

Changing Aerosol Chemistry is Redefining HONO Sources

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This file contains all reviewer reports in order by version, followed by all author rebuttals in order by version.

Version 0:

Reviewer comments:

Reviewer #1

(Remarks to the Author)

The authors focus on the HONO sources in the atmosphere, which are vital to evaluating the atmospheric oxidation capacity. The heterogeneous uptake of NO₂ on aerosol surfaces is one of the most important routes to HONO formation, but the uptake coefficient remains controversial. Previous studies have proposed various parameterization schemes relying on lab and short-term field observations. Zhang et al. provide valuable insights into quantifying γ NO₂ through the integration of machine learning techniques and long-term observation data, offering novel perspectives on the impact of aerosol component variations in China. This paper is generally well-structured and addresses an important knowledge gap in atmospheric HONO chemistry. However, there are a few minor issues requiring clarification before it can be considered for publication.

1. In the Introduction section and Supplementary Table 1, the NO₂ uptake coefficients obtained from lab research and field observation are listed, it is better to add the typical coefficient used in model simulations and the contribution of this route.
2. Fig 1a, b, There seems to be more data missing in the latter three years. Could the decline of annual HONO and γ NO₂ be caused by the possible missing high values?
3. Line 105, The γ NO₂ observed on NaCl used here to compare is in the range of $2.8\text{--}3.7 \times 10^{-4}$. This value is very large, so this is a universal phenomenon or only one literature result? The authors also need to check ref 27, if this is the right reference.
4. In 2023 the HONO concentration increased, but the pH decreased and the yield of HONO product by the heterogeneous reaction of NO₂ on aerosol surfaces in Fig S2 also decreased, more explanation is needed here.
5. Line 141, aqueous nitrites to gaseous HONO is vital to the trend of γ NO₂, so if there are direct observation data to support this hypothesis.
6. The γ in Equation 3, which exclusively represents NO₂ uptake efficiency on aerosol surfaces needs further justification. As the NO₂ heterogeneous reactions on ground surfaces constitute a significant HONO source, could the authors explain why ground surface contributions are not included in this parameterization?
7. Fig S2, the Paerosol in all 5 years was less than 0.1 ppb/hr. That's quite a slow production rate compared to other works. A detailed explanation of the calculation methodology is needed.
8. The definition of "nocturnal" needs explicit clarification.
9. Line 243, it's inappropriate to use a percent increase or decrease for pH.
10. Line 254, in summer, it should be the lowest aerosol pH.
11. Fig. 4b, d, why the mean value is much larger than the median value, near the 75% quartiles.
12. Supplementary Note 1: The rationale for variable selection requires further clarification. Specifically: What criteria were used to determine the included variables? Has the potential impact of excluded variables been evaluated? How might any omitted factors affect the robustness of the conclusions?
13. The pH grouping criteria (Line 140, Supplementary Fig. 4b) are not averaged and lack clear justification. The authors should explain the theoretical or empirical basis for their chosen classification method.

Reviewer #2

(Remarks to the Author)

HONO is a primary source of OH radicals in the atmosphere, affecting the atmospheric oxidative capacity (AOC). Thus, its budget has ever attracted much attention in the atmospheric chemistry community, but the controversy is far from closed due to the uncertainties of related crucial parameters, such as kinetics for heterogeneous reactions and photolysis of nitric acid and nitrate, and so on. Zhang et al. investigated the uptake coefficient of NO₂ (γ NO₂) on ambient aerosol to form HONO

based on 5-year long-term observations in the urban atmosphere in Beijing. They found that the γNO_2 , on the order of 10^{-6} , decreased markedly from $3.07 \pm 5.99 \times 10^{-6}$ in 2019 to $1.43 \pm 3.22 \times 10^{-6}$ in 2023. The underlying reasons for the interannual decrease of γNO_2 were further discussed with the aid of machine learning, and ascribed to the increase in particulate ammonium nitrate opposite to the decrease in particulate ammonium sulfate in Beijing. These results are very interesting and have strong implications for understanding the sources of HONO, the evolution of AOC, and the complicated atmospheric chemistry. Overall, the experiments are well-designed and the data are properly mined. The manuscript is well-organized and clearly written. It is publishable after the following questions have been addressed.

1. Line 40-44: A recent work also support that heterogeneous reaction of NO_2 on ground surfaces is the most important source of HONO in Beijing (Xuan et al., npj Climate and Atmospheric Science, 2024, 7:193). It's better to add some comparison to Zhang et al. in Line 40.
2. Lines 50-51: Although Table S1 summarized the reported γNO_2 , it is unclear what the γNO_2 values were used in these modeling studies when dealing with HONO budget analysis. Please clarify it somewhere.
3. Line 59: It should be noted that only the γNO_2 measured by flow tube showed a increasing trend with decreasing concentration. As for the reactive uptake coefficient determined by FTIR measuring nitrate formation, it increases with increasing concentrations. (Gao et al, Journal of Geophysical Research: Atmospheres, 2021, 126, e2021JD034694.)
4. Some previous studies reported the γNO_2 values based on short-term field observations. To highlight the advantages of the long-term observational dataset, is it possible to show those representatives γNO_2 values in Fig. 1b? A simple discussion may be added to the text.
5. Line 157: Please define the period of nocturnal γNO_2 .
6. In Figs. 2 and 3, relative importance and SHAP values were used to evaluate the role of factors in the γNO_2 and aerosol pH. However, it is unclear how are these values obtained in the model. Please clarify it in the method section.
7. The results of machine learning look good for both the γNO_2 and aerosol pH. How do you make sure they are not overfitted? More details to reduce overfitting should be added.
8. A paper has reported the seasonal variations of aerosol pH in Beijing (Atmos. Chem. Phys. 2019, 19 (12), 7939-7954). It's better to add some comparison in line 224.
9. Temperature is the most important factor governing aerosol pH in Fig. 3, while AN and AS are the second and third ones. The main conclusion suggests that the ratio of AN/AS drives the internal annual evolution of γNO_2 . A clearer explanation is required to clarify the role of temperature in the aerosol pH and the γNO_2 . More discussion might be helpful about the single-factor analysis in supplementary Fig. 9.

Reviewer #3

(Remarks to the Author)

Zhang et al. have conducted studies highlighting the significance of aerosol chemistry in the heterogeneous formation of HONO. Through the combination of 5-year observational with machine learning, this research sheds new light on HONO heterogeneous formation and dynamic NO_2 uptake coefficient on aerosols in the real atmospheric environment, which is essential for comprehending urban air quality, atmospheric oxidizing capacity, and the mechanisms of secondary pollutant formation. The manuscript contents look rich and well fits into the scope of Nat. Commun. It is suitable to publish in Nat. Commun after the following questions have been addressed.

1. In line 102, the mean γNO_2 value is $2.27 \pm 2.58 \times 10^{-6}$, but in Table S1, it is 2.26. The author should check and correct it.
2. In line 125, the term "HONO yield" should be changed to "HONO formation rate" as shown in Fig. 2.
3. In lines 157-160, the author used ALWC rather than RH as input to train and test by RF when evaluating the influence factors affecting the γNO_2 . However, Fig. S4 showed the variations of γNO_2 under different RH. As we all know, ALWC would better reflect the real aerosol physiochemical properties. But when evaluating the influence factor of pH change, RH was as the input rather than ALWC. The authors should unify it or give a proper explanation.
4. Based on RF results, the author claimed the inconsistent trend between NO_2 and γNO_2 would promote the uptake of NO_2 in lines 202-206. This may indicate that in the ambient, the NO_2 concentration is saturated for NO_2 heterogeneous uptake or reaction. Sensitivity tests would help to explain this phenomenon.
5. In lines 250-253, the RF results showed that pH was largely influenced by the temperature. The annual trend of temperature is stable, but shows obvious seasonal variations. The author suggested that temperature is unlikely to drive the increase in aerosol pH from 2019 to 2023 due to the interannual increase trend of pH. Maybe the relationship between temperature and pH in the same season but different years would help to clarify this, given that little uncertainty of temperature in the same season.
6. In Section 3.2, the authors suggested the annual increase in aerosol pH contributed to the decline in γNO_2 , which indicated the important role of aerosol acidity on the uptake of NO_2 on aerosol surface. Thus, the annual variations of NH_3 would also affect the trend of γNO_2 , as the promotional effect of NH_3 for nitrogen dioxide (NO_2) uptake on the wet aerosol surface had been reported in recent studies (eg. doi.org/10.1016/j.aosl.2024.100491). Related discussion was suggested to provided more evidence to the decline in γNO_2 .
7. Fig. S8 was not cited in the manuscript. Please check it.
8. Given the content and style of Nature Communications, it appears that this journal typically does not include a dedicated "Conclusion" section. You should follow the journal's requirements and the format need to be revised.
9. In line 307, the author mentioned that "acidity can modify the phase state of gaseous precursors", this statement would introduce much misunderstanding. Please clarify it.
10. Is the status of LOPAP stable through five-year observation? How is the homogeneity of the calibrated results and backgrounds among different calibrations?
11. Refs 13 and 14, the author lists are not in a similar format. Please check all references, including authors, title, volume,

page, etc. based on the requirements of Nat. Commun.

Reviewer #4

(Remarks to the Author)

I co-reviewed this manuscript with one of the reviewers who provided the listed reports. This is part of the Nature Communications initiative to facilitate training in peer review and to provide appropriate recognition for Early Career Researchers who co-review manuscripts.

Version 1:

Reviewer comments:

Reviewer #1

(Remarks to the Author)

Dear authors, thanks for considering my comments. I have carefully reviewed the manuscript and I have no more comments.

Reviewer #2

(Remarks to the Author)

All my concerns are well addressed. I recommend the manuscript to be accepted.

Reviewer #3

(Remarks to the Author)

Dear Authors,

Thank you for your thorough revisions and detailed responses to my previous comments. You have made substantial improvements to the manuscript(NCOMMS-25-10826A), addressing the concerns raised during the initial review. The additional explanations, refined methodology, and enhanced logical flow have greatly improved the clarity and rigor of the present work.

Congratulations!

Best,

Reviewer #4

(Remarks to the Author)

我与提供所列报告的一位审稿人共同审阅了这份手稿。这是 Nature Communications 计划的一部分，旨在促进同行评审培训，并为共同评审手稿的早期职业研究人员提供适当的认可。

I co-reviewed this manuscript with one of the reviewers who provided the listed reports. This is part of the Nature Communications initiative to facilitate training in peer review and to provide appropriate recognition for Early Career Researchers who co-review manuscripts.

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

Reviewer #1

The authors focus on the HONO sources in the atmosphere, which are vital to evaluating the atmospheric oxidation capacity. The heterogeneous uptake of NO₂ on aerosol surfaces is one of the most important routes to HONO formation, but the uptake coefficient remains controversial. Previous studies have proposed various parameterization schemes relying on lab and short-term field observations. Zhang et al. provide valuable insights into quantifying γ_{NO_2} through the integration of machine learning techniques and long-term observation data, offering novel perspectives on the impact of aerosol component variations in China. This paper is generally well-structured and addresses an important knowledge gap in atmospheric HONO chemistry. However, there are a few minor issues requiring clarification before it can be considered for publication.

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

1. In the Introduction section and Supplementary Table 1, the NO₂ uptake coefficients obtained from lab research and field observation are listed, it is better to add the typical coefficient used in model simulations and the contribution of this route.

Response: Thank you for your good suggestion. We have added the typical NO₂ uptake coefficients used in model simulations and the contribution of this pathway to the HONO budget in the revised **Supplementary Table 1 (Table R1)**.

Table R1. Summary of NO₂ uptake coefficients (γ_{NO_2}) obtained from laboratory studies and field observation methods and used in model simulations.

Method	Type	γ_{NO_2}	Experimental conditions or contribution to HONO sources	Reference
Laboratory	soot	3×10^{-7} - 1×10^{-8}	$m_{\text{soot}}=160$ mg, $[\text{NO}_2]_0=10$ ppm	Kleffmann et al. ¹⁶
Laboratory	soot	1×10^{-5}	T=300 K, RH=80%	Grassian et al., ¹⁷
Laboratory	soot	1.1 - 3.3×10^{-4}	$[\text{NO}_2]_0=10$ ppbv, RH=50%	Ammann et al., ¹⁸
Laboratory	soot	1.54×10^{-6}	$[\text{NO}_2]_0=160$ ppb, RH=7%	Han et al., ¹⁹
Laboratory	soot	$1.54 \times 10^{-6} + 1.96 \times 10^{-7} \times \text{OC}_R^c$	$[\text{NO}_2]_0=160$ ppb, RH=7%	
Laboratory	soot	2.6×10^{-5}	fuel-rich, $[\text{NO}_2]_0=160$ ppb, T=298 K, RH=7%	Han et al., ²⁰
Laboratory	soot	5.9×10^{-6}	fuel-lean, $[\text{NO}_2]_0=160$ ppb, T=298 K, RH=7%	
Laboratory	soot	5.5×10^{-6}	fuel-rich, $[\text{NO}_2]_0=160$ ppb, T=298 K, RH=70%	
Laboratory	soot	7.2×10^{-7}	fuel-lean, $[\text{NO}_2]_0=160$ ppb, T=298 K, RH=70%	
Laboratory	soot	1.6×10^{-8} - 6.1×10^{-6}	Spark generated, NO ₂ (1.6×10^{12} - 2.4×10^{14} molecules cm ⁻³)	Kirchner et al., ²¹
Laboratory	soot	0.48 - 1.17×10^{-5}	Hexane soot, $[\text{NO}_2]_0=2.5 \times 10^{11}$ molecules cm ⁻³ , T=295K	Al-Abadleh et al., ²²

Laboratory	soot	$\leq 4 \times 10^{-8}$	Spark generated, T=294 K, RH=50%,	Saathoff et al. ²³
Laboratory	soot	$1.5\text{--}2.4 \times 10^{-8}$	Hexane soot, BC, T=296 K, RH<1%,	Prince et al. ²⁴
Laboratory	dust	$9.6\text{--}1.2 \times 10^{-4}$	TiO ₂ , RH (15-80%), T=298 K, [NO ₂] ₀ =100 ppb, Irradiation=16 Wm ⁻²	Gustafsson et al., ²⁵
Laboratory	dust	$8.1 \times 10^{-8}\text{--}2.3 \times 10^{-7}$	Kaolinite, T=298 K, RH=0%, [NO ₂] ₀ = $0.56\text{--}8.8 \times 10^{13}$ molecules cm ⁻³	Angelini et al., ²⁶
Laboratory	dust	7.0×10^{-9}	pyrophyllite, T=298 K, RH=0%, [NO ₂] ₀ = 3×10^{14} molecules cm ⁻³	
Laboratory	dust	1.0×10^{-9}	Saharan dust, 1%TiO ₂ /SiO ₂ , SiO ₂ , T=295K,	Ndour et al., ²⁷
Laboratory	dust	1.0×10^{-6}	1%TiO ₂ /SiO ₂ , Irradiation=134 Wm ⁻²	
Laboratory	dust	8.9×10^{-9}	Saharan sand, T=295 K, RH=25%,	Nicolas et al., ²⁸
Laboratory	dust	$4.3\text{--}2.5 \times 10^{-9}$	CaCO ₃ , T=296 K, RH (0-70%),	Li et al., ²⁹
Laboratory	dust	2.0×10^{-8}	γ -Al ₂ O ₃ ^a , S _{BET} =1010 cm ² mg ⁻¹	
Laboratory	dust	7.7×10^{-6}	α -Fe ₂ O ₃ ^b , S _{BET} =23 cm ² mg ⁻¹	
Laboratory	dust	4.0×10^{-6}	γ -Fe ₂ O ₃ ^a , S _{BET} =500 cm ² mg ⁻¹	
Laboratory	dust	1.3×10^{-7}	TiO ₂ ^a , S _{BET} =500 cm ² mg ⁻¹	
Laboratory	dust	$< 4 \times 10^{-10}$	SiO ₂ , S _{BET} =230 cm ² mg ⁻¹	

Laboratory	dust	1.2×10^{-5}	MgO ^b , S _{BET} =150 cm ² mg ⁻¹	
Laboratory	dust	2.2×10^{-5}	CaO ^b , S _{BET} =39 cm ² mg ⁻¹	
Laboratory	dust	2.1×10^{-6}	China loess ^b , S _{BET} =110 cm ² mg ⁻¹	
Laboratory	dust	1.2×10^{-6}	Saharan sand ^b , S _{BET} =31 cm ² mg ⁻¹	
Laboratory	dust	2×10^{-8}	Al ₂ O ₃ , S _{BET} =1010 cm ² mg ⁻¹ , T=298K,	
Laboratory	dust	7×10^{-7}	Fe ₂ O ₃ , S _{BET} =2300 cm ² mg ⁻¹ , T=298K,	Underwood et al., ³⁰
Laboratory	dust	1×10^{-7}	TiO ₂ , S _{BET} =5000 cm ² mg ⁻¹ , T=298K,	
Laboratory	dust	9.7×10^{-6}	α-Fe ₂ O ₃ ^b , S _{BET} =18 cm ² mg ⁻¹	Underwood et al., ³¹
Laboratory	dust	1.2×10^{-9} - 2.6×10^{-8}	Al ₂ O ₃ , T=299 K, [NO ₂] ₀ =10 ¹³ -10 ¹⁵ molecules cm ⁻³	Börensén et al., ³²
Laboratory	dust	6.2×10^{-7}	Saharan sand, T=298 K, S _{BET} =500 cm ² mg ⁻¹	Ullerstam et al., ³³
Laboratory	dust	0.6 - 2.4×10^{-8}	NO ₂ (35-200 ppb), RH (15-50%), irradiation=1.5×10 ¹⁵ photons cm ⁻² s ⁻¹ ,	Dupart et al., ³⁴
Laboratory	dust	1.4×10^{-7}	Kaolin, [NO ₂] ₀ =150 ppb, T=298 K, RH=7%	
Laboratory	dust	4.4×10^{-8}	Kaolin, [NO ₂] ₀ =150 ppb, T=298 K, RH=74%	Liu et al., ³
Laboratory	dust	1.6×10^{-6}	Hematite, [NO ₂] ₀ =150 ppb, T=298 K, RH=7%	

Laboratory	dust	2.8×10^{-7}	Hematite, $[\text{NO}_2]_0 = 150$ ppb, $T = 298$ K, $\text{RH} = 74\%$	
Laboratory	dust	5.3×10^{-6}	MgO (SO_2 -aged), $[\text{NO}_2]_0 = 100$ ppb	Ma et al., ⁴
Laboratory	dust	$1.0\text{-}2.9 \times 10^{-6}$	MgO, SO_2 (40-100 ppb), $[\text{NO}_2]_0 = 100$ ppb	
Laboratory	dust	$9.9 \times 10^{-6}\text{-}1.3 \times 10^{-4}$	TiO_2 , NO_2 (34-400 ppb), $T = 295$ K, $\text{RH} = 15\%$	Dyson et al., ³⁵
Laboratory	humic	$2.6\text{-}3.7 \times 10^{-6}$	NO_2 (5-100 ppb), RH (0-50%), $T = 296$ K	Stemmler et al. ³⁶
Laboratory	humic	$< 1 \times 10^{-7}$	Dark, NO_2 (2.7-280 ppb)	Stemmler et al., ³⁶
Laboratory	humic	1.8×10^{-6}	actinic flux = 1.0×10^{17} photons $\text{cm}^{-2} \text{s}^{-1}$, NO_2 (2.7-280 ppb)	
Laboratory	humic	$1.7\text{-}4.4 \times 10^{-6}$	Irradiation (68.5-194.5 W/m^2)	
Laboratory	humic	1.9×10^{-7}	Dark	
Laboratory	humic	$4.3\text{-}1.6 \times 10^{-6}$	NO_2 (30-160 ppb), Irradiation = 194.5 W/m^2 , $T = 298$ K, $\text{RH} = 22\%$	Han et al., ⁵
Laboratory	humic	3.8×10^{-6}	T (278-308 K), $\text{RH} = 22\%$, $[\text{NO}_2]_0 = 30$ ppb, Irradiation = 194.5 W/m^2	
Laboratory	humic	$3.4\text{-}6.3 \times 10^{-6}$	$T = 298$ K, RH (7-70%), $[\text{NO}_2]_0 = 30$ ppb, Irradiation = 194.5 W/m^2	
Laboratory	grime	$1.1\text{-}5.8 \times 10^{-6}$	$T = 296$ K, RH (0-90%), $[\text{NO}_2]_0 = 46$ ppb, actinic flux = 2.6×10^{15} photons $\text{cm}^{-2} \text{s}^{-1}$	Liu et al., ³⁷
Laboratory	glass	$1.0\text{-}2.7 \times 10^{-7}$	$T = 296$ K, RH (0-90%), $[\text{NO}_2]_0 = 46$ ppb	

Laboratory	grime	5.7×10^{-7} - 4.6×10^{-6}	RH (0-90%), actinicflux= 2.6×10^{15} photons $\text{cm}^{-2} \text{s}^{-1}$	Liu et al., ³⁸
Laboratory	grime	3.2×10^{-6} - 1.1×10^{-6}	NO ₂ (40-120 ppb), RH=60%, actinicflux= 2.6×10^{15} photons $\text{cm}^{-2} \text{s}^{-1}$	
Laboratory	glass	1×10^{-8}	Dark, RH=60%, [NO ₂] ₀ =50 ppb	Liu et al., ³⁹
Laboratory	glass	1.5×10^{-7} - 1.5×10^{-6}	T=296 K, RH (0-90%), Irradiation=8 Wm^{-2}	
Laboratory	grime	2.3 - 4.1×10^{-6}	T=296 K, RH (0-90%), [NO ₂] ₀ =50 ppb, Irradiation=8 Wm^{-2}	
Laboratory	ice	$< 5 \times 10^{-6}$	T (193-243 K)	Saastad et al., ⁴⁰
Laboratory	OA	3 - 7×10^{-6}	Catechol, RH (2-30%), T=298K, NO ₂ (70-103ppb)	Woodill et al., ⁴¹
Laboratory	OA	2.2 - 8.8×10^{-7}	Gentisic acid, tannic acid, UV/Vis light, [NO ₂] ₀ =76 ppb	Sosedova et al. ⁴²
Laboratory	OA	$< 5 \times 10^{-7}$	Solid 1,2,10trihydroxyanthracene, [NO ₂] ₀ =40 ppb	Arens et al. ⁴³
Laboratory	OA	$< 1 \times 10^{-7}$	Solid pyrene, dark	Brigante et al. ⁴⁴
Laboratory	OA	3.5×10^{-6}	Solid pyrene, near-UV	
Laboratory	OA	$< 5 \times 10^{-7}$	pinene/O ₃ , O ₃ =33 ppm, T=298 K, RH=55%	Bröske et al. ⁴⁵
Laboratory	sea salt	2.8 - 3.7×10^{-4}	Deliquesced NaCl	Harrison et al., ⁴⁶
Laboratory	sea salt	5.5×10^{-7} - 1.3×10^{-6}	Chinese sea salt, RH (0-20%), [NO ₂] ₀ = 1.96×10^{15} molecules cm^{-3}	Ye et al. ⁴⁷

Laboratory	sea salt	6×10^{-5}	NaCl, T=298 K, $[\text{NO}_2]_0 = 2.0 \times 10^{14}$ molecules cm^{-3}	Vogt et al. ⁴⁸
Observation	Night	$1-3 \times 10^{-6}$	Beijing, 2020.01-2020.03	Zhang et al., ⁴⁹
Observation	Night	5.9×10^{-6}	Svalbard, 2010.04,	Spataro et al., ⁵⁰
Observation	Night	6.9×10^{-6} - 1.4×10^{-5}	Nanjing, 2017.12-2018.2	Liu et al., ⁵¹
Observation	Night	6.4×10^{-6}	Shijiazhuang, 2020.01	Liu et al., ⁵²
Observation	Night	$2.3-7.6 \times 10^{-5}$	Beijing, 2018.04	Zhang et al., ⁵³
Observation	Night	2.6×10^{-5}	Beijing, 2018.11, Aerosol surface	Zhang et al., ⁵⁴
Observation	Night	1.3×10^{-6}	Beijing, 2018.11, Ground surface	
Observation	Night	2.27×10^{-6}	Beijing, 2019.01-2024.01	This study
Model simulation	WRF- Chem	1×10^{-6} - 2×10^{-7} $^5 \times (\text{illumination}/400)$	Hong Kong, 2011.8, suburban area; 42% (Ground) and 3% (Aerosol) for HONO sources.	Zhang et al., ⁵⁵
Model simulation	CMAQ	5×10^{-5} - 1×10^{-7} $^3 \times (\text{illumination}/400)$	Pearl River Delta, 2017.1, suburban area; 81% (Night) and 52% (Day) for HONO sources.	Fu et al., ⁵⁶
Model simulation	Box model	8×10^{-6} - 1×10^{-7} $^3 \times (\text{J}_{\text{NO}_2}/\text{J}_{\text{NO}_2, \text{noon}})$	Wangdu, 2014.6, rural site; 46% (6:00-8:00) for HONO sources.	Liu et al., ⁵⁷

Model simulation	WRF-Chem	5×10^{-6} - $2.5 \times 10^{-4} \times J_{NO2}$	Beijing, 2006.8, urban area; 27% (Ground) and 20% (Aerosol) for HONO sources.	Zhang et al., ⁵⁸
Model simulation	WRF-Chem	5×10^{-6} - $2.5 \times 10^{-4} \times J_{NO2}$	Wangdu, 2017.11, rural site; 28% (Ground) and 39% (Aerosol) for HONO sources.	Zhang et al., ⁵⁹
Model simulation	Box model	8×10^{-6} - 2×10^{-5}	Changzhou, 2017.4, urban area; 54.4% (Night) and 34.7% (Day) for HONO sources.	Shi et al., ⁶⁰
Model simulation	Box model	1×10^{-6} - 1.35×10^{-5}	Hebei, 2017.12, rural site More than 36% (Daytime) for HONO sources.	Xue et al., ⁶¹
Model simulation	Box model	4.5×10^{-5}	Beijing, 2018.4, urban area; 28% (Ground) and 45% (Aerosol) for HONO sources.	Zhang et al., ⁵³
Model simulation	Box model	1×10^{-6} - 2×10^{-5}	Nanjing, 2015.12, urban area; 11% (Ground) and 35% (Aerosol) for daytime HONO.	Zheng et al., ⁶²
Model simulation	Box model	1.2×10^{-6} - $0.6 \times 10^{-4} \times (J_{NO2}/J_{NO2,noon})$	Beijing, 2018.11-2019.1, urban area; 24.9% (Ground) and 29.7% (Aerosol) for daytime HONO.	Liu et al., ⁶³
Model simulation	WRF-Chem	5×10^{-6} - 5×10^{-5}	Beijing, 2018.10, urban area; 50%-80% (Ground) and <10% (Aerosol) for HONO sources.	Zhang et al., ⁶⁴
Model	Box	2×10^{-6} - 2.5×10^{-5}	Taizhou, 2018.5-2018.6, suburban site;	Ye et al., ⁶⁵

simulation	model		55% (Night) and 71% (Day) for HONO sources.	
Model	Box		Beijing, 2021.3, urban area;	
simulation	model	5×10^{-6} - 2×10^{-5}	63%-76% for HONO sources.	Zhang et al., ⁶⁶
Model	Box		Beijing, 2021.10, urban area;	
simulation	model	8.25×10^{-6} - 1.5×10^{-5}	31.3%-85.6% (Ground) and <3% (Aerosol) for HONO sources.	Xuan et al., ⁶⁷
Model	Box		Beijing, 2018.11, urban area;	
simulation	model	1.3×10^{-6} - 3.9×10^{-5}	68%-91% (severe pollution episodes) for HONO sources.	Zhang et al., ⁵⁴

Note: ^a Sample holder area = 11.88 cm²; ^b Sample holder area = 5.07 cm²; ^c OC_R means OC with a reduced state.

2. Fig 1a, b, there seems to be more data missing in the latter three years. Could the decline of annual HONO and γ_{NO_2} be caused by the possible missing high values?

Response: Thank you for your careful review and insightful comments. Regarding your concern about the potential impact of missing data in the latter three years on the observed decline of annual HONO and γ_{NO_2} , we have compared the HONO concentrations and γ_{NO_2} with the identical degree of data missing by removing the observed data with the same order when a data point is missed in one year. **Figure R1** shows that the trends are consistent with the corresponding pattern presented in **Figure 1d** in the main text after missing data has been ruled out. This suggests that the decline in annual HONO and γ_{NO_2} represents their real trends rather than data missing in the latter three years.

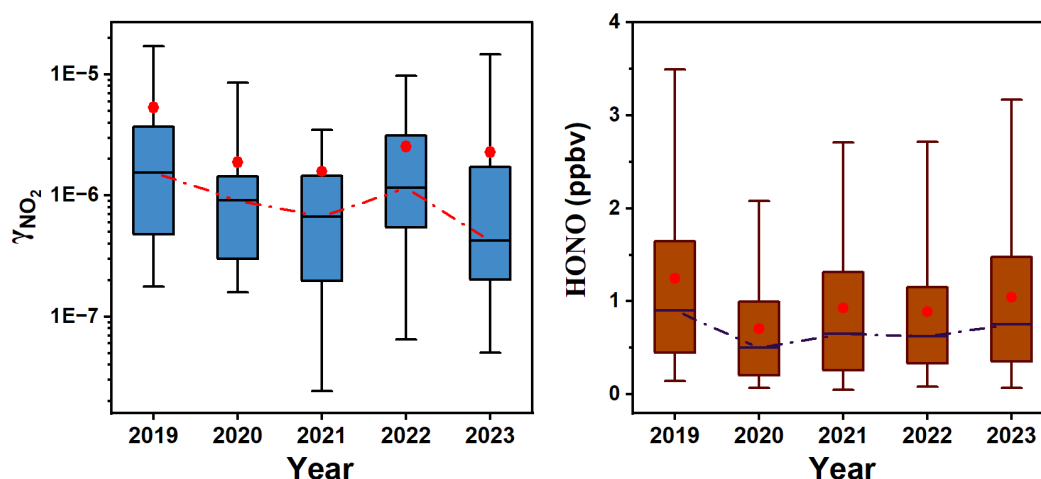


Figure R1. The annual variations of HONO concentration and γ_{NO_2} based on their identical time series in each year by removing the observed data with the same order when a data point is missed in one year.

In [lines 137-139](#) in the revised manuscript, we added a sentence to clarify it “**The decline trends of both HONO concentration and γ_{NO_2} are also confirmed after the missing data have been accounted for**”.

3. Line 105, The γ_{NO_2} observed on NaCl used here to compare is in the range of 2.8-3.7 $\times 10^{-4}$. This value is very large, so this is a universal phenomenon or only one

literature result? The authors also need to check ref 27, if this is the right reference.

Response: Thank you for your careful review and good suggestion. The γ_{NO_2} value of $2.8\text{--}3.7 \times 10^{-4}$ observed on NaCl in this study is based on a specific literature result, which was measured on deliquesced NaCl¹. It is important to note that γ_{NO_2} values vary significantly across different studies due to variations in experimental conditions, such as the state of NaCl (e.g., aqueous, surface, or atmospheric particles) and the specific measurement techniques used. For example, other studies have reported γ_{NO_2} values being 1×10^{-4} over aqueous NaCl solutions², 6×10^{-5} on the surface of NaCl³, and 5.5×10^{-7} – 1.3×10^{-6} on the surface of Chinese sea salt⁴. These discrepancies highlight the complexity and variability of this parameter under different conditions. Regarding Reference 27, we apologize for the error and have corrected the citation accordingly.

In lines 107-109 in the revised manuscript, we revised the sentence “However, it is higher than those measured γ_{NO_2} over kaolinite ($1.4 \pm 0.10 \times 10^{-7}$), but much lower than the γ_{NO_2} observed on deliquesced NaCl ($2.8\text{--}3.7 \times 10^{-4}$)²⁹, NaCl solutions (1×10^{-4})³⁰, dry NaCl (6×10^{-5})³¹ and CaO (2.2×10^{-5})³²”.

4. In 2023 the HONO concentration increased, but the pH decreased and the yield of HONO product by the heterogeneous reaction of NO₂ on aerosol surfaces in Fig S2 also decreased, more explanation is needed here.

Response: Thank you for your good suggestion. The observed increase in HONO concentrations in 2023, accompanied by a decrease in pH levels and a decline in the HONO production yield from NO₂ heterogeneous reactions on particle surfaces (as shown in Fig. S2), suggests that the contribution of heterogeneous reactions of NO₂ on particle surfaces to form HONO is not so important when compared to other sources, such as direct emissions.

In lines 160-167 in the revised manuscript, we added a short paragraph to explain this phenomenon “Interestingly, the HONO concentration increased in 2023, accompanied by a decrease in pH value and a decline of HONO production yield from heterogeneous reactions of NO₂ on particle surfaces (Supplementary Fig. 3). This

suggests heterogeneous reactions of NO₂ on particle surfaces might be a minor source of HONO, whereas other sources, such as direct emissions, might be more important to atmospheric HONO in Beijing. This is consistent with the increase in transport and other economic activities after the relaxation of epidemic control at the end of 2022 in Beijing”.

5. Line 141, aqueous nitrites to gaseous HONO is vital to the trend of γ_{NO_2} , so if there are direct observation data to support this hypothesis.

Response: Thank you for your valuable suggestion. We agree with you that direct observation data of aqueous nitrites is vital to understanding the observed trend of γ_{NO_2} . Unfortunately, it is a challenge to directly observe particle-bound or aqueous nitrites in the atmosphere at present. Thus, the direct observation data of aqueous nitrites were unavailable during our observations. We would like to cite the results of a laboratory study performed by Yang et al.⁵ that observed a similar dependence of the $\gamma_{\text{NO}_2 \rightarrow \text{HONO}}$ on aerosol pH, i.e., the lower the pH levels, the larger the $\gamma_{\text{NO}_2 \rightarrow \text{HONO}}$.

6. The k_{het} in Equation 3, which exclusively represents NO₂ uptake efficiency on aerosol surfaces needs further justification. As the NO₂ heterogeneous reactions on ground surfaces constitute a significant HONO source, could the authors explain why ground surface contributions are not included in this parameterization?

Response: Thank you for your valuable comments. We appreciate your careful review and would like to clarify the treatment of the k_{het} in our parameterization. The k_{het} was calculated based on the total source strength via heterogeneous reactions of NO₂ on the surfaces of both ground and aerosols, while the k_{het} attributed to aerosol surfaces ($k_{\text{het, aerosol}}$) was obtained according to the relative ratio of the surface areas of aerosol to the total surface areas (the surfaces of both ground and aerosols). Because we focus on the properties of aerosols and their impact on the $\gamma_{\text{NO}_2 \rightarrow \text{HONO}}$, we did not include the ground part in our discussion. We are sorry for confusing you because of the unclear expression in our manuscript.

In lines 411-423 in the revised manuscript, we revised the paragraph “It is derived according to Equation (3) and (4),

$$\gamma_{NO_2} = \frac{4 \times k_{het,aerosol}}{A_s \times \omega} = \frac{4 \times k_{het,aerosol}}{A_s \times \sqrt{\frac{8RT}{\pi M}}} \quad (3)$$

$$k_{het,aerosol} = k_{het} \times \frac{A_s}{(A_s + \frac{\delta}{H})} \quad (4)$$

where $k_{het,aerosol}$ is the heterogeneous rate constant of NO₂ on aerosol surfaces, calculated based on the fraction of aerosol surface area concentration in the total surface area concentration (both ground and aerosol surfaces) and the k_{het} ¹⁰. A_s is the surface area concentration of the PM_{2.5} surface (m² m⁻³)¹³, ω is the average molecular velocity (m s⁻¹). R is the ideal gas constant (J K⁻¹·mol⁻¹), T is the air temperature (K), and M is the molecular weight of NO₂ (kg mol⁻¹). δ is the surface roughness, in this study, we used 3.85¹³. H is the planetary boundary layer height (m). The production rate of HONO via heterogeneous reaction is calculated according to Zhang et al.,¹⁰,

$$P_{HONO} = 3600 \times k_{het,aerosol} \times Y_{HONO} \times c_{NO_2} \quad (5)$$

where Y_{HONO} is the HONO yield (0.5), c_{NO_2} is the concentration of NO₂ (ppbv).”

7. Fig S2, the $P_{aerosol}$ in all 5 years was less than 0.1 ppb/hr. That’s quite a slow production rate compared to other works. A detailed explanation of the calculation methodology is needed.

Response: Thank you for your good comment and suggestion. As pointed out in the introduction section, there is a large discrepancy in the $P_{aerosol}$ across different studies. This value definitely depends on the γ_{NO_2} chosen in the model or scheme in budget calculations. As shown in **Table R1** or **Table S1**, most modelers used a large γ_{NO_2} (e.g., $\sim 5 \times 10^{-5}$), which is an order of magnitude larger than the γ_{NO_2} derived from long-term observations in this study. Thus, the HONO production rate is lower than those results. However, our result is consistent with some previous studies^{6,7}. Therefore, our work further underscores the importance of conducting long-term investigations into the γ_{NO_2} .

In lines 411-423 in the revised manuscript, we revised the sentence “It is derived according to Equation (3) and (4),

$$\gamma_{NO_2} = \frac{4 \times k_{het,aerosol}}{A_s \times \omega} = \frac{4 \times k_{het,aerosol}}{A_s \times \sqrt{\frac{8RT}{\pi M}}} \quad (3)$$

$$k_{het,aerosol} = k_{het} \times \frac{A_s}{\left(A_s + \frac{\delta}{H}\right)} \quad (4)$$

where $k_{het,aerosol}$ is the heterogeneous rate constant of NO₂ on aerosol surfaces, calculated based on the fraction of aerosol surface area concentration in the total surface area concentration (both ground and aerosol surfaces) and the k_{het} ¹⁰. A_s is the surface area concentration of the PM_{2.5} surface (m² m⁻³)¹³, ω is the average molecular velocity (m s⁻¹). R is the ideal gas constant (J K⁻¹·mol⁻¹), T is the air temperature (K), and M is the molecular weight of NO₂ (kg mol⁻¹). δ is the surface roughness, in this study, we used 3.85¹³. H is the planetary boundary layer height (m). The production rate of HONO via heterogeneous reaction is calculated according to Zhang et al.,¹⁰,

$$P_{HONO} = 3600 \times k_{het,aerosol} \times Y_{HONO} \times c_{NO_2} \quad (5)$$

where Y_{HONO} is the HONO yield (0.5), c_{NO_2} is the concentration of NO₂ (ppbv)

In lines 133-137 in the revised manuscript, we revised the sentence “The corresponding HONO formation rate from the NO₂ heterogeneous reaction on aerosol surfaces also decreased annually, showing a reduction of over 70% from 2019 to 2023 (Supplementary Fig. 3) although the absolute values were lower than most of those in previous studies calculated based on larger γ_{NO_2} values (Supplementary Table 1)”.

8. The definition of "nocturnal" needs explicit clarification.

Response: Thank you for your good suggestion. In the revised manuscript in lines 410-411, we added a sentence “Thus, we only focus on the nocturnal γ_{NO_2} to form HONO on particle surfaces when UVB is less than 0.01 W m⁻²¹⁴”.

9. Line 243, it's inappropriate to use a percent increase or decrease for pH.

Response: Thank you for your good suggestion. We agree with you that it is inappropriate to use a percent increase or decrease for pH. In lines 265-268 in the

revised manuscript, we deleted the percentage in the brackets, i.e., “When AS was subtracted, the pH ranged from 1.5 to 6.7 with an average of 4.0 ± 0.79 , showing an increase in pH of approximately 0.26. Conversely, removing AN resulted in a lower mean pH of 3.4 ± 0.89 , with a decrease of approximately 0.36.”

10. Line 254, in summer, it should be the lowest aerosol pH.

Response: Thank you for your careful review. We have corrected it to “**lowest**” in line 277 in the revised manuscript.

11. Fig. 4b, d, why the mean value is much larger than the median value, near the 75% quartiles.

Response: Thank you for your good suggestion. In Figures 4b and 4d, the mean values of ALWC and γ_{NO_2} are significantly higher than the median values, approaching the 75th percentile due to the skewed distribution of the data as shown in **Figure R2**.

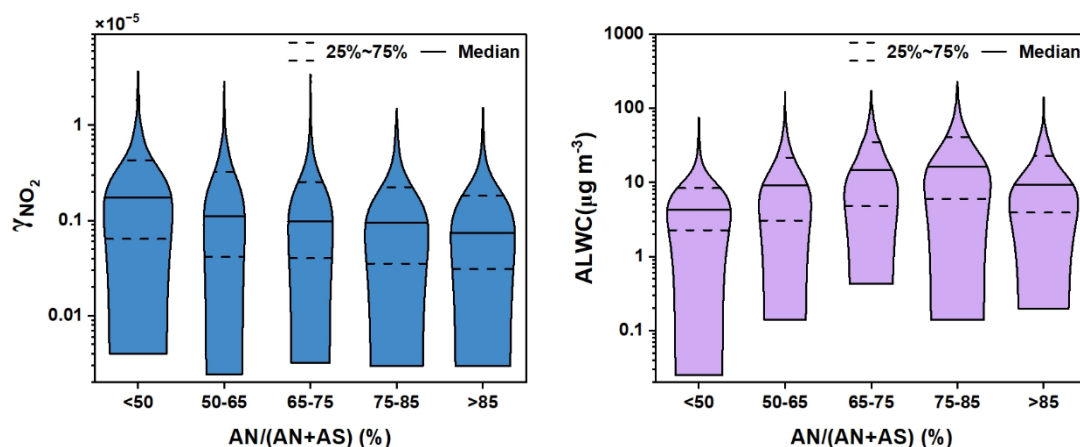


Figure R2. Distribution of γ_{NO_2} and ALWC based on the fraction of NH_4NO_3 in SNA.

Although the data are not in a normal distribution and there is a gap between the mean and median values, both the mean and median values exhibit the same trends as the fraction of AN increases. Thus, in [lines 302-304](#) and [lines 310-313](#) in the manuscript, we have also shown the trends of the corresponding median values “Fig. 4b shows that the mean aerosol pH increases from 2.68 to 4.31, with the median pH increasing from 2.54 to 4.31 as the AN fraction in SNA rises from less than 50% to higher than 85%”

and “As the proportion of AN relative to SNA increases in the particles, the mean γ_{NO_2} decreases from $4.17 \pm 7.19 \times 10^{-6}$ to $1.76 \pm 4.24 \times 10^{-6}$, with the median value dropping from 1.73×10^{-6} to 7.42×10^{-7} , representing a reduction of about 58%”.

In addition, we conducted a Mann-Whitney U test due to the skewed distribution of the dataset. The trends are significant at a 0.05 level. Therefore, we believe that this data distribution does not affect the accuracy of our conclusions.

In lines 321-324 in the revised manuscript, we added a sentence “It should be noted that there are some gaps between the mean values and median values of both ALWC and γ_{NO_2} in Fig. 4 due to the skewed distribution of the datasets. The dependence of ALWC or γ_{NO_2} on the AN/(AN+AS) is significant at a 0.05 level according to a Mann-Whitney U test”.

12. Supplementary Note 1: The rationale for variable selection requires further clarification. Specifically: What criteria were used to determine the included variables? Has the potential impact of excluded variables been evaluated? How might any omitted factors affect the robustness of the conclusions?

Response: Thank you for your instructive comment. We appreciate your detailed review and would like to provide clarification regarding the variable selection process. The selection of variables was based on a comprehensive evaluation of two primary criteria: model interpretability and model accuracy. Specifically, we aimed to include variables that were most relevant to the target parameters (pH and γ_{NO_2}) while ensuring that the model remained interpretable. Thus, we screened the parameters according to the following criteria:

(1) Variable Relevance: We drew on existing studies to identify key factors influencing pH and γ_{NO_2} . For pH, the primary factors included components of PM_{2.5}, temperature (T), and relative humidity (RH)⁸. For γ_{NO_2} , the key variables were NO₂, NO, SO₂, NH₃, ALWC, pH, T, and RH^{5,9-13}.

(2) Model Accuracy and Parsimony: While maintaining model interpretability, we aimed to optimize model performance. To this end, we excluded certain environmental

variables (e.g., wind speed, wind direction, boundary layer height, CO, and PM_{2.5} mass concentration) that were found to have minimal or redundant contributions to the model's predictive power. This was determined through rigorous tests, in which the inclusion of these variables did not significantly improve model accuracy but increased complexity.

(3) Evaluation of Excluded Variables: We conducted a thorough assessment of the excluded variables by incorporating them into the model and evaluating their impacts on the model performance. The results showed that adding these variables led to a significant decline in both the interpretability and accuracy of the model. This validated our decision to exclude them from the final model.

(4) Robustness of Conclusions: Given the careful selection process and the evaluation of excluded variables, we are confident that the omitted factors have a minimal impact on the robustness of our conclusions.

In summary, the variable selection process was systematic, balancing both scientific relevance and model performance. We believe this approach ensures the validity and robustness of our conclusions.

In the revised Supplementary Note 1, we added the details about the variable selection in the random forest model as follows:

“The selection of variables was based on a comprehensive evaluation of two primary criteria: model interpretability and model accuracy. Specifically, we aimed to include variables that were most relevant to the target parameters (pH and γ_{NO_2}) while ensuring that the model remained interpretable. We drew on existing studies to identify key factors influencing pH and γ_{NO_2} . For pH, the primary factors included particulate matter components, temperature (T), and relative humidity (RH)². For γ_{NO_2} , the screened key variables were NO₂, NO, SO₂, NH₃, ALWC, pH, T, and RH³⁻⁸. While maintaining model interpretability, we aimed to optimize model performance. To this end, we excluded certain environmental variables (e.g., wind speed, wind direction, boundary layer height, CO, and PM_{2.5} mass concentration) that were found to have minimal or redundant contributions to the model's predictive power. We conducted a

thorough assessment of the excluded variables by incorporating them into the model and evaluating their impact. The results showed that adding these variables led to a significant decline in both model interpretability and accuracy. We are confident that the omitted factors have a minimal impact on the robustness of our conclusions.”

13. The pH grouping criteria (Line 140, Supplementary Fig. 4b) are not averaged and lack clear justification. The authors should explain the theoretical or empirical basis for their chosen classification method.

Response: Thank you for your suggestion. We appreciate your careful review.

The pH grouping method was carefully designed to ensure the statistical robustness and reliability of our analysis. Specifically, when analyzing how a variable changes across different bins, it is crucial to ensure that each bin contains a comparable number of data points. This approach minimizes potential biases and ensures that the observed trends are statistically meaningful and accurate. By maintaining balanced data distribution across the bins, we can avoid artifacts that might arise from uneven sampling. This methodological choice allows for a more reliable interpretation of the relationships observed in the data.

In Supplementary Fig. 5, we revised the caption “The number of data points in each bin is generally the same to avoid possible artifacts arising from uneven sampling”.

Reviewer #2

HONO is a primary source of OH radicals in the atmosphere, affecting the atmospheric oxidative capacity (AOC). Thus, its budget has ever attracted much attention in the atmospheric chemistry community, but the controversy is far from closed due to the uncertainties of related crucial parameters, such as kinetics for heterogeneous reactions and photolysis of nitric acid and nitrate, and so on. Zhang et al. investigated the uptake coefficient of NO₂ (γ_{NO_2}) on ambient aerosol to form HONO based on 5-year long-term observations in the urban atmosphere in Beijing. They found that the γ_{NO_2} , on the order of 10⁻⁶, decreased markedly from $3.07 \pm 5.99 \times 10^{-6}$ in 2019 to $1.43 \pm 3.22 \times 10^{-6}$ in 2023. The underlying reasons for the interannual decrease of γ_{NO_2} were further discussed with the aid of machine learning, and ascribed to the increase in particulate ammonium nitrate opposite to the decrease in particulate ammonium sulfate in Beijing. These results are very interesting and have strong implications for understanding the sources of HONO, the evolution of AOC, and the complicated atmospheric chemistry. Overall, the experiments are well-designed and the data are properly mined. The manuscript is well-organized and clearly written. It is publishable after the following questions have been addressed.

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

1. Line 40-44: A recent work also support that the heterogeneous reaction of NO₂ on ground surfaces is the most important source of HONO in Beijing (Xuan et al., npj Climate and Atmospheric Science, 2024, 7:193). It's better to add some comparison to Zhang et al. in Line 40.

Response: Thank you for your suggestion. We have modified it in the revised manuscript to “In contrast, Zhang et al.,³ and Xuan et al.⁴ found that heterogeneous reaction of NO₂ on ground surfaces accounted for 42% and 85.6% of the HONO, respectively, as the dominant source in Hong Kong and Beijing” in lines 42-44.

2. Lines 50-51: Although Table S1 summarized the reported γ_{NO_2} , it is unclear what the γ_{NO_2} values were used in these modeling studies when dealing with HONO budget analysis. Please clarify it somewhere.

Response: Thank you for your good suggestion. According to your suggestion, we have added the typical NO_2 uptake coefficients commonly used in model simulations and the contribution of this route in the revised Supplementary Table 1 (Table R1) as follows:

Table R1. Summary of NO₂ uptake coefficients (γ_{NO_2}) obtained from laboratory studies and field observation methods and used in model simulations.

Method	Type	γ_{NO_2}	Experimental conditions or contribution to HONO sources	Reference
Laboratory	soot	3×10^{-7} - 1×10^{-8}	$m_{\text{soot}}=160$ mg, $[\text{NO}_2]_0=10$ ppm	Kleffmann et al. ¹⁶
Laboratory	soot	1×10^{-5}	T=300 K, RH=80%	Grassian et al., ¹⁷
Laboratory	soot	1.1 - 3.3×10^{-4}	$[\text{NO}_2]_0=10$ ppbv, RH=50%	Ammann et al., ¹⁸
Laboratory	soot	1.54×10^{-6}	$[\text{NO}_2]_0=160$ ppb, RH=7%	Han et al., ¹⁹
Laboratory	soot	$1.54 \times 10^{-6} + 1.96 \times 10^{-7} \times \text{OC}_R^c$	$[\text{NO}_2]_0=160$ ppb, RH=7%	
Laboratory	soot	2.6×10^{-5}	fuel-rich, $[\text{NO}_2]_0=160$ ppb, T=298 K, RH=7%	Han et al., ²⁰
Laboratory	soot	5.9×10^{-6}	fuel-lean, $[\text{NO}_2]_0=160$ ppb, T=298 K, RH=7%	
Laboratory	soot	5.5×10^{-6}	fuel-rich, $[\text{NO}_2]_0=160$ ppb, T=298 K, RH=70%	
Laboratory	soot	7.2×10^{-7}	fuel-lean, $[\text{NO}_2]_0=160$ ppb, T=298 K, RH=70%	
Laboratory	soot	1.6×10^{-8} - 6.1×10^{-6}	Spark generated, NO ₂ (1.6×10^{12} - 2.4×10^{14} molecules cm ⁻³)	Kirchner et al., ²¹
Laboratory	soot	0.48 - 1.17×10^{-5}	Hexane soot, $[\text{NO}_2]_0=2.5 \times 10^{11}$ molecules cm ⁻³ , T=295K	Al-Abadleh et al., ²²

Laboratory	soot	$\leq 4 \times 10^{-8}$	Spark generated, T=294 K, RH=50%,	Saathoff et al. ²³
Laboratory	soot	$1.5\text{--}2.4 \times 10^{-8}$	Hexane soot, BC, T=296 K, RH<1%,	Prince et al. ²⁴
Laboratory	dust	$9.6\text{--}1.2 \times 10^{-4}$	TiO ₂ , RH (15-80%), T=298 K, [NO ₂] ₀ =100 ppb, Irradiation=16 Wm ⁻²	Gustafsson et al., ²⁵
Laboratory	dust	$8.1 \times 10^{-8}\text{--}2.3 \times 10^{-7}$	Kaolinite, T=298 K, RH=0%, [NO ₂] ₀ =0.56-8.8×10 ¹³ molecules cm ⁻³	Angelini et al., ²⁶
Laboratory	dust	7.0×10^{-9}	pyrophyllite, T=298 K, RH=0%, [NO ₂] ₀ =3×10 ¹⁴ molecules cm ⁻³	
Laboratory	dust	1.0×10^{-9}	Saharan dust, 1%TiO ₂ /SiO ₂ , SiO ₂ , T=295K,	Ndour et al., ²⁷
Laboratory	dust	1.0×10^{-6}	1%TiO ₂ /SiO ₂ , Irradiation=134 Wm ⁻²	
Laboratory	dust	8.9×10^{-9}	Saharan sand, T=295 K, RH=25%,	Nicolas et al., ²⁸
Laboratory	dust	$4.3\text{--}2.5 \times 10^{-9}$	CaCO ₃ , T=296 K, RH (0-70%),	Li et al., ²⁹
Laboratory	dust	2.0×10^{-8}	γ -Al ₂ O ₃ ^a , S _{BET} =1010 cm ² mg ⁻¹	
Laboratory	dust	7.7×10^{-6}	α -Fe ₂ O ₃ ^b , S _{BET} =23 cm ² mg ⁻¹	
Laboratory	dust	4.0×10^{-6}	γ -Fe ₂ O ₃ ^a , S _{BET} =500 cm ² mg ⁻¹	
Laboratory	dust	1.3×10^{-7}	TiO ₂ ^a , S _{BET} =500 cm ² mg ⁻¹	
Laboratory	dust	$< 4 \times 10^{-10}$	SiO ₂ , S _{BET} =230 cm ² mg ⁻¹	

Laboratory	dust	1.2×10^{-5}	MgO ^b , S _{BET} =150 cm ² mg ⁻¹	
Laboratory	dust	2.2×10^{-5}	CaO ^b , S _{BET} =39 cm ² mg ⁻¹	
Laboratory	dust	2.1×10^{-6}	China loess ^b , S _{BET} =110 cm ² mg ⁻¹	
Laboratory	dust	1.2×10^{-6}	Saharan sand ^b , S _{BET} =31 cm ² mg ⁻¹	
Laboratory	dust	2×10^{-8}	Al ₂ O ₃ , S _{BET} =1010 cm ² mg ⁻¹ , T=298K,	
Laboratory	dust	7×10^{-7}	Fe ₂ O ₃ , S _{BET} =2300 cm ² mg ⁻¹ , T=298K,	Underwood et al., ³⁰
Laboratory	dust	1×10^{-7}	TiO ₂ , S _{BET} =5000 cm ² mg ⁻¹ , T=298K,	
Laboratory	dust	9.7×10^{-6}	α-Fe ₂ O ₃ ^b , S _{BET} =18 cm ² mg ⁻¹	Underwood et al., ³¹
Laboratory	dust	1.2×10^{-9} - 2.6×10^{-8}	Al ₂ O ₃ , T=299 K, [NO ₂] ₀ =10 ¹³ -10 ¹⁵ molecules cm ⁻³	Börensén et al., ³²
Laboratory	dust	6.2×10^{-7}	Saharan sand, T=298 K, S _{BET} =500 cm ² mg ⁻¹	Ullerstam et al., ³³
Laboratory	dust	0.6 - 2.4×10^{-8}	NO ₂ (35-200 ppb), RH (15-50%), irradiation=1.5×10 ¹⁵ photons cm ⁻² s ⁻¹ ,	Dupart et al., ³⁴
Laboratory	dust	1.4×10^{-7}	Kaolin, [NO ₂] ₀ =150 ppb, T=298 K, RH=7%	
Laboratory	dust	4.4×10^{-8}	Kaolin, [NO ₂] ₀ =150 ppb, T=298 K, RH=74%	Liu et al., ³
Laboratory	dust	1.6×10^{-6}	Hematite, [NO ₂] ₀ =150 ppb, T=298 K, RH=7%	

Laboratory	dust	2.8×10^{-7}	Hematite, $[\text{NO}_2]_0 = 150$ ppb, $T = 298$ K, $\text{RH} = 74\%$	
Laboratory	dust	5.3×10^{-6}	MgO (SO_2 -aged), $[\text{NO}_2]_0 = 100$ ppb	Ma et al., ⁴
Laboratory	dust	$1.0\text{-}2.9 \times 10^{-6}$	MgO, SO_2 (40-100 ppb), $[\text{NO}_2]_0 = 100$ ppb	
Laboratory	dust	$9.9 \times 10^{-6}\text{-}1.3 \times 10^{-4}$	TiO_2 , NO_2 (34-400 ppb), $T = 295$ K, $\text{RH} = 15\%$	Dyson et al., ³⁵
Laboratory	humic	$2.6\text{-}3.7 \times 10^{-6}$	NO_2 (5-100 ppb), RH (0-50%), $T = 296$ K	Stemmler et al. ³⁶
Laboratory	humic	$< 1 \times 10^{-7}$	Dark, NO_2 (2.7-280 ppb)	Stemmler et al., ³⁶
Laboratory	humic	1.8×10^{-6}	actinic flux = 1.0×10^{17} photons $\text{cm}^{-2} \text{s}^{-1}$, NO_2 (2.7-280 ppb)	
Laboratory	humic	$1.7\text{-}4.4 \times 10^{-6}$	Irradiation (68.5-194.5 W/m^2)	
Laboratory	humic	1.9×10^{-7}	Dark	
Laboratory	humic	$4.3\text{-}1.6 \times 10^{-6}$	NO_2 (30-160 ppb), Irradiation = 194.5 W/m^2 , $T = 298$ K, $\text{RH} = 22\%$	Han et al., ⁵
Laboratory	humic	3.8×10^{-6}	T (278-308 K), $\text{RH} = 22\%$, $[\text{NO}_2]_0 = 30$ ppb, Irradiation = 194.5 W/m^2	
Laboratory	humic	$3.4\text{-}6.3 \times 10^{-6}$	$T = 298$ K, RH (7-70%), $[\text{NO}_2]_0 = 30$ ppb, Irradiation = 194.5 W/m^2	
Laboratory	grime	$1.1\text{-}5.8 \times 10^{-6}$	$T = 296$ K, RH (0-90%), $[\text{NO}_2]_0 = 46$ ppb, actinic flux = 2.6×10^{15} photons $\text{cm}^{-2} \text{s}^{-1}$	Liu et al., ³⁷
Laboratory	glass	$1.0\text{-}2.7 \times 10^{-7}$	$T = 296$ K, RH (0-90%), $[\text{NO}_2]_0 = 46$ ppb	

Laboratory	grime	5.7×10^{-7} - 4.6×10^{-6}	RH (0-90%), actinicflux= 2.6×10^{15} photons $\text{cm}^{-2} \text{s}^{-1}$	Liu et al., ³⁸
Laboratory	grime	3.2×10^{-6} - 1.1×10^{-6}	NO ₂ (40-120 ppb), RH=60%, actinicflux= 2.6×10^{15} photons $\text{cm}^{-2} \text{s}^{-1}$	
Laboratory	glass	1×10^{-8}	Dark, RH=60%, [NO ₂] ₀ =50 ppb	Liu et al., ³⁹
Laboratory	glass	1.5×10^{-7} - 1.5×10^{-6}	T=296 K, RH (0-90%), Irradiation=8 Wm^{-2}	
Laboratory	grime	2.3 - 4.1×10^{-6}	T=296 K, RH (0-90%), [NO ₂] ₀ =50 ppb, Irradiation=8 Wm^{-2}	
Laboratory	ice	$< 5 \times 10^{-6}$	T (193-243 K)	Saastad et al., ⁴⁰
Laboratory	OA	3 - 7×10^{-6}	Catechol, RH (2-30%), T=298K, NO ₂ (70-103ppb)	Woodill et al., ⁴¹
Laboratory	OA	2.2 - 8.8×10^{-7}	Gentisic acid, tannic acid, UV/Vis light, [NO ₂] ₀ =76 ppb	Sosedova et al. ⁴²
Laboratory	OA	$< 5 \times 10^{-7}$	Solid 1,2,10trihydroxyanthracene, [NO ₂] ₀ =40 ppb	Arens et al. ⁴³
Laboratory	OA	$< 1 \times 10^{-7}$	Solid pyrene, dark	Brigante et al. ⁴⁴
Laboratory	OA	3.5×10^{-6}	Solid pyrene, near-UV	
Laboratory	OA	$< 5 \times 10^{-7}$	pinene/O ₃ , O ₃ =33 ppm, T=298 K, RH=55%	Bröske et al. ⁴⁵
Laboratory	sea salt	2.8 - 3.7×10^{-4}	Deliquesced NaCl	Harrison et al., ⁴⁶
Laboratory	sea salt	5.5×10^{-7} - 1.3×10^{-6}	Chinese sea salt, RH (0-20%), [NO ₂] ₀ = 1.96×10^{15} molecules cm^{-3}	Ye et al. ⁴⁷

Laboratory	sea salt	6×10^{-5}	NaCl, T=298 K, $[\text{NO}_2]_0 = 2.0 \times 10^{14} \text{ molecules cm}^{-3}$	Vogt et al. ⁴⁸
Observation	Night	$1\text{-}3 \times 10^{-6}$	Beijing, 2020.01-2020.03	Zhang et al., ⁴⁹
Observation	Night	5.9×10^{-6}	Svalbard, 2010.04,	Spataro et al., ⁵⁰
Observation	Night	$6.9 \times 10^{-6}\text{-}1.4 \times 10^{-5}$	Nanjing, 2017.12-2018.2	Liu et al., ⁵¹
Observation	Night	6.4×10^{-6}	Shijiazhuang, 2020.01	Liu et al., ⁵²
Observation	Night	$2.3\text{-}7.6 \times 10^{-5}$	Beijing, 2018.04	Zhang et al., ⁵³
Observation	Night	2.6×10^{-5}	Beijing, 2018.11, Aerosol surface	Zhang et al., ⁵⁴
Observation	Night	1.3×10^{-6}	Beijing, 2018.11, Ground surface	
Observation	Night	2.27×10^{-6}	Beijing, 2019.01-2024.01	This study
Model simulation	WRF- Chem	$1 \times 10^{-6}\text{-}2 \times 10^{-5} \times (\text{illumination}/400)$	Hong Kong, 2011.8, suburban area; 42% (Ground) and 3% (Aerosol) for HONO sources.	Zhang et al., ⁵⁵
Model simulation	CMAQ	$5 \times 10^{-5}\text{-}1 \times 10^{-4} \times (\text{illumination}/400)$	Pearl River Delta, 2017.1, suburban area; 81% (Night) and 52% (Day) for HONO sources.	Fu et al., ⁵⁶
Model simulation	Box model	$8 \times 10^{-6}\text{-}1 \times 10^{-4} \times (\text{J}_{\text{NO}_2}/\text{J}_{\text{NO}_2, \text{noon}})$	Wangdu, 2014.6, rural site; 46% (6:00-8:00) for HONO sources.	Liu et al., ⁵⁷

Model simulation	WRF-Chem	5×10^{-6} - $2.5 \times 10^{-4} \times J_{NO2}$	Beijing, 2006.8, urban area; 27% (Ground) and 20% (Aerosol) for HONO sources.	Zhang et al., ⁵⁸
Model simulation	WRF-Chem	5×10^{-6} - $2.5 \times 10^{-4} \times J_{NO2}$	Wangdu, 2017.11, rural site; 28% (Ground) and 39% (Aerosol) for HONO sources.	Zhang et al., ⁵⁹
Model simulation	Box model	8×10^{-6} - 2×10^{-5}	Changzhou, 2017.4, urban area; 54.4% (Night) and 34.7% (Day) for HONO sources.	Shi et al., ⁶⁰
Model simulation	Box model	1×10^{-6} - 1.35×10^{-5}	Hebei, 2017.12, rural site More than 36% (Daytime) for HONO sources.	Xue et al., ⁶¹
Model simulation	Box model	4.5×10^{-5}	Beijing, 2018.4, urban area; 28% (Ground) and 45% (Aerosol) for HONO sources.	Zhang et al., ⁵³
Model simulation	Box model	1×10^{-6} - 2×10^{-5}	Nanjing, 2015.12, urban area; 11% (Ground) and 35% (Aerosol) for daytime HONO.	Zheng et al., ⁶²
Model simulation	Box model	1.2×10^{-6} - $0.6 \times 10^{-4} \times (J_{NO2}/J_{NO2,noon})$	Beijing, 2018.11-2019.1, urban area; 24.9% (Ground) and 29.7% (Aerosol) for daytime HONO.	Liu et al., ⁶³
Model simulation	WRF-Chem	5×10^{-6} - 5×10^{-5}	Beijing, 2018.10, urban area; 50%-80% (Ground) and <10% (Aerosol) for HONO sources.	Zhang et al., ⁶⁴
Model	Box	2×10^{-6} - 2.5×10^{-5}	Taizhou, 2018.5-2018.6, suburban site;	Ye et al., ⁶⁵

simulation	model		55% (Night) and 71% (Day) for HONO sources.	
Model	Box	5×10^{-6} - 2×10^{-5}	Beijing, 2021.3, urban area;	Zhang et al., ⁶⁶
simulation	model		63%-76% for HONO sources.	
Model	Box	8.25×10^{-6} - 1.5×10^{-5}	Beijing, 2021.10, urban area;	Xuan et al., ⁶⁷
simulation	model		31.3%-85.6% (Ground) and <3% (Aerosol) for HONO sources.	
Model	Box	1.3×10^{-6} - 3.9×10^{-5}	Beijing, 2018.11, urban area;	Zhang et al., ⁵⁴
simulation	model		68%-91% (severe pollution episodes) for HONO sources.	

Note: ^a Sample holder area = 11.88 cm²; ^b Sample holder area = 5.07 cm²; ^c OC_R means OC with a reduced state.

3. Line 59: It should be noted that only the γ_{NO_2} measured by flow tube showed an increasing trend with decreasing concentration. As for the reactive uptake coefficient determined by FTIR measuring nitrate formation, it increases with increasing concentrations. (Gao et al, Journal of Geophysical Research: Atmospheres, 2021, 126, e2021JD034694.)

Response: Thank you for your good suggestion. We agree with you that the reactive uptake coefficient determined by FTIR measuring nitrate formation increases with increasing concentration of NO_2 (from 2.46×10^{13} to 1.72×10^{15} molecules cm^{-3}) as reported by Gao et al.¹⁴. However, a negative dependence of γ_{NO_2} on NO_2 concentration (from 1.48×10^{12} to 2.09×10^{13} molecules cm^{-3}) has also been observed using a flow tube, conducted in the same work. This should be ascribed to the difference in surface coverage of NO_2 on samples, leading to different reaction orders or mechanisms under different reaction conditions. We think it is more reasonable to take the kinetics that are measured at the NO_2 concentrations close to ambient values.

In lines 59-64 in the revised manuscript, we added a sentence “Liu et al.¹⁸ and Gao et al.¹⁹ observed that high NO_2 concentrations partially inhibited the γ_{NO_2} owing to surface saturation according to the Langmuir-Hinshelwood mechanism, measured using a flow tube at NO_2 concentrations close to ambient values, whereas, high NO_2 concentrations facilitate the uptake of NO_2 measured using a Diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS)¹⁹”.

4. Some previous studies reported the γ_{NO_2} values based on short-term field observations. To highlight the advantages of the long-term observational dataset, is it possible to show those representative γ_{NO_2} values in Fig. 1b? A simple discussion may be added to the text.

Response: Thank you for your valuable suggestion. We agree that highlighting the advantages of the long-term observational dataset is important. However, the periods of the short-term field observations reported in the literature do not align with the time series in this study, making it inconvenient to directly incorporate those representative

γ_{NO_2} values into **Fig. 1b** for comparison. Nevertheless, we averaged the hourly data in five years in this study to generate an hourly mean dataset in one year and replaced the date with the order of a day in one year (**Figure R3**). As shown in **Figure R3** (**Supplementary Fig. 2**), the derived γ_{NO_2} across short-term campaign observations varies greatly, whereas most of those γ_{NO_2} values are in the range of this study. This highlights the unique advantages of our long-term dataset in providing a more robust and comprehensive understanding of the temporal variations in γ_{NO_2} .

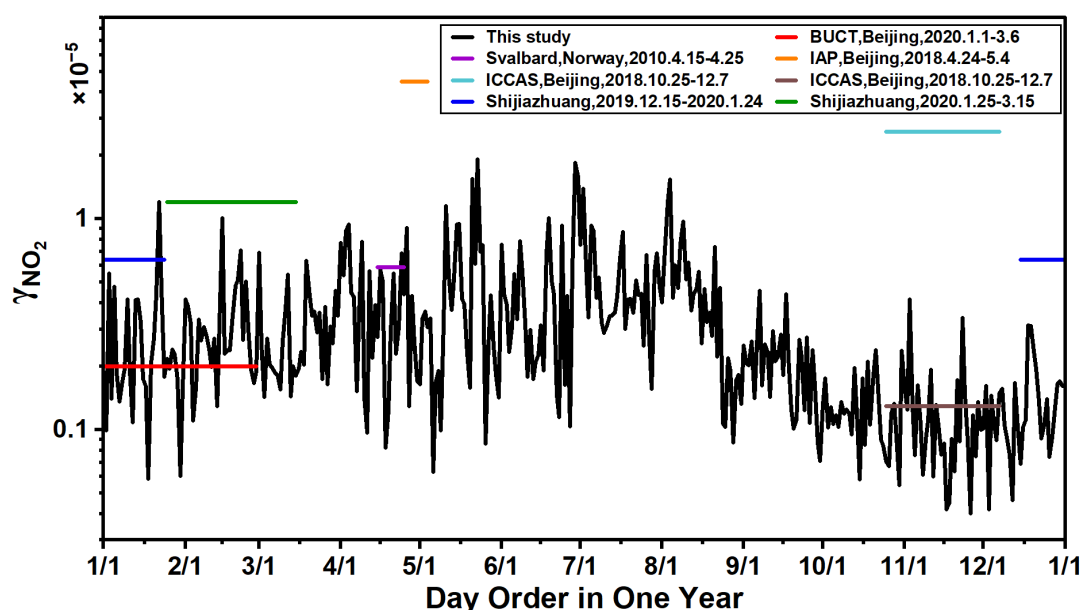


Figure R3. Comparison of the γ_{NO_2} time series from this study with short-term observational values reported in the literature.

In lines 113-116 in the revised manuscript, we added a sentence “As shown in Supplementary Fig. 2, the derived γ_{NO_2} on ambient aerosol particles across short-term campaign observations varies greatly, whereas most of those γ_{NO_2} values are in the range of this study.”

5. Line 157: Please define the period of nocturnal γ_{NO_2} .

Response: Thank you for your good suggestion. We defined it in lines 410-411 in the revised manuscript “Thus, we only focus on the nocturnal γ_{NO_2} to form HONO on particle surfaces when UVB is less than 0.01 W m^{-2} .”.

6. In Figs. 2 and 3, relative importance and SHAP values were used to evaluate the role of factors in the γ_{NO_2} and aerosol pH. However, it is unclear how are these values obtained in the model. Please clarify it in the method section.

Response: Thank you for your good suggestion. The SHAP values in our study were computed using the SHAP (SHapley Additive exPlanations) library, which is a widely used tool for interpreting the contributions of input features in machine learning models. The process involved the following steps: (1) Model Training: A random forest model was trained and fitted using our training dataset. (2) SHAP Value Calculation: We utilized the TreeExplainer from the SHAP library, which is specifically designed for tree-based models. The trained random forest model was passed to the TreeExplainer, and SHAP values were calculated using *shap_values = explainer.shap_values(X)*, where *X* is the input feature matrix. (3) Analysis and Visualization: The computed SHAP values, which represent the contribution of each feature to the model's predictions, were aggregated and visualized. This process allowed us to quantify and illustrate the relative importance of each input variable. These methods were used to obtain the SHAP values mentioned in the manuscript, which were then used to analyze the importance of variables in the model. The Relative importance is the mean of absolute SHAP values.

In the revised Supplementary Note 1, we added the details about how are SHAP values obtained in the model. The added content is as follows:

“The SHAP (SHapley Additive exPlanations) values were calculated using the SHAP library, a widely adopted tool for interpreting feature contributions in machine learning models. The computation process included the following steps: (1) Model Training: A random forest model was trained on the dataset, serving as the basis for SHAP value computation. (2) SHAP Value Calculation: Using the TreeExplainer class from the SHAP library, which is optimized for tree-based models, we computed the SHAP values for the input features. Specifically, the trained model was passed to the explainer, and SHAP values were obtained using *explainer.shap_values(X)*, where *X* represents the feature matrix. (3) Analysis and Visualization: The resulting SHAP

values, indicative of each feature's contribution to model predictions, were summarized and visualized to quantify feature importance. This approach enabled us to systematically assess and communicate the relative influence of each variable in the model.”

The relative importance is the mean of absolute SHAP values. In lines 184-185 in the revised manuscript, we revised the sentence to clarify the meaning of relative importance “Thus, we obtained the relative importance (the mean of absolute SHAP values) of various factors affecting γ_{NO_2} ”.

7. The results of machine learning look good for both the γ_{NO_2} and aerosol pH. How do you make sure they are not overfitted? More details to reduce overfitting should be added.

Response: Thank you for your good suggestion. To reduce the risk of overfitting in the RF algorithm and improve the model's generalization ability, we optimized the number of decision trees to minimize variance and bias. Then, we performed 10-fold cross-validation i.e., by randomly dividing the dataset into 10 subsets and alternately taking one subset as testing data and the rest as training data. By doing this, every data point has an equal chance of being trained and tested. Then all network configuration parameters (i.e., N estimators, Max depth, min split, and so on) were modified by a trial and error method to obtain the optimized network structure. The optimized RF model parameters are shown in Supplementary Table 5.

In the revised Supplementary Note 1, we revised the paragraph “To reduce the risk of overfitting in the RF algorithm and improve the model's generalization ability, we optimized the number of decision trees to minimize variance and bias. In addition, 10-fold cross-validation (CV) along with grid search was performed to obtain more stable predictions through random sampling and feature selection. Briefly, we randomly divided the data into 10 subsets, then alternately took one subset as testing data along with the rest as training data. By doing this, every data point generally has an equal chance of being trained and tested. And then all network configuration parameters (i.e.,

N estimators, Max depth, min split, and so on) were modified by a trial and error method to obtain the optimized network structure. The optimized RF model parameters are shown in Supplementary Table 5. The model's performance was evaluated based on the correlation coefficient (R^2), root mean square error (RMSE), and mean absolute error (MAE). The Shapley additive explanation (SHAP value) is used to quantify the relative contributions of the driving factors of pH and γ_{NO_2} in Beijing.”

8. A paper has reported the seasonal variations of aerosol pH in Beijing (Atmos. Chem. Phys. 2019, 19 (12), 7939-7954). It's better to add some comparison in line 224.

Response: Thank you for your good suggestion. In lines 242-247 in the revised manuscript, we added a sentence “The pH values observed in this study show a similar seasonal variation, i.e., 4.5 ± 0.7 (winter) $> 4.4 \pm 1.2$ (spring) $> 4.3 \pm 0.8$ (autumn) $> 3.8 \pm 1.2$ (summer), observed between 2016 and 2017 (around 7 months) in Beijing⁴⁶ and Shanghai⁴⁹. Whereas, slight differences are observed among different seasons. These discrepancies may stem from differences in the data collection periods (7 months vs. 5 years) and changes in air pollution levels”.

9. Temperature is the most important factor governing aerosol pH in Fig. 3, while AN and AS are the second and third ones. The main conclusion suggests that the ratio of AN/AS drives the internal annual evolution of γ_{NO_2} . A clearer explanation is required to clarify the role of temperature in the aerosol pH and the γ_{NO_2} . More discussion might be helpful about the single-factor analysis in supplementary Fig. 9.

Response: Thank you for your valuable comments. The aerosol pH is the positive proportion to the concentration of H^+ in a solution, while the rate constant of the dissociation reaction of acids to release H^+ is exponentially dependent on the reciprocal of temperature¹⁵, i.e.,

$$k_{\text{diss}}(T) = \exp \left[-\frac{\sum_i v_i \mu_i^0(T)}{RT} \right] \quad (\text{R1})$$

where $k_{\text{diss}}(T)$ is the dissociation reaction rate of acids to release H^+ , R is the universal gas constant, $\mu_i^0(T)$ is the standard chemical potential of species i at 1 atm pressure and

temperature T (in K).

Thus, temperature shows the largest influence on the aerosol pH. It should be pointed out that the annual mean temperature is almost constant for those five years, while the temperature difference is around 26.4 K between winter and summer. This strongly suggests that the temperature dependence of pH should be related to seasonal temperature changes.

To rule out the contribution of temperature to aerosol pH, we further analyzed the mean aerosol pH during the same month (October) from 2019 to 2023. As shown in **Figure R4 (Supplementary Fig. 9a)**, the mean pH shows significant differences among different years at a 0.05 level, while the mean temperature does not exhibit significant changes. This further suggests that the interannual variations in aerosol pH should be dominantly driven by changes in aerosol composition. This is well consistent with the single-factor analysis results that temperature is the dominant factor affecting ΔpH among different seasons (**Supplementary Fig. 9c**), while the chemical composition is the dominant one between different years (**Supplementary Fig. 9b**).

Similarly, temperature is also identified as a factor affecting γ_{NO_2} , consistent with findings reported in the literature¹¹, but less important compared to chemical factors. Given that temperature has remained relatively stable over the past five years, it is considered unlikely to be the primary driver behind the annual decline in γ_{NO_2} . Additionally, the influence of temperature on γ_{NO_2} may be indirectly mediated through aerosol pH and activation energy of the reaction.

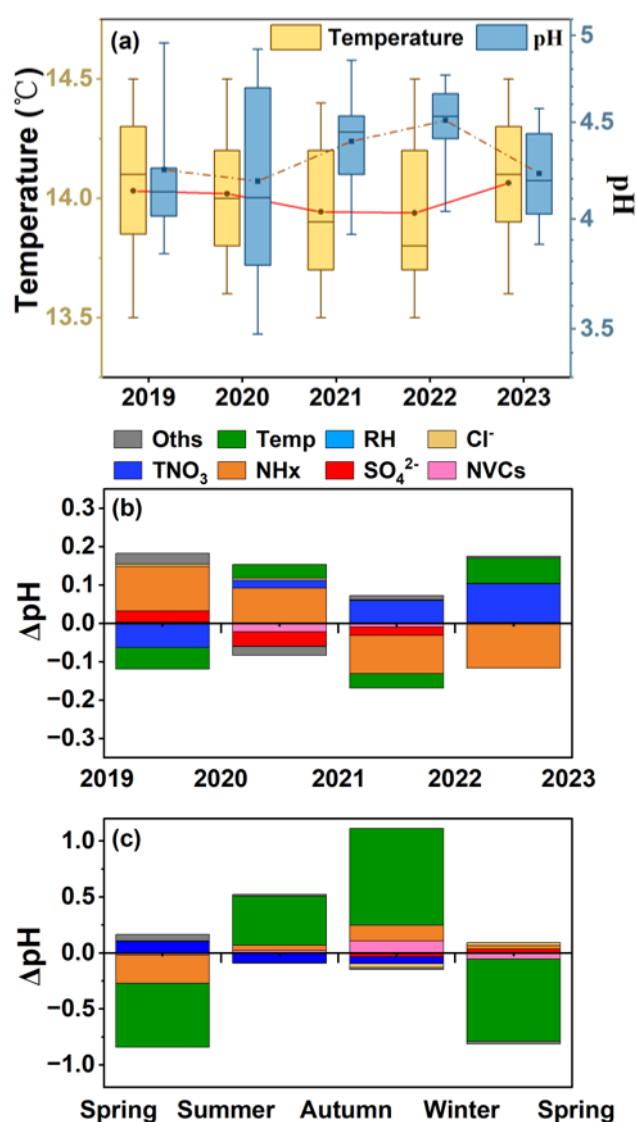


Figure R4. Driver Factor Analysis of pH and the fractional contribution of individual drivers to the variations in aerosol pH from average conditions (i.e., averages of all observational data) during 2019–2023. (a) Temporal Variations in Temperature and pH During the Same Season (October) from 2019 to 2023: Significant Differences in pH Mean and Variance but Not in Temperature Parameters at the 0.05 Significance Level; (b) Annual variation; (c) Seasonal variation. The meanings of the abbreviations: Temp, temperature; RH, relative humidity; TNO₃, total nitrate; NHx, total ammonia; NVCs, non-volatile cations. The center lines in the box plots represent the median; the dots indicate the mean; the whiskers mean 1.5 times the interquartile range (IQR); and the boxes span the 25th to 75th percentiles.

In lines 214-216 in the revised manuscript, we revised the sentence “Although laboratory studies have shown minimal effects of temperature on γ_{NO_2} ¹⁷, our results suggest that temperature does affect the uptake of NO₂ in the real atmosphere, but is less important compared to chemical factors”.

In lines 254-256 in the revised manuscript, we added a sentence “This is consistent with the fact that the rate constant of the dissociation reaction of acids to release H⁺ is exponentially dependent on the reciprocal of temperature⁵⁰”.

In lines 283-289 in the revised manuscript, we added a paragraph “In addition, as shown in Supplementary Fig. 9a, the mean pH in the same month (October) from 2019 to 2023 shows significant differences among different years at a 0.05 level, while the mean temperature does not exhibit significant changes, to decrease the contribution of temperature to aerosol pH. This is well consistent with the single-factor analysis results that temperature is the dominant factor affecting ΔpH among different seasons (Supplementary Fig. 9c), while the chemical composition is the dominant one between different years (Supplementary Fig. 9b)”.

Reviewer #3

Zhang et al. have conducted studies highlighting the significance of aerosol chemistry in the heterogeneous formation of HONO. Through the combination of 5-year observational with machine learning, this research sheds new light on HONO heterogeneous formation and dynamic NO₂ uptake coefficient on aerosols in the real atmospheric environment, which is essential for comprehending urban air quality, atmospheric oxidizing capacity, and the mechanisms of secondary pollutant formation. The manuscript contents look rich and well fits into the scope of Nat. Commun. It is suitable to publish in Nat. Commun after the following questions have been addressed.

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

1. In line 102, the mean γ_{NO_2} value is $2.27 \pm 2.58 \times 10^{-6}$, but in Table S1, it is 2.26. The author should check and correct it.

Response: Thank you for your good suggestion. We have double-checked the numbers. It should be $2.27 \pm 2.58 \times 10^{-6}$.

In the revised **Supplementary Table 1**, we have corrected it.

2. In line 125, the term “HONO yield” should be changed to “HONO formation rate” as shown in Fig. 2.

Response: Thank you for your good suggestion. We have modified it in the revised manuscript to “**HONO formation rate**” in [lines 133-134](#).

3. In lines 157-160, the author used ALWC rather than RH as input to train and test by RF when evaluating the influence factors affecting the γ_{NO_2} . However, Fig. S4 showed the variations of γ_{NO_2} under different RH. As we all know, ALWC would better reflect the real aerosol physiochemical properties. But when evaluating the influence factor of pH change, RH was as the input rather than ALWC. The authors should unify it or give a proper explanation.

Response: Thank you for your suggestion. We agree that ALWC better reflects the real physicochemical properties of aerosols, and thus we used ALWC instead of RH as the input to train and test the random forest (RF) model when evaluating the factors influencing γ_{NO_2} . However, when assessing the influence of pH changes, we chose RH as the input rather than ALWC. This is because pH is calculated using the formula:

$$\text{pH} = -\log_{10} \frac{1000\gamma_{\text{H}^+}c_{\text{H}^+}}{\text{ALWC}} \quad (\text{R2})$$

where γ_{H^+} is the activity coefficient of H^+ , c_{H^+} is the concentration of H^+ . Thus, pH value has a quantitative relationship with ALWC. Therefore, ALWC is not suitable as an input parameter for the model. Additionally, our calculations revealed that the model performs better when RH is used as the input than ALWC. As a result, we used RH and ALWC as input variables in the two models, respectively, based on the specific requirements of each analysis.

In Supplementary Note 1. Random forest (RF), we added a paragraph to clarify this point “It should be pointed out that pH value has a quantitative relationship with ALWC according to eq (6). Therefore, RH is more suitable as an input parameter for the model than ALWC although reflects the real physicochemical properties of aerosols”.

4. Based on RF results, the author claimed the inconsistent trend between NO_2 and γ_{NO_2} would promote the uptake of NO_2 in lines 202-206. This may indicate that in the ambient, the NO_2 concentration is saturated for NO_2 heterogeneous uptake or reaction. Sensitivity tests would help to explain this phenomenon.

Response: Thank you for your good suggestion. Here, we did not intend to suggest that the NO_2 concentration is saturated for NO_2 heterogeneous uptake or reaction in the atmosphere. Our statement “It is important to note that annual mean concentrations of NO_2 in Beijing were 18.9 ± 14.4 , 15.5 ± 12.8 , 19.4 ± 13.2 , 12.2 ± 10.1 , and 13.6 ± 10.7 ppb, respectively, from 2019 to 2023. This suggests that a downtrend of NO_2 should facilitate the uptake of NO_2 , while it is in contrast with the decreased γ_{NO_2} ” (in lines 221-225 in the revised manuscript) aimed to highlight that the slight decrease in

ambient NO₂ concentrations should facilitate the uptake of NO₂, indicating a slight increase in γ_{NO_2} if NO₂ concentration decreasing, according to previous findings that lower NO₂ concentrations correspond to higher γ_{NO_2} values because of the weakened saturation effect on aerosol surfaces. However, the annual variation of NO₂ concentrations generally shows a downward trend, and NO₂ showed the greatest relative importance to γ_{NO_2} based on RF simulations. Thus, we would expect γ_{NO_2} to exhibit an increasing trend over time. However, the γ_{NO_2} shows a decreasing trend. This discrepancy suggests that changes in NO₂ concentration cannot explain the observed annual decrease in γ_{NO_2} . Additionally, as can be observed from the distribution of NO₂ feature values in **Figure R5 (Figure 2d)**, higher feature values are concentrated in areas where SHAP values are below zero, and vice versa. This indeed reflects the sensitivity results you suggested. This means that an increase in NO₂ concentration imposes a certain inhibitory effect on γ_{NO_2} , which indirectly supports our viewpoint.

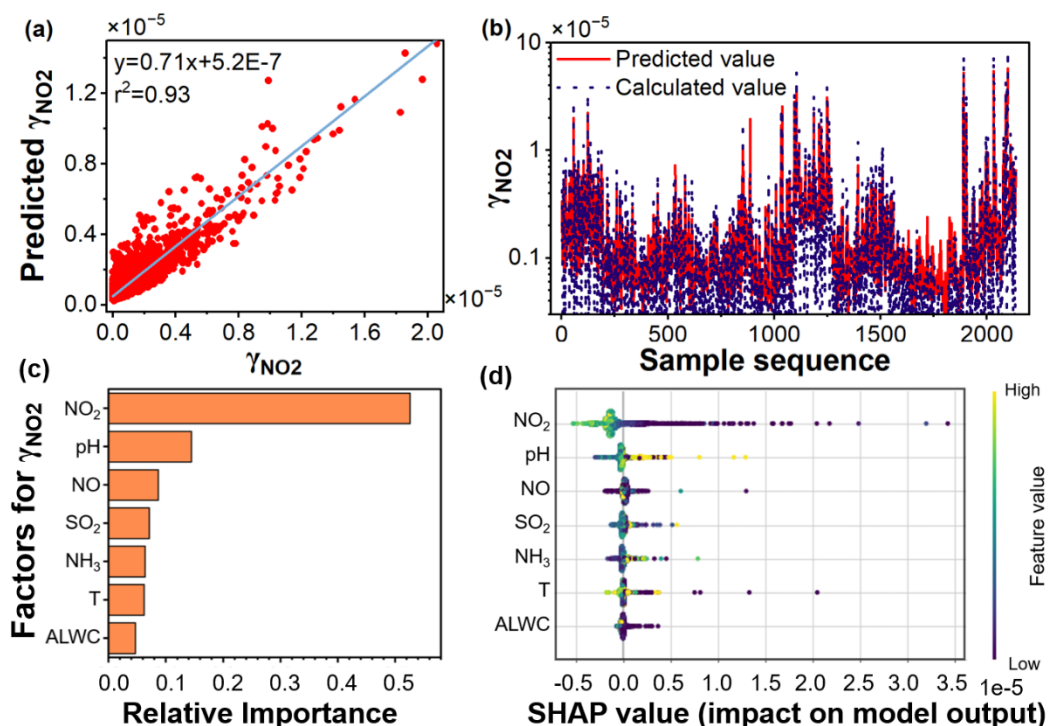


Fig. R5. Performance of the RF model for predicting γ_{NO_2} and the relative importance of individual factors. (a) The linear relationship between the observed γ_{NO_2} and the predicted γ_{NO_2} ; (b) the time series of the observed and the predicted γ_{NO_2} ;

(c) the relative importance of each factor for the γ_{NO_2} ; (d) the SHAP value of each feature variable.

5. In lines 250-253, the RF results showed that pH was largely influenced by the temperature. The annual trend of temperature is stable, but shows obvious seasonal variations. The author suggested that temperature is unlikely to drive the increase in aerosol pH from 2019 to 2023 due to the interannual increase trend of pH. Maybe the relationship between temperature and pH in the same season but different years would help to clarify this, given that little uncertainty of temperature in the same season.

Response: Thank you for your valuable comments. To address the potential influence of temperature on pH, we further analyzed the temporal variations in temperature and pH during the same month (October) from 2019 to 2023 (Figure R4). Through a comparative study of the five-year dataset, we found that at the 0.05 significance level, both the overall mean and variance of pH showed significant differences, while the overall mean and variance of temperature did not exhibit significant changes. Furthermore, in different years, even under similar temperature conditions, significant differences in pH were observed, while the annual trend of temperature remained relatively stable. These results suggest that temperature is unlikely to be the primary driver of the interannual variations in aerosol pH.

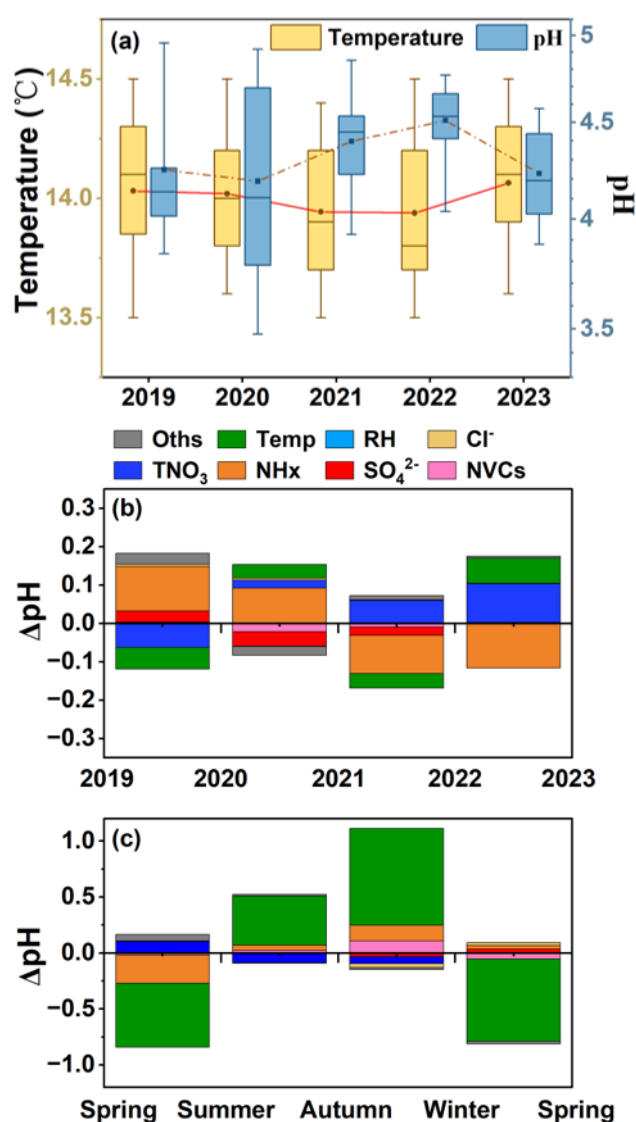


Figure R4. Driver Factor Analysis of pH and the fractional contribution of individual drivers to the variations in aerosol pH from average conditions (i.e., averages of all observational data) during 2019–2023. (a) Temporal Variations in Temperature and pH During the Same Season (October) from 2019 to 2023: Significant Differences in pH Mean and Variance but Not in Temperature Parameters at the 0.05 Significance Level; (b) Annual variation; (c) Seasonal variation. The meanings of the abbreviations: Temp, temperature; RH, relative humidity; TNO₃, total nitrate; NHx, total ammonia; NVCs, non-volatile cations. The center lines in the box plots represent the median; the dots indicate the mean; the whiskers mean 1.5 times the interquartile range (IQR); and the boxes span the 25th to 75th percentiles.

In lines 283-289 in the revised manuscript, we added a paragraph “In addition, as shown in Supplementary Fig. 9a, the mean pH in the same month (October) from 2019 to 2023 shows significant differences among different years at a 0.05 level, while the mean temperature does not exhibit significant changes, to decrease the contribution of temperature to aerosol pH. This is well consistent with the single-factor analysis results that temperature is the dominant factor affecting ΔpH among different seasons (Supplementary Fig. 9c), while the chemical composition is the dominant one between different years (Supplementary Fig. 9b)”

6. In Section 3.2, the authors suggested the annual increase in aerosol pH contributed to the decline in γ_{NO_2} , which indicated the important role of aerosol acidity on the uptake of NO_2 on aerosol surface. Thus, the annual variations of NH_3 would also affect the trend of γ_{NO_2} , as the promotional effect of NH_3 for nitrogen dioxide (NO_2) uptake on the wet aerosol surface had been reported in recent studies (eg. doi.org/10.1016/j.aosl.2024.100491). Related discussion was suggested to provided more evidence to the decline in γ_{NO_2} .

Response: Thank you for your insightful comments. We agree that NH_3 can promote the uptake of NO_2 on the surface of wet aerosols, as suggested by recent studies¹⁶. However, based on our analysis, the influence of NH_3 on γ_{NO_2} appears to be indirect, primarily through its role in regulating aerosol pH. Some studies have suggested that the distribution of $\text{NH}_4^+/\text{NH}_3$ can regulate the aerosol pH, thus affecting the conversion of NO_2 to HONO ¹⁷. Our study found that NH_4^+ is a key factor affecting aerosol pH, which in turn plays a critical role in driving the variations in γ_{NO_2} . While NH_3 may influence γ_{NO_2} through pH adjustments, its annual variations do not directly indicate the trends in γ_{NO_2} . In lines 206-208 in the revised manuscript, we have pointed out “Additionally, SO_2 and NH_3 can not only compete with NO_2 for surface active sites but also alter the particle acidity^{41, 42}. Both SO_2 and NH_3 can react with NO_2 , impacting the NO_2 uptake process^{21, 43}”. Therefore, we focused our discussion on aerosol pH as the primary driver of the observed decline in γ_{NO_2} . We appreciate your suggestion and

will consider incorporating further discussion on this aspect in future work.

7. Fig. S8 was not cited in the manuscript. Please check it.

Response: Thank you for your careful review. Figure S8 is included in the Supporting Information (SI) to describe the annual variation characteristics of AS and AN, and it is not directly cited in the main manuscript. We corrected the order of **Supplementary Fig. 8** and adjusted **Supplementary Fig. 8** to **Supplementary Fig. 11** in the revised SI to make sure to properly cite the figures.

8. Given the content and style of Nature Communications, it appears that this journal typically does not include a dedicated “Conclusion” section. You should follow the journal's requirements and the format need to be revised.

Response: Thank you for your valuable comment. We understand that Nature Communications typically does not require a separate "Conclusion" section, but the journal allows for flexibility based on the needs of the research. We believe that the conclusion section in this manuscript effectively highlights the significance and value of our research, and thus we have chosen to include it as a separate section. We will ensure the format complies with the journal's requirements during the revision process.

9. In line 307, the author mentioned that “acidity can modify the phase state of gaseous precursors”, this statement would introduce much misunderstanding. Please clarify it.

Response: Thank you for your good suggestion. We have modified it in [lines 337-339](#) in the revised manuscript to “This aligns with previous studies showing that **aerosol** acidity can **influence the uptake of gaseous precursors onto particle surfaces** and the rates of related chemical reactions, thereby affecting secondary aerosol formation^{37,56}”.

10. Is the status of LOPAP stable through five-year observation? How is the homogeneity of the calibrated results and backgrounds among different calibrations?

Response: Thank you for your good comment. Based on our observations over five years, the stability of the LOPAP has been maintained at a consistent level. To

ensure the homogeneity of the calibrated results and backgrounds across different calibrations, we have implemented a rigorous calibration and maintenance protocol. Specifically, the instrument undergoes zero-point calibration every two days and a comprehensive maintenance procedure approximately once a month. This maintenance includes replacing components such as the peristaltic pump tubing, gas filter in the safety bottle, and liquid filter in the optical fiber pool. After each maintenance, the instrument is recalibrated to ensure that parameters such as the response signal, liquid flow rate, and gas flow rate remain within their set values. Frequent maintenance helps maintain the stability of the instrument.

For calibration, we use standard HONO solutions of known concentrations of nitrite. As shown in **Figure R6 (Supplementary Fig. 10)**, the response signals corresponding to two different concentrations of standard HONO solutions have remained stable over the years, demonstrating the robust stability of our instrument. These consistent results indicate that our calibration process effectively ensures the homogeneity of the data across different calibrations.

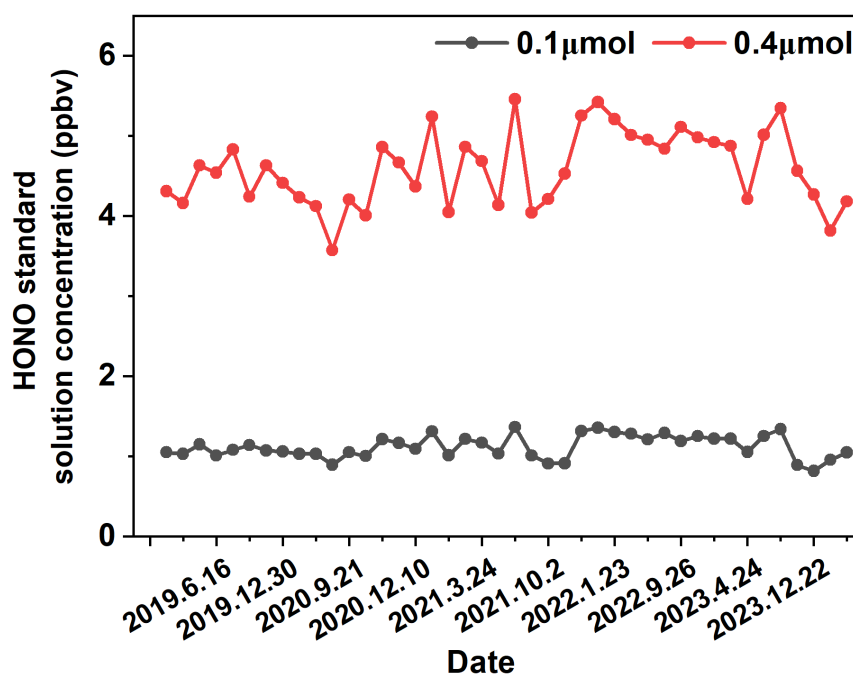


Figure R6. Time Series of Concentration-Response Signals for Calibrated Solutions from 2019 to 2023.

In lines 379-380 in the revised manuscript, we added a sentence “The status of the LOPAP is stable through five-year observation as shown in Supplementary Fig. 10”.

11. Refs 13 and 14, the author lists are not in a similar format. Please check all references, including authors, title, volume, page, etc. based on the requirements of Nat. Commun.

Response: Thank you for your suggestion. We have carefully checked all references to ensure they comply with the formatting requirements of Nature Communications. Regarding the author lists, we have standardized the format according to the journal's guidelines: for papers with fewer than five authors, all authors are listed in full; for papers with more than five authors, only the first author is listed, followed by "et al." Additionally, we have consolidated all references from the main text into a single "References" section at the end of the manuscript, as per the journal's formatting requirements.

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