

Supporting information of

Changing Aerosol Chemistry is Redefining HONO Sources

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Supplementary Note 1. Random forest (RF)

Random Forest (RF) is an ensemble learning model that combines multiple weak classifiers (decision trees) to build a strong classifier. It exhibits robustness and high accuracy in handling high-dimensional data and complex relationships. It assesses feature importance by calculating the contributions of each feature to decisions across all trees. RF is commonly used for both classification and regression tasks. In the RF model, a bagging algorithm is employed, which involves randomly selecting samples (with replacement) from the training dataset and their corresponding predictive features. Each decision tree is grown based on various decision rules that optimize the fit between the observed pollutant concentration (response variable) and its predictor features. The selection of predictor features for each tree node is randomized to achieve the best split. The predicted pollutant concentration is determined by aggregating the results of all individual decision trees using a weighted average. The bagging process helps reduce variance and mitigate overfitting in the model by averaging the predictions of the bootstrap samples. The input dataset is randomly divided into a training dataset (80% of the total data) for building the RF model and a test dataset (20% of the total data) for evaluating the model's performance on an unseen dataset. The RF model is an ensemble method consisting of many individual decision trees¹.

In our study, the parameters of the RF model are as follows: hourly concentrations of pH and γ_{NO_2} as dependent variables, trace gases (NO_2 , NO,

NH₃, SO₂), meteorological parameters (RH, T), chemical components, and properties (NH₄NO₃ (AN), (NH₄)₂SO₄ (AS), Ca²⁺, Mg²⁺, Na⁺, K⁺, Cl⁻, OA, Dust, pH, and ALWC) with the same temporal resolution as independent predictors. 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. The training set consists of a randomly selected 80% of the data, with the remaining 20% used as the test set. 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 (R²), 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_{NO2} in Beijing.

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 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.

Supplementary Note 2. Model performance evaluation

The evaluation metrics for the model can be found in Supplementary Table 5 and Figs. 2 and 3. The random forest model performed well in predicting the data compared to the observations in the dataset. These extremely high correlation values indicate a strong relationship between the predicted and observed values, demonstrating that the characteristics of the established model are excellent. Similarly, lower MAE (mean absolute error) and RMSE (root mean squared error) values indicate that our model performs well. Based on the verification of various indicators, we believe that the model has strong predictive ability.

Supplementary Note 3. Characteristics of AN and AS in Beijing from 2019 to 2023

The observation period spans from September 1, 2019, to December 31, 2023. Supplementary Fig. 1a shows the hourly average concentrations of PM_{2.5}, AS,

and AN. PM_{2.5} concentrations range from 1.0 to 662 $\mu\text{g m}^{-3}$, with an average of $37 \pm 39 \mu\text{g m}^{-3}$, slightly exceeding China's first-stage air quality standard of 35 $\mu\text{g m}^{-3}$ ⁹. AS concentrations range from 0.01 to 110 $\mu\text{g m}^{-3}$, with an average concentration of $5.0 \pm 6.7 \mu\text{g m}^{-3}$, while AN ranges from 0.01 to 120 $\mu\text{g m}^{-3}$, averaging $13 \pm 16 \mu\text{g m}^{-3}$. AS and AN contribute, on average, $14 \pm 20\%$ and $28 \pm 38\%$ to PM_{2.5}, respectively, with a combined average contribution of $42 \pm 26\%$. Supplementary Fig. 11 presents the absolute concentrations and relative contributions of AS and AN across different PM_{2.5} and relative humidity ranges. As pollution levels and relative humidity increase, so do the concentrations of AS and AN, with their combined contribution ranging from 27% to 52%. Compared to previous studies, the average contribution of AN to PM_{2.5} in Beijing is lower than the 40-66% observed in Salt Lake City, USA, during the winter of 2009, while the contribution of AS in Beijing is slightly higher than that observed in Salt Lake City (6.5%)¹⁰.

The average concentration of AN is highest in spring at $19 \pm 20 \mu\text{g m}^{-3}$, followed by autumn ($17 \pm 20 \mu\text{g m}^{-3}$) and winter ($13 \pm 15 \mu\text{g m}^{-3}$). Summer concentrations are significantly lower at $8.0 \pm 10 \mu\text{g m}^{-3}$. In contrast, AS concentrations show smaller seasonal variations. Average concentrations in spring, summer, autumn, and winter are 5.2 ± 6.0 , 5.0 ± 4.6 , 4.2 ± 5.0 , and $5.8 \pm 11 \mu\text{g m}^{-3}$, respectively. AS concentrations are significantly lower in autumn ($P < 0.05$), with no substantial differences between spring, summer, and winter. Seasonal variations in AS and AN concentrations closely match the trends of

sulfates and nitrates in Beijing^{11,12}. These differences are linked to the formation mechanisms of sulfates and nitrates. During the observation period, the annual average NH_3 concentration in Beijing was $11 \pm 6.6 \mu\text{g m}^{-3}$ (ranging from 0.30 to $55 \mu\text{g m}^{-3}$), similar to Xi'an⁸ but higher than in Shanghai¹³. Additionally, the molar ratio of cations to anions is 1.2 ± 0.13 , and the $\text{NH}_4^+/(2\text{SO}_4^{2-}+\text{NO}_3^-)$ ratio is 1.1 ± 0.16 . These results indicate that NH_3 neutralizes particulate sulfate and nitrate, suggesting that the formation of AS and AN is primarily controlled by sulfuric and nitric acid concentrations. This is consistent with previous studies indicating that SNA ($\text{SNA}=\text{NO}_3^-+\text{SO}_4^{2-}+\text{NH}_4^+$) formation in many regions of China is dominated by sulfuric and nitric acid¹⁴.

Supplementary Note 4. Drivers of aerosol pH variations

To investigate the drivers of aerosol pH changes, we conducted sensitivity experiments using the one-at-a-time method¹⁵ to assess the impact of various factors, including temperature, relative humidity, SO_4^{2-} , TNO_3 ($\text{HNO}_3 + \text{NO}_3^-$), NH_x ($\text{NH}_3 + \text{NH}_4^+$), Cl^- , and non-volatile cations (NVCs: Ca^{2+} , Mg^{2+} , Na^+ , K^+), on pH variations. Specifically, if the aerosol pH under Scenario I (pH_I) differs from that under Scenario II (pH_II), the pH difference ($\Delta\text{pH} = \text{pH}_\text{II} - \text{pH}_\text{I}$) is attributed to changes in these factors. To quantify the contribution of each factor, we altered the value of factor i from its value in Scenario I to its value in Scenario II, while keeping all other factors constant. The resulting pH change, ΔpH_i , represents the contribution of that specific factor to the overall pH change. Due to the nonlinear interactions between factors, the sum of the individual

contributions may differ slightly from the total contribution of all factors combined. The unexplained portion of the pH difference, $\Delta\text{pH} - \sum_i \Delta\text{pH}_i$, is attributed to “other” factors, which likely represent the covariation among the factors. The method is applied to the results shown in Supplementary Fig. 6b and Supplementary Fig. 8b, representing annual and seasonal averages. Supplementary Fig. 11b illustrates the contributions of various factors to ΔpH from 2019 to 2023. The pH increase from 2019 to 2021 is primarily driven by TNO_3 , NH_x , and temperature, while the pH decrease from 2021 to 2022 is mainly due to temperature and NH_x . The pH increase from 2022 to 2023 is largely influenced by temperature and TNO_3 . Overall, interannual pH variation is mainly driven by NH_x and TNO_3 . As shown in Supplementary Fig. 11c, temperature is the dominant factor influencing seasonal pH variation, followed by NH_x and TNO_3 . In summary, temperature, TNO_3 , NH_x , and SO_4^{2-} are key factors affecting aerosol pH, consistent with the RF model results, which identified temperature, AN, and AS as the primary drivers of aerosol pH.

Supplementary Table 1. 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	1.54×10^{-6} $+1.96 \times 10^{-7} \times \text{OC}_{\text{R}}^{\text{c}}$	$[\text{NO}_2]_0=160$ 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 , $S_{\text{BET}}=150 \text{ cm}^2\text{mg}^{-1}$	
Laboratory	dust	2.2×10^{-5}	CaO ^b , $S_{\text{BET}}=39 \text{ cm}^2\text{mg}^{-1}$	
Laboratory	dust	2.1×10^{-6}	China loess ^b , $S_{\text{BET}}=110 \text{ cm}^2\text{mg}^{-1}$	
Laboratory	dust	1.2×10^{-6}	Saharan sand ^b , $S_{\text{BET}}=31 \text{ cm}^2\text{mg}^{-1}$	
Laboratory	dust	2×10^{-8}	Al ₂ O ₃ , $S_{\text{BET}}=1010 \text{ cm}^2\text{mg}^{-1}$, T=298K,	
Laboratory	dust	7×10^{-7}	Fe ₂ O ₃ , $S_{\text{BET}}=2300 \text{ cm}^2\text{mg}^{-1}$, T=298K,	Underwood et al., ³⁰
Laboratory	dust	1×10^{-7}	TiO ₂ , $S_{\text{BET}}=5000 \text{ cm}^2\text{mg}^{-1}$, T=298K,	
Laboratory	dust	9.7×10^{-6}	α -Fe ₂ O ₃ ^b , $S_{\text{BET}}=18 \text{ cm}^2\text{mg}^{-1}$	Underwood et al., ³¹
Laboratory	dust	1.2×10^{-9} - 2.6×10^{-8}	Al ₂ O ₃ , T=299 K, $[\text{NO}_2]_0=10^{13}$ - $10^{15} \text{ molecules cm}^{-3}$	Börensén et al., ³²
Laboratory	dust	6.2×10^{-7}	Saharan sand, T=298 K, $S_{\text{BET}}=500 \text{ cm}^2\text{mg}^{-1}$	Ullerstam et al., ³³
Laboratory	dust	0.6 - 2.4×10^{-8}	NO ₂ (35-200 ppb), RH (15-50%), irradiation= $1.5 \times 10^{15} \text{ photons cm}^{-2} \text{ s}^{-1}$,	Dupart et al., ³⁴
Laboratory	dust	1.4×10^{-7}	Kaolin, $[\text{NO}_2]_0=150 \text{ ppb}$, T=298 K, RH=7%	
Laboratory	dust	4.4×10^{-8}	Kaolin, $[\text{NO}_2]_0=150 \text{ ppb}$, T=298 K, RH=74%	Liu et al., ³
Laboratory	dust	1.6×10^{-6}	Hematite, $[\text{NO}_2]_0=150 \text{ ppb}$, 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	Han et al., ⁵
Laboratory	humic	$4.3\text{-}1.6 \times 10^{-6}$	NO_2 (30-160 ppb), Irradiation = 194.5 W/m^2 , $T = 298$ K, $\text{RH} = 22\%$	
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%, $[\text{NO}_2]_0=50$ 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%), $[\text{NO}_2]_0=50$ ppb, Irradiation=8 Wm^{-2}	Saastad et al., ⁴⁰
Laboratory	ice	$< 5 \times 10^{-6}$	T (193-243 K)	
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, $[\text{NO}_2]_0=76$ ppb	Sosedova et al. ⁴²
Laboratory	OA	$< 5 \times 10^{-7}$	Solid 1,2,10trihydroxyanthracene, $[\text{NO}_2]_0=40$ 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 , $\text{O}_3=33$ 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%), $[\text{NO}_2]_0=1.96 \times 10^{15}$ 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	$1\text{-}3 \times 10^{-6}$	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} - $2.5 \times 10^{-4} \times \text{JNO}_2$	Beijing, 2006.8, urban area; 27% (Ground) and 20% (Aerosol) for HONO sources.	Zhang et al., ⁵⁸
Model simulation	WRF-Chem	5×10^{-6} - $2.5 \times 10^{-4} \times \text{JNO}_2$	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} - $0.6 \times 10^{-4} \times (\text{JNO}_2/\text{JNO}_{2,\text{noon}})$	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 simulation	Box model	5×10^{-6} - 2×10^{-5}	Beijing, 2021.3, urban area; 63%-76% for HONO sources.	Zhang et al., ⁶⁶
Model simulation	Box model	8.25×10^{-6} - 1.5×10^{-5}	Beijing, 2021.10, urban area; 31.3%-85.6% (Ground) and <3% (Aerosol) for HONO sources.	Xuan et al., ⁶⁷
Model simulation	Box model	1.3×10^{-6} - 3.9×10^{-5}	Beijing, 2018.11, urban area; 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.

Supplementary Table 2. Instruments used in the measurement.

Parameter	Instrument	Time resolution	Detection limit	Accuracy
HONO	LOPAP ^a	60 s	0.01 ppb	10%
NO ₂	Thermo Scientific 42 _b	60 s	0.05 ppb	5%
SO ₂	Thermo Scientific 43i ^c	60 s	0.12 ppb	5%
Temperature	AWS310 ^d	60 s	-	1%
Relative humidity	AWS310 ^d	60 s	-	1%
Organic carbon	Sunset OCEC RT-4 _e	3600 s	0.40 µg m ⁻³	5%
Element carbon	Sunset OCEC RT-4 _e	3600 s	0.20 µg m ⁻³	5%
Heavy metals	XHAM-2000A ^f	3600 s	1.0-99 ng m ⁻³	10%
Organic aerosol	ACSM ^g	120 s	198 ng m ⁻³	10%
NH ₃	MARGA ^h	3600 s	9.2 ng m ⁻³	10%
Nitrate	MARGA ^h	3600 s	0.70 ng m ⁻³	5%
Sulfate	MARGA ^h	3600 s	2.0 ng m ⁻³	5%
Chloride	MARGA ^h	3600 s	0.30 ng m ⁻³	5%
Ammonium	MARGA ^h	3600 s	9.2 ng m ⁻³	5%
Calcium	MARGA ^h	3600 s	18 ng m ⁻³	5%
Magnesium	MARGA ^h	3600 s	31 ng m ⁻³	10%
Potassium	MARGA ^h	3600 s	3.7 ng m ⁻³	15%
Sodium	MARGA ^h	3600 s	3.0 ng m ⁻³	15%

^a Long Optical Path Absorption Photometer, Homemade by Institute of Chemistry, CAS, China

^b NO₂ Analyzer, Thermo Scientific 42i, Thermo Fisher Scientific, USA

^c SO₂ Analyzer, Thermo Scientific 43i, Thermo Fisher Scientific, USA

^d Weather station, AWS 310, Vaisala, Finland

^e OC/EC Analyzer, Sunset OCEC RT-4, Hebei Sailhero Environmental Protection High-tech Co., Ltd. China

^f Heavy metal analyzer, XHAM-2000A, Hebei Sailhero Environmental Protection High-tech Co., Ltd. China

^g Time-of-Flight Aerosol Chemical Speciation Monitor, Aerodyne, America

^h Monitor for aerosols and gases in air, 2060R, Metrohm, Netherlands

Supplementary Table 3. Date and mean values (mean $\pm$ standard deviation) of nighttime HONO, γ_{NO_2} , NO_2 , NH_3 , $\text{PM}_{2.5}$, $(\text{NH}_4)_2\text{SO}_4$ (AS), NH_4NO_3 (AN), the ratio in $\text{PM}_{2.5}$, and the proportion of AN in AN and AS, NO_3^- , SO_4^{2-} , NH_4^+ , PH, and ALWC in field observation.

Date	2019	2020	2021	2022	2023
HONO(ppb)	1.26 $\pm$ 1.16	0.78 $\pm$ 0.66	0.93 $\pm$ 0.92	0.81 $\pm$ 0.76	0.99 $\pm$ 0.91
γ_{NO_2} ($\times 10^{-6} \text{ s}^{-1}$)	3.07 $\pm$ 5.99	2.27 $\pm$ 4.03	1.69 $\pm$ 3.19	2.05 $\pm$ 4.19	1.43 $\pm$ 3.22
NO_2 (ppb)	18.9 $\pm$ 14.4	15.5 $\pm$ 12.8	19.4 $\pm$ 13.2	12.2 $\pm$ 10.1	13.6 $\pm$ 10.7
NH_3 ($\mu\text{g}/\text{m}^3$)	11.6 $\pm$ 5.76	11.7 $\pm$ 6.35	14.3 $\pm$ 7.85	10.0 $\pm$ 5.97	8.27 $\pm$ 4.67
$\text{PM}_{2.5}$ ($\mu\text{g}/\text{m}^3$)	43.3 $\pm$ 43.0	39.3 $\pm$ 38.5	35.5 $\pm$ 41.4	32.3 $\pm$ 33.5	36.0 $\pm$ 37.6
AS($\mu\text{g}/\text{m}^3$)	6.59 $\pm$ 8.66	5.23 $\pm$ 6.26	5.65 $\pm$ 7.13	3.37 $\pm$ 4.05	3.04 $\pm$ 3.43
AS ratio(%)	16.3 $\pm$ 31.3	13.8 $\pm$ 10.4	17.0 $\pm$ 14.6	10.9 $\pm$ 10.6	6.80 $\pm$ 5.76
AN($\mu\text{g}/\text{m}^3$)	12.8 $\pm$ 14.9	12.8 $\pm$ 16.6	15.8 $\pm$ 19.2	12.2 $\pm$ 15.7	12.3 $\pm$ 15.3
AN ratio(%)	26.8 $\pm$ 50.1	24.8 $\pm$ 17.4	32.3 $\pm$ 21.3	24.7 $\pm$ 17.6	20.4 $\pm$ 12.3
AN/(AN+AS) (%)	59.3 $\pm$ 23.9	62.0 $\pm$ 23.0	67.8 $\pm$ 19.2	68.6 $\pm$ 22.1	72.6 $\pm$ 20.6
NO_3^- ($\mu\text{g}/\text{m}^3$)	9.41 $\pm$ 11.9	9.06 $\pm$ 12.3	9.53 $\pm$ 13.3	6.64 $\pm$ 10.5	5.70 $\pm$ 9.08
SO_4^{2-} ($\mu\text{g}/\text{m}^3$)	4.85 $\pm$ 6.10	4.15 $\pm$ 4.80	3.97 $\pm$ 4.99	2.41 $\pm$ 2.79	2.10 $\pm$ 2.27
NH_4^+ ($\mu\text{g}/\text{m}^3$)	4.91 $\pm$ 5.35	5.24 $\pm$ 5.39	5.64 $\pm$ 6.41	3.46 $\pm$ 4.32	3.12 $\pm$ 4.13
pH	3.54 $\pm$ 0.90	3.62 $\pm$ 0.99	3.83 $\pm$ 0.78	3.67 $\pm$ 0.80	3.87 $\pm$ 0.93
ALWC ($\mu\text{g m}^{-3}$)	13.1 $\pm$ 31.9	20.6 $\pm$ 33.6	26.4 $\pm$ 52.1	13.3 $\pm$ 20.9	10.8 $\pm$ 22.7

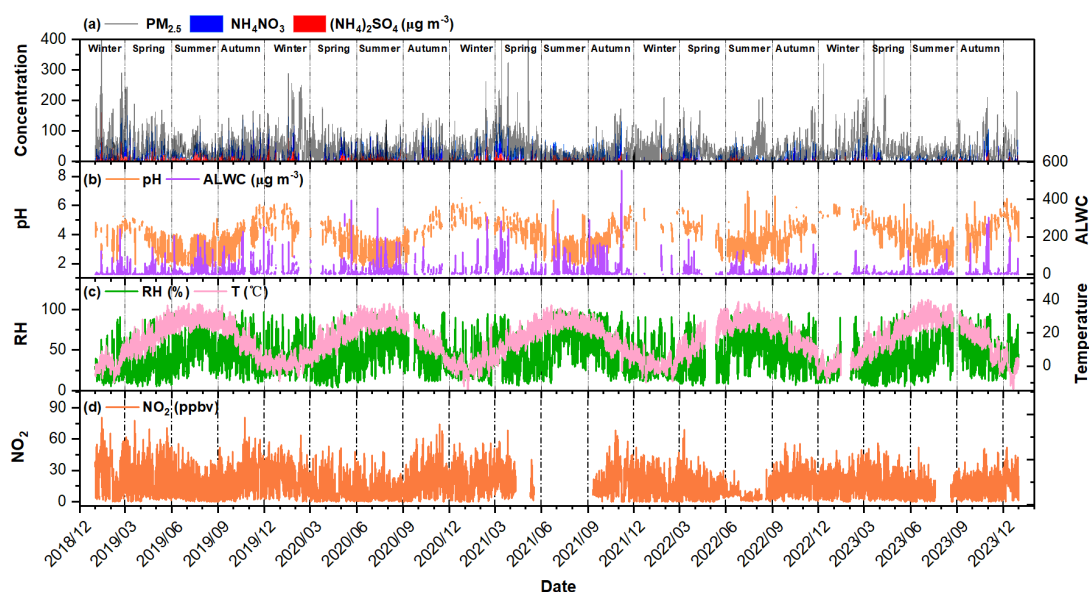
Supplementary Table 4. Mean values (mean $\pm$ standard deviation) of nighttime HONO, γ_{NO_2} , NO_2 , NH_3 , $\text{PM}_{2.5}$, $(\text{NH}_4)_2\text{SO}_4$ (AS), NH_4NO_3 (AN), the ratio in $\text{PM}_{2.5}$, and the proportion of AN in AN and AS, NO_3^- , SO_4^{2-} , NH_4^+ , PH, and ALWC in different seasons.

Date	Spring	Summer	Autumn	Winter
HONO (ppb)	1.30 $\pm$ 1.21	0.97 $\pm$ 0.81	1.04 $\pm$ 0.82	1.30 $\pm$ 1.12
γ_{NO_2} ($\times 10^{-6} \text{ s}^{-1}$)	2.50 $\pm$ 4.57	4.16 $\pm$ 7.09	1.17 $\pm$ 2.04	1.80 $\pm$ 3.64
NO_2 (ppb)	17.3 $\pm$ 12.5	10.7 $\pm$ 7.81	21.4 $\pm$ 13.3	22.1 $\pm$ 14.2
NH_3 ($\mu\text{g}/\text{m}^3$)	12.0 $\pm$ 7.97	11.7 $\pm$ 5.08	10.9 $\pm$ 5.86	8.69 $\pm$ 7.19
$\text{PM}_{2.5}$ ($\mu\text{g}/\text{m}^3$)	43.0 $\pm$ 41.1	26.2 $\pm$ 18.5	38.3 $\pm$ 37.0	48.6 $\pm$ 53.0
AS ($\mu\text{g}/\text{m}^3$)	5.15 $\pm$ 5.98	4.97 $\pm$ 4.64	4.21 $\pm$ 4.97	5.75 $\pm$ 11.0
AS ratio (%)	10.3 $\pm$ 8.68	17.8 $\pm$ 18.8	11.2 $\pm$ 14.4	11.3 $\pm$ 28.6
AN ($\mu\text{g}/\text{m}^3$)	19.0 $\pm$ 19.8	8.01 $\pm$ 9.89	16.5 $\pm$ 19.8	12.6 $\pm$ 15.2
AN ratio (%)	30.2 $\pm$ 18.3	27.7 $\pm$ 46.0	31.5 $\pm$ 40.8	21.3 $\pm$ 39.3
AN/(AN+AS) (%)	72.6 $\pm$ 21.4	56.8 $\pm$ 21.2	71.1 $\pm$ 21.4	65.8 $\pm$ 21.1
NO_3^- ($\mu\text{g}/\text{m}^3$)	10.3 $\pm$ 0.70	5.18 $\pm$ 0.63	9.19 $\pm$ 0.85	8.36 $\pm$ 0.72
SO_4^{2-} ($\mu\text{g}/\text{m}^3$)	3.49 $\pm$ 3.92	3.57 $\pm$ 3.34	2.85 $\pm$ 3.33	3.98 $\pm$ 7.48
NH_4^+ ($\mu\text{g}/\text{m}^3$)	4.94 $\pm$ 6.00	3.55 $\pm$ 3.45	4.89 $\pm$ 5.46	4.59 $\pm$ 6.19
pH	4.09 $\pm$ 0.64	3.13 $\pm$ 0.62	3.99 $\pm$ 0.72	4.84 $\pm$ 0.68
ALWC ($\mu\text{g m}^{-3}$)	16.1 $\pm$ 28.1	15.4 $\pm$ 27.4	23.5 $\pm$ 49.3	18.6 $\pm$ 33.9

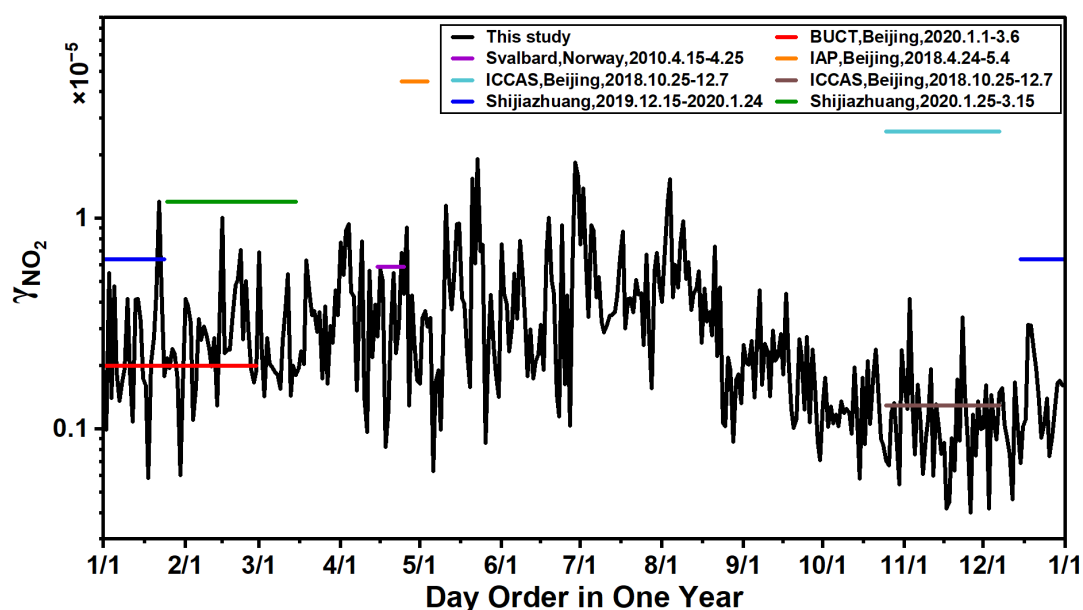
Supplementary Table 5. The values of the parameters for optimizing the RF model and the values of the five key parameters for evaluating the performance of the RF model.

Species		pH	r _{NO2}
N estimators		180	240
	Max depth	20	12
	min split	2	2
	min leaf	2	1
	random state	42	42
Evaluating	Slope	0.98	0.71
	MSE	0.0057	1.049e-12
	RMSE	0.0755	1.02e-06
	MAE	0.0472	6.36e-07
	R ²	0.988	0.931

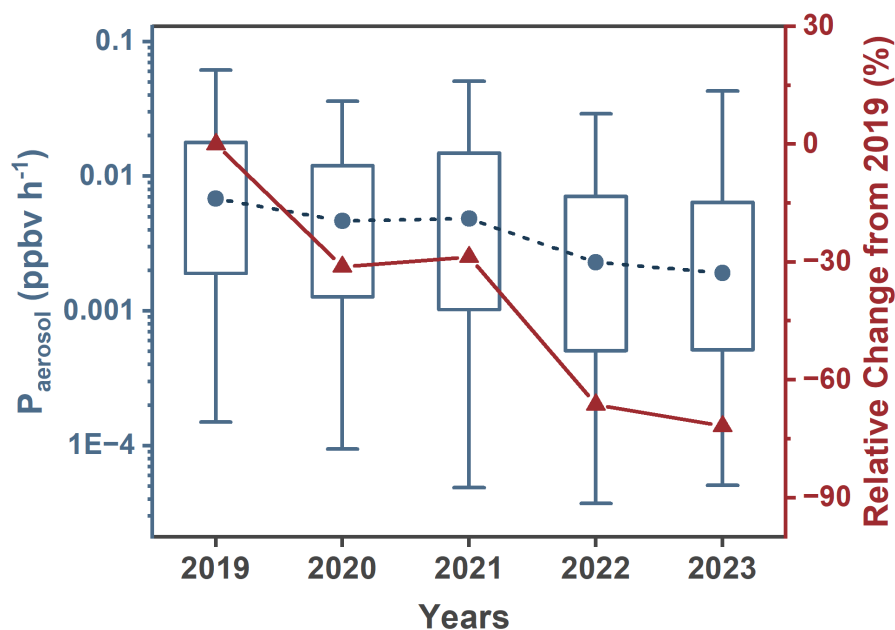
Note: MSE (mean squared error), RMSE (root mean squared error), MAE (mean absolute error).



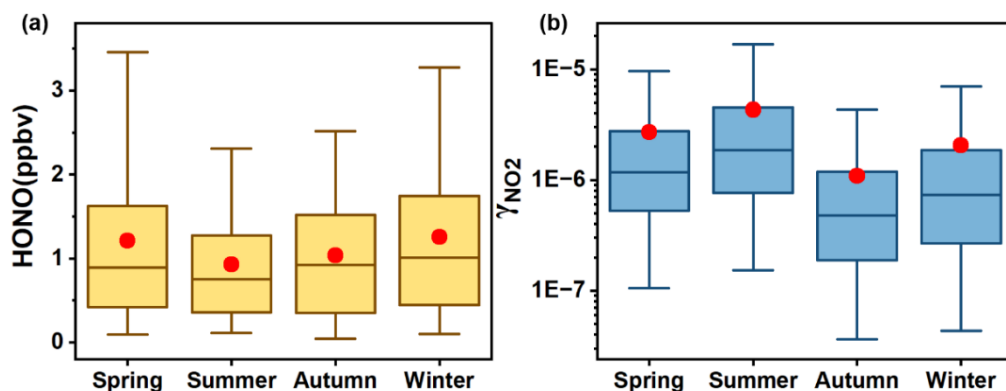
Supplementary Fig. 1. Time series of atmospheric composition and meteorological parameters with hourly time resolution from January 1, 2019, to December 31, 2023, in Beijing. (a) the mass concentrations of $\text{PM}_{2.5}$, NH_4NO_3 , and $(\text{NH}_4)_2\text{SO}_4$; (b) pH and aerosol liquid water content (ALWC); (c) relative humidity (RH) and Temperature (T); (d) NO_2 concentration.



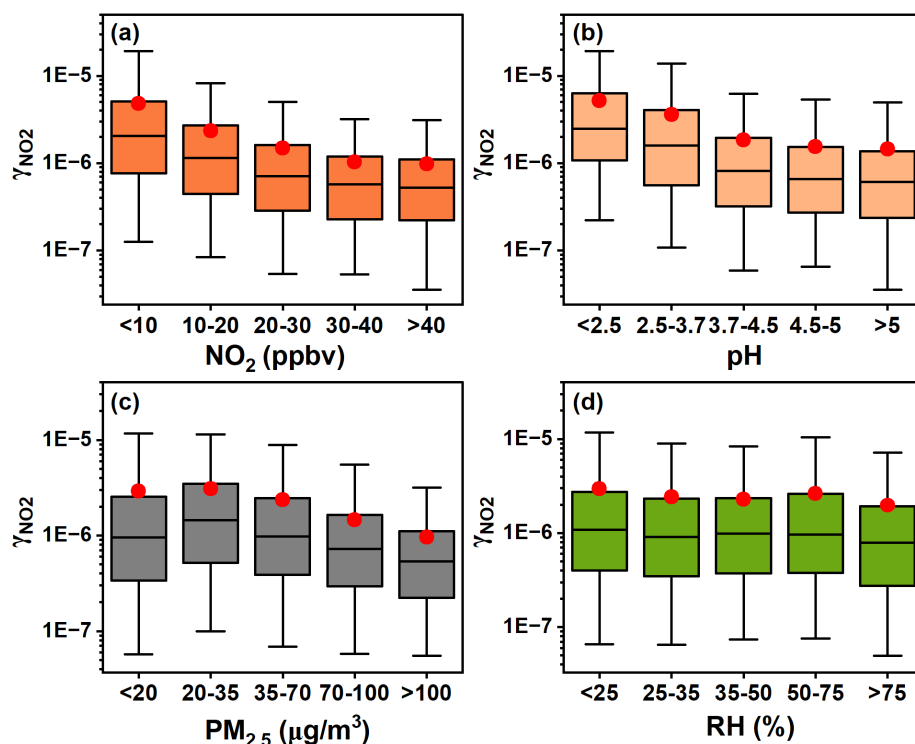
Supplementary Fig. 2. Comparison of the γ_{NO_2} time series from this study with short-term observational values reported in the literature.



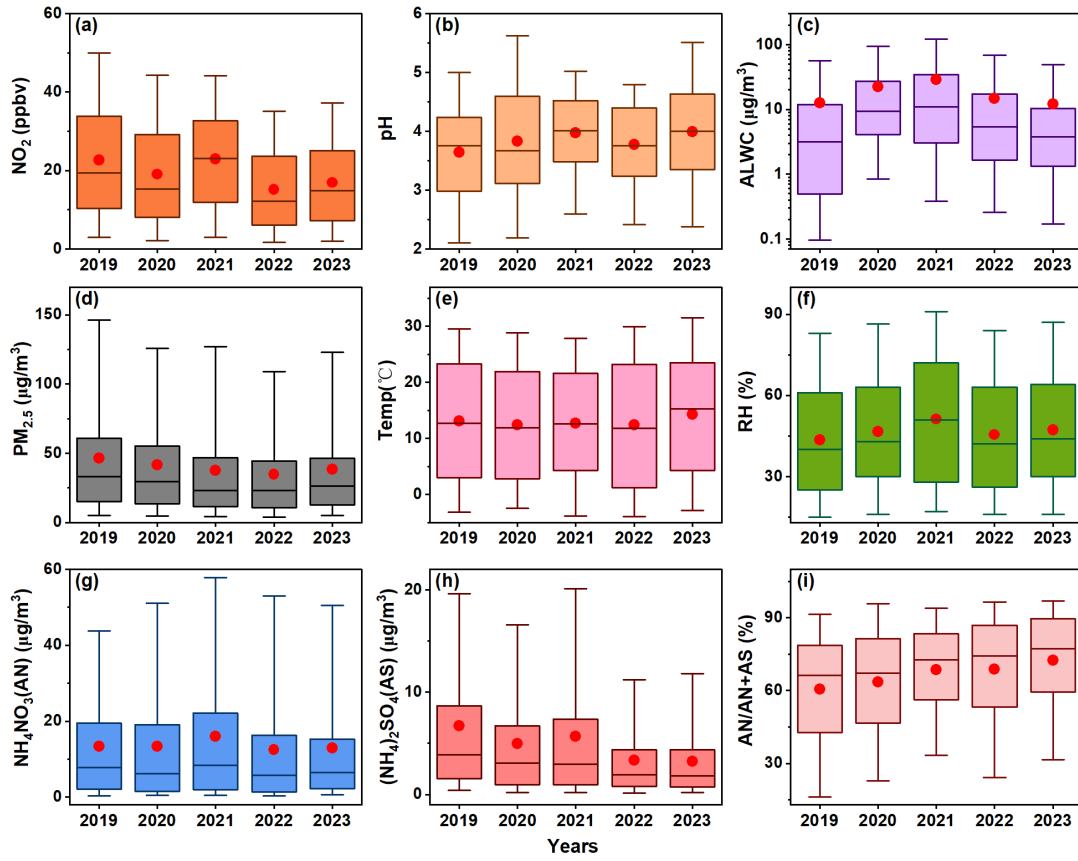
Supplementary Fig. 3. Annual variations in the yield of HONO product by the heterogeneous reaction of NO₂ on aerosol surfaces; the left axis is the HONO yield of this process, and the right axis is the percentage change of each year relative to 2019. The center lines in the box plots represent the median; the red dots indicate the mean; the whiskers mean 1.5 times the interquartile range (IQR); and the boxes span the 25th to 75th percentiles.



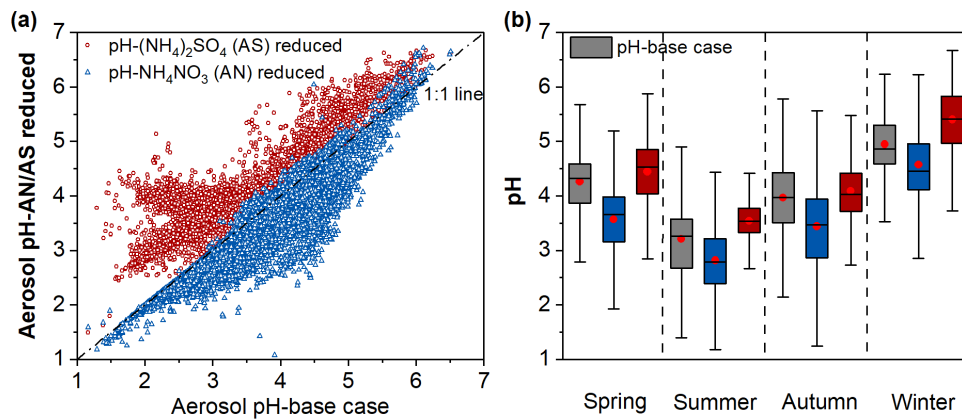
Supplementary Fig. 4. Seasonal variation of HONO and γ_{NO_2} . (a) HONO; (b) γ_{NO_2} . The center lines in the box plots represent the median; the red dots indicate the mean; the whiskers mean 1.5 times the interquartile range (IQR); and the boxes span the 25th to 75th percentiles.



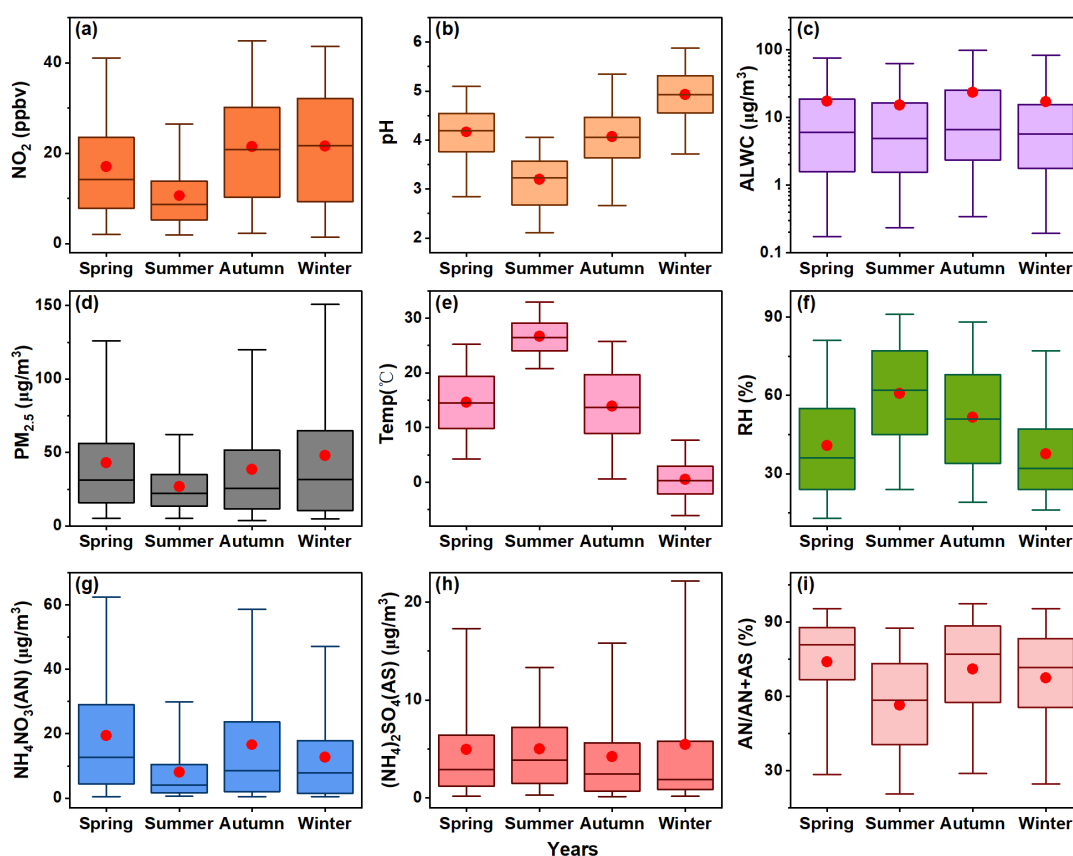
Supplementary Fig. 5. Dependence of γ_{NO_2} on key atmospheric factors. The variations of γ_{NO_2} under different (a) NO_2 concentrations, (b) pH levels, (c) $\text{PM}_{2.5}$ and (d) RH bins. The number of data points in each bin is generally the same to avoid possible artifacts arising from uneven sampling. The center lines in the box plots represent the median; the red dots indicate the mean; the whiskers mean 1.5 times the interquartile range (IQR); and the boxes span the 25th to 75th percentiles.



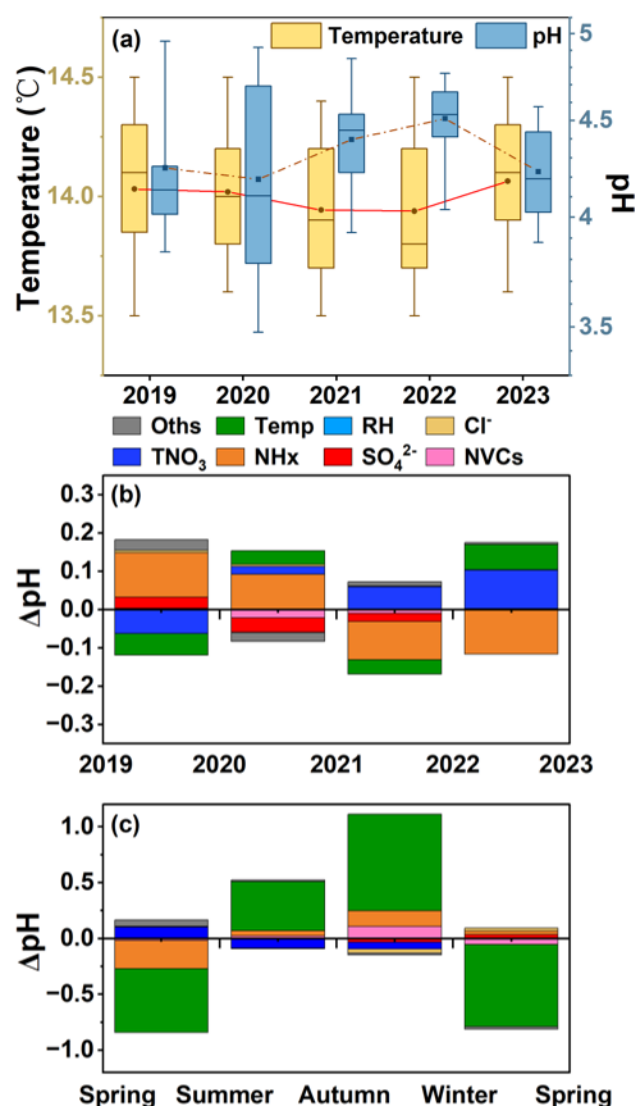
Supplementary Fig. 6. Annual variations of key atmospheric parameters and aerosol components during 2019-2023 in Beijing. The center lines in the box plots represent the median; (a) NO_2 ; (b) aerosol pH; (c) ALWC; (d) $\text{PM}_{2.5}$; (e) T; (f) RH; (g) NH_4NO_3 (AN); (h) $(\text{NH}_4)_2\text{SO}_4$ (AS), and (i) AN/AN+AS. The red dots indicate the mean; the whiskers mean 1.5 times the interquartile range (IQR); and the boxes span the 25th to 75th percentiles.



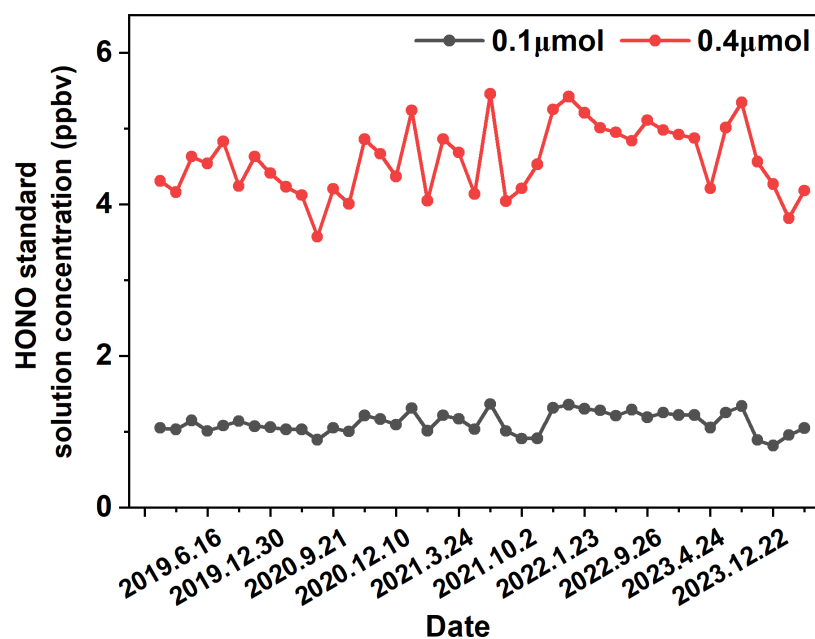
Supplementary Fig. 7. Influence of $(\text{NH}_4)_2\text{SO}_4$ (AS) and NH_4NO_3 (AN) on aerosol pH. (a) Scatter plot of aerosol pH variation after reduction of $(\text{NH}_4)_2\text{SO}_4$ (red dots) and NH_4NO_3 (blue dots); (b) Box plots of aerosol pH change in different seasons before and after reduction, The center lines in the box plots represent the median; the red dots indicate the mean; the whiskers mean 1.5 times the interquartile range (IQR); and the boxes span the 25th to 75th percentiles.



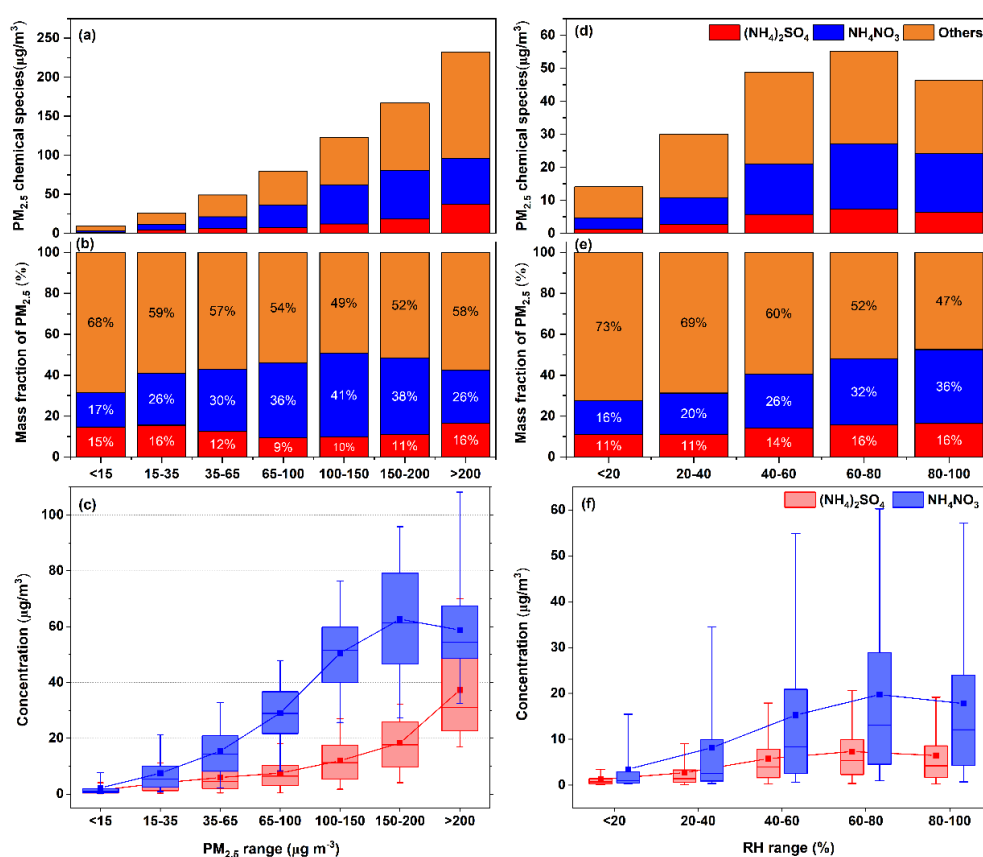
Supplementary Fig. 8. Seasonal variations of key atmospheric parameters and aerosol components during 2019-2023 in Beijing. (a) NO_2 ; (b) aerosol pH; (c) ALWC; (d) $\text{PM}_{2.5}$; (e) T; (f) RH; (g) NH_4NO_3 (AN); (h) $(\text{NH}_4)_2\text{SO}_4$ (AS), and (i) AN/AN+AS. The center lines in the box plots represent the median; the red dots indicate the mean; the whiskers mean 1.5 times the interquartile range (IQR); and the boxes span the 25th to 75th percentiles.



Supplementary Fig. 9. 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.



Supplementary Fig. 10. Time Series of Concentration-Response Signals for Calibrated Solutions from 2019 to 2023.



Supplementary Fig. 11. Relative contributions of PM_{2.5} components and nitrous species under different pollution levels and relative humidity conditions. Aerosol components in different pollution levels: (a) Stacked concentrations; (b)

Relative contributions; (c) Box plots; Aerosol components in different RH range:
(d) Stacked concentrations; (e) Relative contributions; (f) Box plots; The red is $(\text{NH}_4)_2\text{SO}_4$, blue is NH_4NO_3 . 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.

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