

1 **Supplementary information for**

2 **Surface nitrate photochemistry explains the**
3 **long-standing missing source of nitrous acid**

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Text S1. Grime model construction

Based on the principle of mass balance, this study constructed a mechanistic model to simulate the photolysis of surface nitrate (sNO_3) in grime as a source of nitrous acid (HONO). The core framework assumes that the temporal variation in sNO_3 concentration results from the balance between its production via the dry deposition of

particulate nitrate (pNO_3) and gaseous nitric acid (HNO_3), and its removal through photolysis and precipitation scavenging. The partitioning of HNO_3 between the atmosphere and the grime layer may represent an important secondary source or sink of sNO_3 , depending on the direction of redistribution. However, this dynamic exchange process is not explicitly accounted in the current model framework. This omission is primarily due to the lack of robust, measurement constrained physical and chemical parameters, such as grime pH, required to mechanistically represent the bidirectional flux of HNO_3 . The model is mathematically expressed by the following governing differential equation (S1):

$$\frac{d[\text{sNO}_3]}{dt} = GR - 3600 \times J_{\text{sNO}_3} \times \text{sNO}_3 - L_{\text{precipitation}} \quad (\text{S1})$$

where $[\text{sNO}_3]$ is the surface nitrate concentration (mol m^{-2}), GR is the gross depositional growth rate ($\text{mol m}^{-2} \text{h}^{-1}$), J_{sNO_3} is the photolysis frequency of sNO_3 (s^{-1}), $L_{\text{precipitation}}$ is the loss rate due to precipitation ($\text{mol m}^{-2} \text{h}^{-1}$), and 3600 is a conversion factor from seconds to hours. The model was solved numerically using an iterative time-stepping method. Each simulation is initialized 30 days before the start of observational period, with an initial sNO_3 concentration assumed to be zero.

The growth rate (GR) is defined as the sum of the dry deposition fluxes of pNO_3 and HNO_3 , equation (S2). These fluxes are calculated as the product of the respective concentrations of near-surface species and their deposition velocities:

$$GR = v_{\text{d, pNO}_3} \times [\text{pNO}_3] + v_{\text{d, HNO}_3} \times [\text{HNO}_3] \quad (\text{S2})$$

where $v_{\text{d, pNO}_3}$ and $v_{\text{d, HNO}_3}$ are the deposition rates of pNO_3 and HNO_3 (m h^{-1}), respectively. $[\text{pNO}_3]$ and $[\text{HNO}_3]$ are the mol concentration of pNO_3 and HNO_3 (mol m^{-3}), respectively. A key improvement in this model is a novel parameterization for predicting pNO_3 concentrations to address common overestimations in chemical transport models (CTMs)(Norman et al., 2025). Based on 870 concurrent measurements of $\text{PM}_{2.5}$ and pNO_3 compiled from various field campaigns, a robust power-law relationship was established, equation (S3):

$$[\text{pNO}_3]_{\text{mass}} = a \times [\text{PM}_{2.5}]_{\text{mass}}^b \quad (\text{S3})$$

where $a = 0.12 \pm 0.03$ and $b = 1.18 \pm 0.06$ ($R^2 = 0.76$, $RMSE = 7.26 \mu\text{g m}^{-3}$). $[\text{pNO}_3]_{\text{mass}}$ and $[\text{PM}_{2.5}]_{\text{mass}}$ is the mass concentration of pNO_3 and $\text{PM}_{2.5}$ ($\mu\text{g m}^{-3}$), respectively. This relationship captures the non-linear, accelerated increase in pNO_3 fraction within $\text{PM}_{2.5}$ under polluted conditions, driven by self-amplifying processes like N_2O_5 heterogeneous hydrolysis(Lin et al., 2020). For consistency, $\text{PM}_{2.5}$ data is provided by the EAC4 reanalysis(CAMS global reanalysis ECMWF Atmospheric Composition Reanalysis 4, n.d.). Furthermore, HNO_3 concentration data are obtained directly from the EAC4 multi-level product.

The deposition velocities (v_{d}) for both species are computed using the resistance-in-series model as implemented in the GEOS-Chem chemical transport model, which

accounts for aerodynamic resistance (R_a), quasi-laminar boundary layer resistance (R_b), and surface resistance (R_c), with an additional parallel term for gravitational settling velocity (v_g) for particles, equation (S4):

$$v_d = \frac{1}{R_a + R_b + R_c} + v_g \quad (\text{S4})$$

Meteorological parameters required for calculating deposition velocities (e.g., wind speed, temperature, friction velocity) were obtained from the MERRA-2 reanalysis(MERRA-2 `tavg1_2d_slv_Nx`: 2d,1-Hourly,Time-Averaged,Single-Level,Assimilation,Single-Level Diagnostics V5.12.4, n.d.; MERRA-2 `tavg1_2d_flux_Nx`: 2d,1-Hourly,Time-Averaged,Single-Level,Assimilation,Surface Flux Diagnostics 0.625 x 0.5 degree V5.12.4, n.d.; MERRA-2 `tavg1_2d_aer_Nx`: 2d,1-Hourly,Time-averaged,Single-Level,Assimilation,Aerosol Diagnostics V5.12.4, n.d.; MERRA-2 `inst3_3d_aer_Nv`: 3d,3-Hourly,Instantaneous,Model-Level,Assimilation,Aerosol Mixing Ratio V5.12.4, n.d.), while land cover types, which critically influence the surface resistance (R_c), were obtained from the MODIS MOD15A2H V061 dataset(MODIS/Terra Leaf Area Index/FPAR 8-Day L4 Global 500m SIN Grid V061, n.d.).

The primary loss pathway, photolysis, was calculated as the product of the modeled $s\text{NO}_3$ concentration and the corresponding photolysis frequency ($J_{s\text{NO}_3}$). To reflect surface-dependent variability, $J_{s\text{NO}_3}$ is parameterized according to the empirical function developed by Ye et al.(Ye et al., 2016) (equation (S5)), which is based on field measurements of $J_{s\text{NO}_3}$ on various environmental surfaces (Table S7 and Figure 1b).

$$J_{s\text{NO}_3} = \frac{k_1}{k_2} \times \ln(1 + k_2 \times [s\text{NO}_3]) + k_3 \quad (\text{S5})$$

where $k_1 = 8.70 \times 10^{-4} \text{ s}^{-1}$, $k_2 = 2.50 \times 10^7 \text{ m}^2 \text{ mol}^{-1}$, and $k_3 = 1.14 \times 10^{-5} \text{ s}^{-1}$, which is independent of surface type and solar spectral actinic flux.

Precipitation scavenging ($L_{\text{precipitation}}$) was parameterized based on the relationship between rainfall intensity (P , mm h^{-1}) and grime scavenging measurements (equation (S6)), recommended by I. Andrés-Doménech et al.(Andrés-Doménech et al., 2018) This relationship was further validated using grime scavenging data at various locations (Figure S5 and Table S8).Note that, rainfall intensity data was also sourced from the MERRA-2 reanalysis.

$$L_{\text{precipitation}} = e^{-0.016 \times \frac{(P-1)^2}{P-1+10}} \times [s\text{NO}_3] \quad (\text{S6})$$

Text S2. Dataset for Grime Model Construction and Validation

Text S2.1 Validation of GR Source

As mentioned above, the mechanistic model for simulating $s\text{NO}_3$ dynamics was fundamentally grounded in a mass balance framework applied to the grime layer. This

conceptual approach treats sNO_3 as a grime component whose concentration is governed by depositional sources and photolysis, precipitation losses, and is adapted from established grime evolution models (Diamond et al., 2001; Sarwar et al., 2008). This framework was developed based on two key datasets necessary for model construction and validation.

First, the model is driven by globally consistent reanalysis data. These data sources include meteorological fields (e.g., wind, radiation, and precipitation) from the MERRA-2 reanalysis, aerosol and precursor gas concentrations ($\text{PM}_{2.5}$, PM_{10} , pNO_3 , and HNO_3) from the EAC4 reanalysis, and land cover information from the MODIS MOD15A2H V061 dataset. The MERRA-2 and MODIS datasets were used to calculate the deposition velocities, accounting for aerosol size distribution. Meanwhile, the EAC4 reanalysis was used to provide atmospheric pollutant concentrations ($\text{PM}_{2.5}$, PM_{10} , and HNO_3).

Second, the model's parameterizations and outputs are empirically anchored and validated against a compilation of direct, independent measurements from diverse environments (urban, roadside, and suburban). This not only supports the mechanistic model framework for predicting grime concentration and sNO_3 photolysis rates but also demonstrates the reliability of the reanalysis datasets. As shown in Figure. S1, the model reproduces the measured grime concentrations well (Tables S1 and S2) showing strong agreement ($R^2 = 0.87$, $\text{NMB} = +24\%$).

The model framework for sNO_3 simulation incorporates necessary modifications driven by both mechanistic considerations and data availability constraints. While pNO_3 deposition is a recognized source of sNO_3 , the pNO_3 concentrations provided by the EAC4 reanalysis fail to adequately capture their spatiotemporal variability (Figs. S3c, f, and i). Alternative AI-based datasets, such as the TAP (Tracking Air Pollution) reanalysis (Geng et al., 2021; Liu et al., 2022), demonstrate substantially improved predictions of pNO_3 relative to the EAC4 reanalysis (Figs. S3b, e, and h). However, the spatial and temporal coverage of such specialized datasets is more limited compared to the globally consistent EAC4 reanalysis.

To address this limitation while maintaining broad applicability, we introduced a novel parameterization to estimate pNO_3 concentrations associated with EAC4 $\text{PM}_{2.5}$ data. This approach is based on previous studies (Tao et al., 2023) that established a robust power-law relationship between ambient pNO_3 and $\text{PM}_{2.5}$ concentrations. In this paper, this relationship is further validated using concurrently measured $\text{PM}_{2.5}$ and pNO_3 data across multiple campaigns (Table S1 and Figure S2). Consequently, this pNO_3 parameterization yields predictions comparable to the TAP dataset while maintaining

the full spatial and temporal coverage of the parent EAC4 PM_{2.5} reanalysis (Figs. S3a, d, and g).

For the other source, HNO₃ deposition, the parameterization relies directly on the HNO₃ concentrations from EAC4, and the deposition velocity calculated using the resistance-in-series model. It is acknowledged that the EAC4 HNO₃ dataset is subject to considerable uncertainties (Norman et al., 2025), nearly 50-100%, primarily due to the scarcity of direct atmospheric HNO₃ measurements available for assimilation and validation. Unlike pNO₃, improvements through a simple proxy-based parameterization are not currently feasible for HNO₃, as no similarly robust and universally applicable predictive relationship has been established. Indeed, the identification of HNO₃ deposition as a major contributor to sNO₃ accumulation underscores the critical need for more accurate atmospheric HNO₃ concentrations (Figure S4, Tables S4 and S5). The current reliance on reanalysis datasets like the EAC4—introduces significant uncertainty into the modeled sNO₃ source strength.

Overall, the validation of the depositional growth rate (*GR*) of sNO₃ is directly enabled by measurements from light-shielded grime samples, which collect deposited materials while avoiding photolytic loss and precipitation scavenging (Figure S4 and Tables S4 and S5). This comparison yields a strong agreement between the modeled and measured *GR* of sNO₃ ($R^2 = 0.93$), despite the potential inherent uncertainties in the HNO₃ deposition flux calculations. However, notable discrepancies emerge during specific periods, i.e., immediately following the deployment of a new grime sampler. In these cases, the modeled *GR* significantly underestimates the initial measured accumulation rates. This systematic deviation appears to result from a key omission of HNO₃ partitioning between the atmosphere and the grime layer in the current model framework. In reality, a new or rain-washed surface may initially act as a net sink for atmospheric HNO₃ through adsorption, but as the grime layer develops and its chemistry evolves, equilibrium partitioning could lead to a reduced net uptake rate or even temporary re-emission, particularly under changing temperature and humidity conditions (Cao et al., 2023; Pusede et al., 2015; Tuite et al., 2021). The absence of this buffering mechanism in the model is probably responsible for the underestimation of sNO₃ during these initial growth phases. Notably, this discrepancy diminishes and effectively disappears as sNO₃ accumulation progresses. This latter scenario—where the modeled *GR* consistent with measurements—represents the predominant condition throughout the modeling periods. Once an initial surface film is established, the system behaves more consistently with the model's assumption of irreversible deposition, validating the use of the simpler, unidirectional flux parameterization. (Please refer to the results and discussion section of the main text).

Text S2.2 Validation of Photolysis and Precipitation Loss

The photolytic loss of sNO_3 and the associated production of HONO arise from the same chemical process. Therefore, the validation of the sNO_3 photolysis frequency and the calculated HONO production flux is presented together in this context. Data used to evaluate sNO_3 photolysis and the quantum yield of HONO (ϕ_{HONO}) are provided in Tables S6 and S7.

Parameterization of precipitation scavenging ($L_{\text{precipitation}}$) was directly adapted from an established and validated model framework developed for simulating the removal of urban grime by rain (Andrés-Doménech et al., 2018). This approach is justified by field studies (Chen and Adams, 2006; Wijesiri et al., 2015) indicating that individual grime components, including inorganic salts like sNO_3 , exhibit precipitation scavenging efficiencies (W_E) similar to those of the overall grime mass (Figure S5). Consequently, applying the grime-level removal scheme, based on rainfall intensity, to the sNO_3 is a well-supported simplification. Data used to validate the parameterization of precipitation scavenging are presented in Table S8.

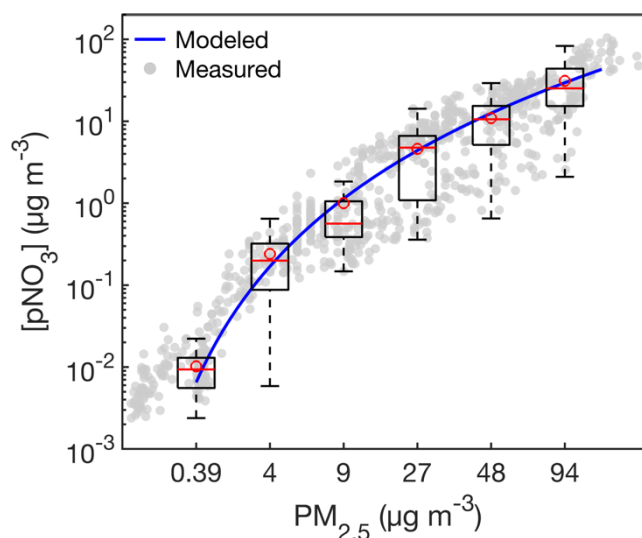
Text S3. Box Model Construction for HONO Budget Calculation

A chemical box model was employed to simulate the surface-layer HONO budget, focusing on the two dominant direct photolytic pathways. The source term is represented by HONO production from sNO_3 photolysis, while the sink term is defined as HONO loss via its own photolysis. To estimate the photo-steady-state concentration of HONO ($[\text{HONO}]_{\text{PSS}}$) under this simplified condition, a mixing layer height (MLH) of 100 m is assumed. This value is typical for nocturnal or early morning stable boundary layer conditions (Tang et al., 2016), which are often conducive to HONO accumulation. Photolysis frequencies for both J_{HONO} and J_{HNO_3} were calculated using the Tropospheric Ultraviolet and Visible (TUV) radiation transfer model (Madronich and Flocke, 1999), incorporating site-specific solar zenith angles and atmospheric conditions. To enable direct and consistent comparisons of the sNO_3 photolysis rate, the derived HONO production flux, and $[\text{HONO}]_{\text{PSS}}$ across diverse atmospheric environments (Tables S9 and S10), all calculated values were normalized to standard noontime solar conditions. Therefore, $[\text{HONO}]_{\text{PSS}}$ is obtained by equation (S7):

$$[\text{HONO}]_{\text{PSS}} = \frac{J_{\text{sNO}_3}^{\text{N}} \times [\text{sNO}_3]}{MLH \times J_{\text{HONO}}^{\text{N}}} \quad (\text{S7})$$

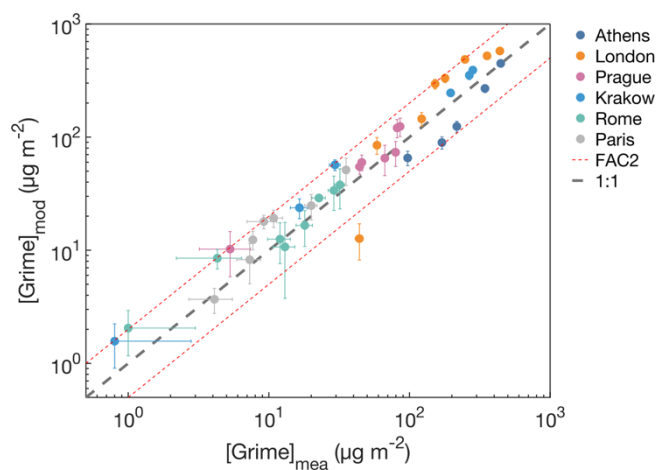
where $J_{\text{sNO}_3}^{\text{N}}$ and $J_{\text{HONO}}^{\text{N}}$ are the photolysis frequencies normalized to standard noontime solar conditions.

236 **Supplementary Figures**



237

238 **Figure S1.** Mass concentration of particulate nitrate ([pNO₃]) as a function of mass
 239 concentration of PM_{2.5} ([PM_{2.5}]). The blue solid line denotes $[pNO_3] = a \times (PM_{2.5})^b$
 240 where $a=0.12\pm0.03$, $b=1.18\pm0.06$, $R^2 = 0.76$, $RMSE = 7.26 \mu g m^{-3}$, $NMB = +4\%$. The
 241 grey scatters denote concurrent field measurement of both [pNO₃] and [PM_{2.5}].



242

243 **Figure S2.** Comparison of measured and modeled [Grime]. $R^2 = 0.93$, $NMB = +23.72\%$
 244 and $RMSE = 3.43 \times 10^{-5}$. 95.12% modeled [Grime] are within a factor of 2 (FAC2)
 245 measured [Grime] (red dashed line).

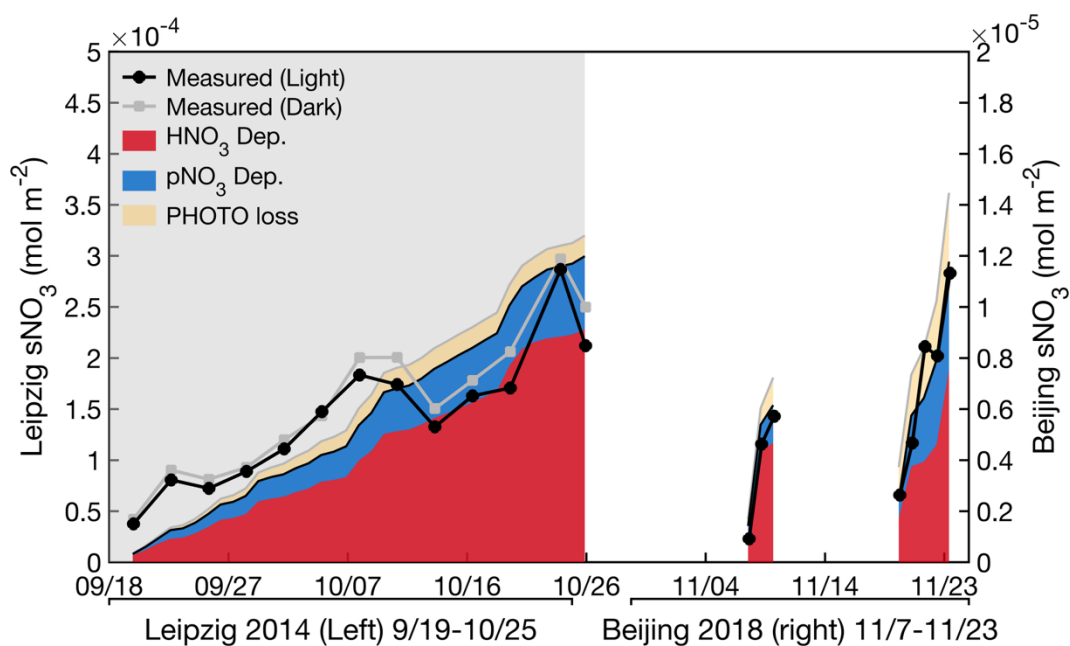


Figure S3. Time series of measured and modeled $[sNO_3]$ at Leipzig and Beijing, respectively. R^2 between measured and modeled $[sNO_3]$ is 0.80 at Leipzig and 0.92 at Beijing.

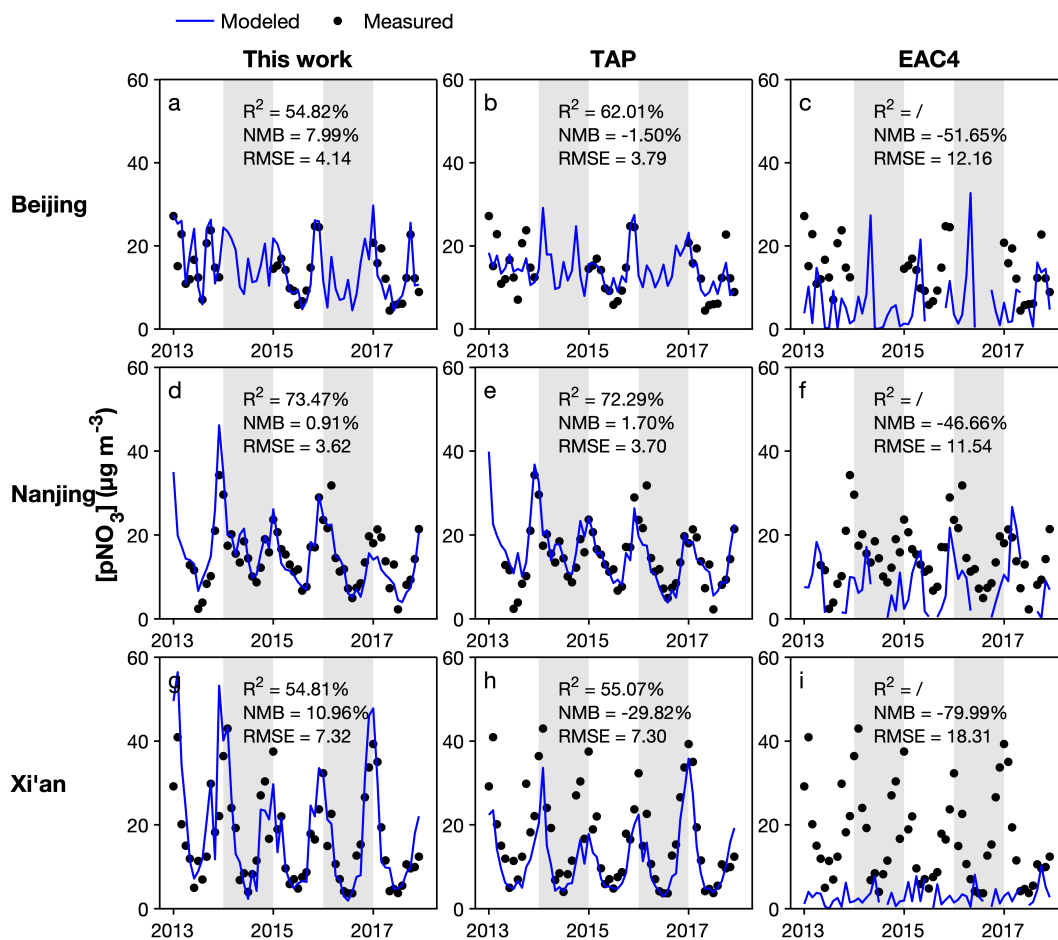


Figure S4. Comparison of measured and modeled mass concentration of particulate nitrate ($[pNO_3]$). Modeled results are from this study (a, d, g), TAP (b, e, h) and EAC4 (c, f, i), respectively. The measured data is collected from. Zhang et al. supporting information(Zhang et al., 2019).

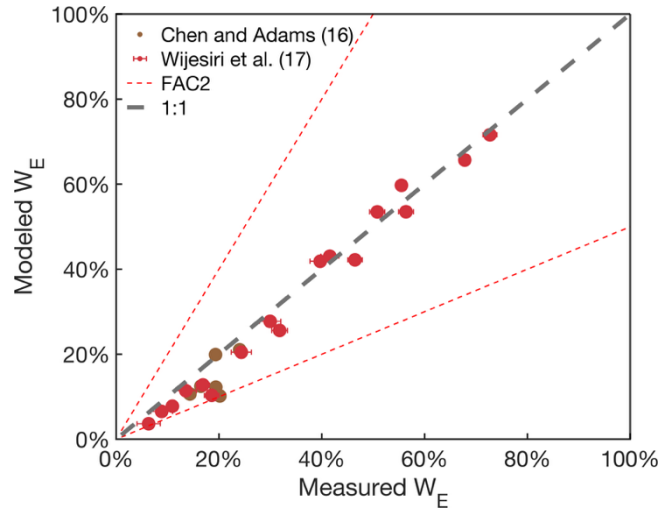


Figure S5. Comparison of measured and modeled W_E . The grey dashed line denoted linear fit between measured and modeled W_E . Modeled $W_E = 1.012 \times \text{Measured } W_E - 0.042$. $R^2 = 0.91$, $NMB = -12.04\%$, $RMSE = 6.38 \times 10^{-5} \mu g m^{-2}$. 96% data points within 2σ prediction interval (red dashed line). Note that, W_E is calculated using $W_E = e^{-0.016 \times \frac{(P-1)^2}{P-1+10}}$ from I. Andr s-Dom nech et al.(Andr s-Dom nech et al., 2018)

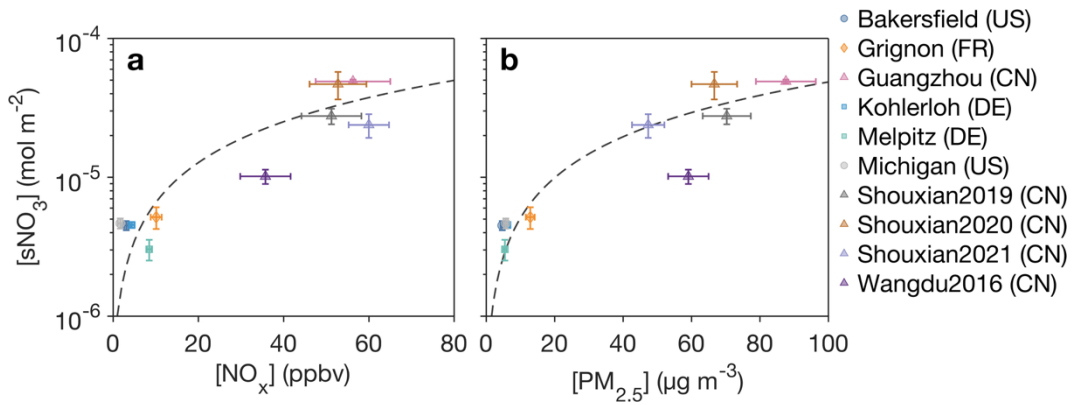


Figure S6. Variation of modeled $[sNO_3]$ with pollution levels, shown in $[NO_x]$ (a) or $[PM_{2.5}]$ (b). The black dashed line denoted linear fit between pollution levels and $[sNO_3]$, with $R^2 = 0.70$ and 0.74 from left to right.

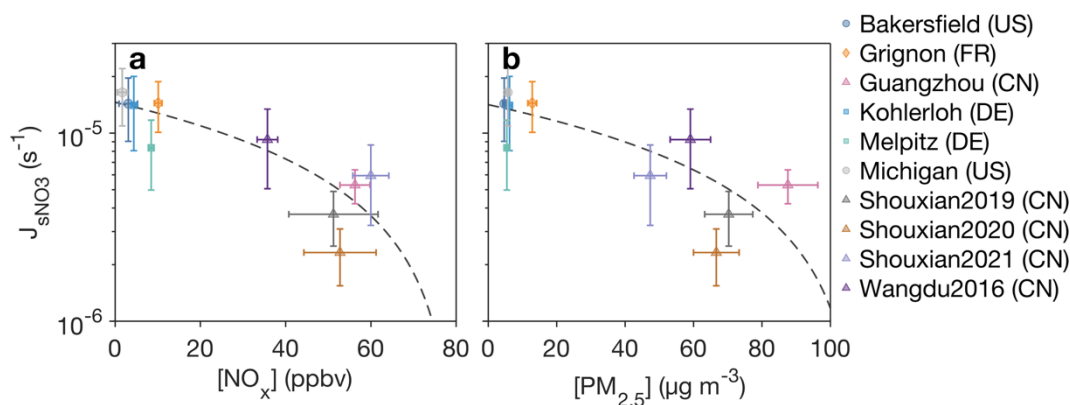


Figure S7. Variation of modeled J_{sNO_3} with pollution levels, shown in $[\text{NO}_x]$ (a) or $[\text{PM}_{2.5}]$ (b). The black dashed line denoted linear fit between pollution levels and J_{sNO_3} , with $R^2 = 0.77$ and 0.66 from left to right.

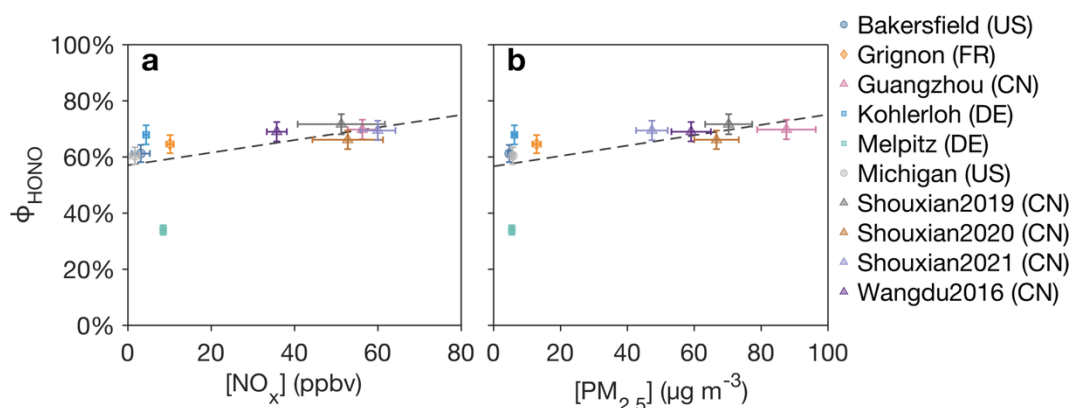


Figure S8. Variation of modeled ϕ_{HONO} with pollution levels, shown in $[\text{NO}_x]$ (a) or $[\text{PM}_{2.5}]$ (b). The black dashed line denoted linear fit between pollution levels and ϕ_{HONO} , with $R^2 = 0.21$ and 0.17 from left to right.

Supplementary Tables

Table S1. Concurrent measurements of $[\text{PM}_{2.5}]$ and $[\text{pNO}_3]$ used to derive a new $[\text{pNO}_3]$ parameterization. Data are expressed as mean $\pm$ SD.

Sampling site	Sampling duration & samples	Time resolution	$[\text{PM}_{2.5}]$ ($\mu\text{g m}^{-3}$)	$[\text{pNO}_3]$ ($\mu\text{g m}^{-3}$)	Description	Ref.
Mingshan	2017/4/29-2017/05/13 & 30	12 hours	57.80 ± 28.61	5.65 ± 5.38	rural site, surrounded by	(24)

	samples				agricultural land and distant from urban centers and major roads	(24)
Wenjiang	2017/04/29- 2017/05/14 & 31 samples	12 hours	72.67 ± 33.51	7.81 ± 6.18		
7 Chinese cities in NCP*	2017/12/01- 2019/01/12 & 26 samples	1 day	147.18 ± 75.72	33.45 ± 20.90	urban sites, experiences severe air pollution due to intensive anthropogen ic emissions	(25)
Beijing	2023/12/15- 2024/01/01 & 474 samples	1 hour	38.95 ± 40.00	11.75 ± 16.87		This stud y
CONUS [#]	2019/07/24- 2019/09/05 & 116 samples	1 hour	22.37 ± 21.07	0.79 ± 0.84	clean marine boundary, far from anthropogen ic emissions	(26)
Gulf of Alaska and the Bering Sea ^{\$}	2015/11/12- 2015/11/23 & 2016/05/18- 2016/06/01 & 2017/09/04- 2017/09/19 & 193 samples	1 hour	0.90 ± 1.31	0.04 ± 0.06	free troposphere measureme nt over CONUS.	(27)

276 * 7 Chinese cities include Zhengzhou, Zibo, Shijiazhuang, Tianjin, Dezhou, Jinan and
277 Handan.

278 [#] Aloft samples and were collected from a wide geographic area. The flight track is
279 available at <https://www-air.larc.nasa.gov/missions/firex-aq/>.

280 \$ Aloft samples and were collected from a wide geographic area. The flight track is
 281 available at <https://science-data.larc.nasa.gov/naames-data/data2015.html>

282 **Table S2. Summary of observational datasets and their applications in this study.**

Dataset	Application	Relevant figures	Relevant tables
[Grime] observation	Evaluation of [Grime] parameterization	Figure S2	Tables S3-S4
[PM _{2.5}] and [pNO ₃] concurrent measurement	Development of [pNO ₃] parametrization	Figure S1	Table S1
TAP and PM _{2.5} filter analysis data	Evaluation of [pNO ₃] parametrization	Figure S4	/
[sNO ₃] observation	Evaluation of [sNO ₃] parameterization	Figures 1a and S3	Tables S5-S6
sNO ₃ photolysis constant (J_{sNO_3}) measurement	Development of J_{sNO_3} parametrization	Figure 1b	Table S7
HONO branching ratio (ϕ_{HONO}) measurement	Development of ϕ_{HONO} parametrization	Figure 1c	Table S9
wash-off efficiency (W_{E}) measurement	Development of W_{E} parametrization	Figure S5	Table S8
HONO flux field measurement	Calculation of sNO ₃ -derived HONO flux contribution	Figure 2	Tables S10-S11
[HONO] measurement	Evaluation of updated GEOS- Chem	Figure 5	Tables S12

283

284 **Table S3. Detailed sampling information of [Grime] measurements.**

Sample name	Latitude	Longitude	Sampling duration & Samples	Time resolution	Description	Reference
Athens	37.99 °N	23.73 °E	2002/12/10-2004/03/10, 5 samples in 548 days	30-120 days	urban grime samples, glass panes silico-soda-lime in composition (Planilux®)	(21-23)
London	50.06 °N	19.94 °E	2003/1/23-2005/03/03, 8 samples in 790 days			
Prague	51.59 °N	0.23 °E	2002/12/9-2005/02/09, 7 samples in 793 days			
Krakow	50.08 °N	14.43 °E	2003/1/7-2004/11/07, 6 samples in 670 days			
Paris	48.86 °N	2.34 °E	2002/10/15-2005/02/15, 8 samples in 854 days			
Rome	42.14 °N	12.74 °E	2002/12/12-2005/02/12, 8 samples in 793 days		Suburban grime samples, glass panes silico-soda-lime in composition (Planilux®)	

285

Table S4. Results of measured and modeled Grime concentration at sampling locations listed in Table S3. Data are expressed as mean $\pm$ SD. Modeled [Grime] is calculated considering accumulated PM₁₀ deposition flux in sampling duration.

Sample name	Sampling time	Measured [Grime] ($\mu\text{g cm}^{-2}$)	Modeled [Grime] ($\mu\text{g cm}^{-2}$)
Athens	2003/3/10	97.0 ± 3.9	50.3 ± 7.3
	2003/6/10	170.0 ± 5.4	68.8 ± 8.5
	2003/9/10	217.0 ± 6.3	95.5 ± 10.6
	2003/12/10	344.0 ± 8.9	206.9 ± 16.5
	2004/3/10	445.0 ± 10.9	344.7 ± 18.0
London	2003/4/23	44.0 ± 2.9	9.7 ± 3.4
	2003/7/23	58.7 ± 3.2	65.2 ± 11.1
	2003/10/23	122.0 ± 4.4	111.4 ± 15.2
	2004/1/23	152.0 ± 5.0	226.8 ± 21.8
	2004/4/23	179.0 ± 5.6	255.0 ± 21.6
	2004/7/23	248.0 ± 7.0	373.8 ± 17.2
	2005/1/23	356.0 ± 9.1	402.3 ± 26.8
	2005/5/23	439.0 ± 10.8	443.6 ± 21.0
	2003/3/9	5.3 ± 2.1	7.9 ± 3.4
	2003/6/9	44.2 ± 2.9	42.1 ± 6.1
Prague	2003/9/9	45.8 ± 2.9	46.0 ± 7.3
	2003/12/9	66.7 ± 3.3	50.1 ± 15.0
	2004/3/9	79.7 ± 3.6	56.4 ± 14.1
	2004/12/9	81.7 ± 3.6	92.8 ± 17.0
	2005/4/9	85.7 ± 3.7	95.6 ± 17.6
	2003/4/7	0.8 ± 2.0	1.2 ± 0.5
	2003/7/7	16.5 ± 2.3	18.3 ± 3.6
Krakow	2003/10/7	29.5 ± 2.6	43.7 ± 4.7
	2004/4/7	196.0 ± 5.9	189.0 ± 12.4
	2004/10/7	266.0 ± 7.3	270.5 ± 22.4
	2005/1/7	282.0 ± 7.6	301.0 ± 10.9
	2002/11/15	4.1 ± 1.4	2.8 ± 0.7
Paris	2002/12/15	7.3 ± 1.4	6.3 ± 2.5
	2003/1/15	7.7 ± 0.5	9.5 ± 1.8
	2003/4/15	10.8 ± 1.7	14.8 ± 2.6
	2003/7/15	9.2 ± 2.2	13.8 ± 1.9
	2003/10/15	20.0 ± 2.0	19.1 ± 4.8

Rome	2005/2/15	35.4 ± 2.1	39.4 ± 10.7
	2003/3/12	1.0 ± 2.0	1.6 ± 0.7
	2003/6/12	4.3 ± 2.1	6.5 ± 1.3
	2003/9/12	13.0 ± 2.3	8.2 ± 5.3
	2003/12/12	12.0 ± 2.2	9.6 ± 3.8
	2004/3/12	18.0 ± 2.4	12.8 ± 4.5
	2004/6/12	22.7 ± 2.5	22.3 ± 1.5
	2004/9/12	29.0 ± 2.6	26.0 ± 8.8
	2005/4/12	32.0 ± 2.6	29.1 ± 11.3

289

Table S5. Detailed sampling information of [sNO₃] measurement.

Sample name	Latitude	Longitude	Sampling duration & Samples	Time resolution	Description	Reference
Leipzig	51.33 °N	12.38 °E	2014/09/19 - 2014/10/25 & 13 samples in 39 days	3 days	urban grime samples, shield from precipitation, soda-lime glass beads	(28)
Leipzig dark					urban grime samples, shield from precipitation and light, soda-lime glass beads	
Toronto dark	43.65 °N	79.38 °W	2014/10/1 - 2015/08/27	~ 30 days	urban grime samples, shield from precipitation and light, quartz crystal microbalance (QCM) crystals	(29)
Beijing	39.99 °N	116.32 °E	2018/11/07 - 2018/11/23 & 8 samples in 8 days	1 day	urban grime samples, no precipitation. during sampling, Teflon filters	This study
Syracuse*	[42.99 °N, 43.05 °N]	[76.09 °W, 76.15 °W]	2017/2/20- 2017/9/24		urban grime samples, room window	(30)
Scranton*	[41.34 °N, 41.44 °N]	[75.64 °W, 75.77 °W]	2017/5/11- 2017/10/07			
Michigan*	45.30 °N	84.42 °W	2008/07/1/ - 2008/08/07		clean forest grime samples, live leaves	(31)
Köhlerloh*	50.08 °N	11.52 °E	2011/06/01-		clean forest grime samples, live leaves	(32)

2011/07/31

291 * means grime already exists on the impervious environmental surface for unknown time before sampling.

Table S6. Results of measured and modeled [sNO₃] at sampling locations listed in Table S5. Data are expressed as mean ± SD. Modeled [sNO₃] was calculated considering accumulated pNO₃ deposition, accumulated HNO₃ deposition. sNO₃ photolysis and precipitation wash-off were also considered according to sampling design.

Sample name	Sampling time	Measured [sNO ₃]	Modeled [sNO ₃]
		(μmol m ⁻²)	(μmol m ⁻²)
Leipzig*	2014/9/19	37.56 ± 8.69	8.07 ± 3.07
	2014/9/22	80.65 ± 18.65	31.42 ± 6.02
	2014/9/25	72.36 ± 16.74	47.15 ± 9.07
	2014/9/28	88.93 ± 20.57	64.94 ± 7.78
	2014/10/1	111.03 ± 25.68	86.09 ± 10.92
	2014/10/4	147.48 ± 34.11	104.99 ± 8.86
	2014/10/7	183.38 ± 42.42	134.10 ± 20.37
	2014/10/10	173.99 ± 40.24	170.14 ± 22.40
	2014/10/13	132.57 ± 30.66	189.32 ± 19.57
	2014/10/16	162.95 ± 37.69	209.66 ± 73.57
	2014/10/19	170.68 ± 39.48	251.49 ± 33.77
	2014/10/23	286.68 ± 66.31	289.63 ± 32.09
	2014/10/25	212.11 ± 49.06	299.73 ± 20.81
	2014/9/19	42.15 ± 9.75	8.49 ± 3.24
	2014/9/22	90.23 ± 20.87	33.79 ± 6.90
Leipzig dark*	2014/9/25	81.20 ± 18.78	51.86 ± 9.95
	2014/9/28	92.92 ± 21.49	72.33 ± 8.79
	2014/10/1	119.97 ± 27.75	96.45 ± 13.13
	2014/10/4	143.41 ± 33.17	118.39 ± 10.12
	2014/10/7	200.45 ± 46.36	150.66 ± 21.62
	2014/10/10	200.61 ± 46.40	190.33 ± 39.49
	2014/10/13	150.55 ± 34.82	209.50 ± 30.84
	2014/10/16	178.11 ± 41.20	229.85 ± 45.83
	2014/10/19	206.20 ± 47.70	271.68 ± 33.77
	2014/10/23	297.07 ± 68.71	309.81 ± 30.63
Toronto dark*	2014/10/25	249.88 ± 57.80	319.91 ± 38.62
	2014/10/29	14.00 ± 1.70	26.91 ± 7.58
	2014/12/4	14.00 ± 3.40	24.74 ± 2.33
	2015/1/12	15.00 ± 2.30	20.56 ± 3.72
	2015/2/20	27.00 ± 6.20	30.39 ± 6.19

	2015/4/2	12.00 ± 1.00	23.04 ± 7.39
	2015/5/15	32.00 ± 2.30	48.83 ± 4.44
	2015/6/26	45.00 ± 20.00	56.71 ± 15.97
	2015/7/28	26.00 ± 5.10	46.89 ± 8.57
	2015/8/27	30.00 ± 2.00	37.32 ± 3.26
	2018/11/7	0.92 ± 0.01	1.42 ± 2.40
	2018/11/8	4.63 ± 0.02	5.39 ± 3.18
	2018/11/9	5.72 ± 0.01	6.15 ± 0.95
Beijing*	2018/11/19	2.63 ± 0.06	2.47 ± 5.53
	2018/11/20	4.67 ± 0.05	5.75 ± 1.19
	2018/11/21	8.45 ± 0.09	6.43 ± 1.11
	2018/11/22	8.08 ± 0.03	7.91 ± 2.36
	2018/11/23	11.32 ± 0.02	11.78 ± 3.06
Syracuse#	2017/2/20- 2017/9/24	28.52 ± 6.03	25.15 ± 2.95
Scranton#	2017/5/11- 2017/10/07	37.24 ± 4.49	43.47 ± 5.86
Michigan#	2008/8/7	8.30 ± 3.10	5.66 ± 1.85
Köhlerloh#	2011/7/31	17.00 ± 7.00	12.00 ± 2.28

297 * means no model spin-up to represent grime accumulation on clean surface at the
298 start of sampling.

299 # means model spin-up for 14 days to represent grime already exists on the
300 impervious environmental surface before sampling.

301 **Table S7. Results of photolysis of sNO₃ on the surfaces of artificial materials and**
302 **plants.** Data from Ye et al.(Ye et al., 2016) Table 1 and Table 2.

[sNO ₃] (μmol m ⁻²)	Normalized J_{sNO_3} (×10 ⁻⁵ s ⁻¹)	Surface type and conditions	Category
28.0	2.0	Wood board	Building materials
9.1	2.9	Red brick	
9.0	1.7	Granite	
4.8	1.7	Zn-plated metal sheet	Metals
1.1	0.6	Stainless steel	
11.6	5.7	Al (unpolished)	
0.4	15.3	Al (polished)	

0.6	13.6	Al (polished)	
4.7	10.3	Al (polished)	
25.1	6.3	Al (polished)	
18.6	3.2	Maple	
3.4	3.7	Maple	
2.4	4.4	Maple	
5.1	3.0	Maple	Maple leaves
31.7	0.9	Maple	
38.0	0.9	Maple	
2.2	3.4	Maple	
17.0	4.9	Maple	
17.4	1.6	Oak	
11	2.4	Oak	
3.3	5.1	Oak	Oak leaves
0.54	16.0	Oak	
0.3	37.0	Oak	
18.3	3.4	Brich	
6.7	5.8	Grass	other plants
10.7	5.3	Kentia palm	
14.8	1.4	Pine	

Table S8. Results of measured and modeled grime wash-off efficiency (W_E) due to precipitation. Data are expressed as mean $\pm$ SD. Modeled W_E is calculated using W_E

$$= e^{-0.016 \times \frac{(P-1)^2}{P-1+10}}$$

Precipitation (mm)	Measured W_E	Modeled W_E	Reference
15	16.48%	12.49%	
23	24.04%	21.05%	
13	20.17%	10.18%	(16)
15	19.39%	12.26%	
22	19.33%	19.91%	
14	14.35%	10.64%	
89	72.72 $\pm$ 1.37%	71.63%	
57	56.39 $\pm$ 1.44%	53.51%	
77	67.82 $\pm$ 0.41%	65.70%	(17)
43	46.47 $\pm$ 1.40%	42.20%	
27	31.80 $\pm$ 1.53%	25.60%	

13	$18.59 \pm 1.41\%$	10.33%
11	$10.95 \pm 0.77\%$	7.79%
15	$16.88 \pm 1.25\%$	12.80%
22	$24.35 \pm 1.96\%$	20.50%
44	$41.57 \pm 1.74\%$	43.07%
67	$55.52 \pm 0.58\%$	59.74%
7	$6.33 \pm 2.25\%$	3.65%
10	$8.85 \pm 2.12\%$	6.55%
14	$13.56 \pm 2.06\%$	11.44%
29	$29.95 \pm 2.09\%$	27.75%
43	$39.69 \pm 1.97\%$	41.87%
57	$50.80 \pm 1.46\%$	53.49%

306 **Table S9. Results of sNO₃ photolysis HONO branching ratio (ϕ_{HONO}) within**
307 **different nitrate mixture. Data are expressed as mean $\pm$ SD.**

f_{OC}	ϕ_{HONO}	Mixture type	Reference
88.68%	$84.97 \pm 14.91\%$	Urban particulate matter filter sample	(33)
90.42%	$69.88 \pm 8.32\%$		
95.10%	$69.42 \pm 28.77\%$		
97.47%	$69.21 \pm 9.43\%$		
99.46%	$84.03 \pm 11.81\%$		
67.78%	75.68%	Urban particulate matter filter sample	(34)
68.06%	68.85%		
16.22%	66.23%		
22.18%	71.81%		
38.73%	70.57%		
23.63%	72.30%		
$35.52 \pm 11.85\%$	$68.09 \pm 11.97\%$	Organic compounds and nitrate artificial mixture	(35)
$91.59 \pm 4.67\%$	$70.11 \pm 15.78\%$		

308 **Table S10. Sample name, Location and sampling period of each HONO flux field**
309 **measurement.**

Sample name	Latitude	Longitude	Sampling duration	Reference
Bakersfield	35.2 °N	118.57 °W	2010/05/16 - 2010/06/29	(14)

Grignon	48.9 °N	1.95 °E	2011/08/16 - 2011/08/30	(36)
Guangzhou	23.1 °N	113.22 °E	2020/11/04 - 2020/11/24	(37)
Köhlerloh	50.08 °N	11.52 °E	2011/06/15 - 2011/07/31	(32)
Melpitz	51.53 °N	12.93 °E	2020/09/27 - 2020/10/02	(38)
Michigan	45.3 °N	84.42 °W	2008/07/17 - 2008/08/07	(31)
Shouxian2019	32.25 °N	116.47 °E	2019/11/15 - 2019/11/25	(39)
Shouxian2020	32.25 °N	116.47 °E	2019/12/15 - 2020/01/02	(40)
Shouxian2021	32.25 °N	116.47 °E	2021/05/29 - 2021/06/13	(41)
Wangdu2016	38.67 °N	115.25 °E	2016/08/02 - 2016/08/12	(42)

311 **Table S11. Results of modeled [sNO₃], modeled and measured sNO₃ photolysis HONO flux and related parameters at sampling locations**
312 **listed in Table S10.** Data are expressed as mean ± SD. [PM_{2.5}], [NO_x] and [sNO₃] are averages of modeled data in sampling duration at each
313 sampling location. Note that, both “Modeled sNO₃ photolysis HONO flux” and “Measured HONO flux” are daytime average (9:00-18:00, LT).
314 Contribution is the ratio of “Modeled sNO₃ photolysis HONO flux” and “Measured HONO flux”.

Sample name	[PM _{2.5}] (μg m ⁻³)	[NO _x] (ppbv)	Predicted [sNO ₃] (μmol m ⁻²)	Predicted sNO ₃ photolysis HONO flux (μmol m ⁻² h ⁻¹)	Measured HONO flux (μmol m ⁻² h ⁻¹)	Contribution
Bakersfield	9.37 ± 1.93	3.86 ± 2.16	4.50 ± 0.34	0.16 ± 0.00	0.32 ± 0.11	48.74 ± 0.99%
Grignon	25.73 ± 4.42	12.63 ± 0.90	5.17 ± 0.92	0.17 ± 0.01	0.34 ± 0.16	47.37 ± 2.24%
Guangzhou	175.15 ± 26.58	70.33 ± 3.53	48.96 ± 1.59	0.21 ± 0.01	0.74 ± 0.39	27.03 ± 1.82%
Köhlerloh	12.43 ± 1.42	5.46 ± 0.67	4.54 ± 0.22	0.16 ± 0.01	0.17 ± 0.06	87.11 ± 5.94%
Melpitz	10.88 ± 2.28	10.57 ± 0.48	3.03 ± 0.52	0.08 ± 0.00	0.13 ± 0.08	59.99 ± 0.64%
Michigan	11.40 ± 0.79	2.10 ± 1.20	4.66 ± 0.39	0.19 ± 0.01	0.37 ± 0.14	49.05 ± 1.48%
Shouxian2019	140.59 ± 25.91	64.02 ± 10.47	27.63 ± 3.54	0.17 ± 0.02	0.88 ± 0.47	21.45 ± 1.78%
Shouxian2020	133.32 ± 26.57	65.94 ± 8.47	46.86 ± 10.49	0.20 ± 0.02	0.61 ± 0.22	31.05 ± 5.55%
Shouxian2021	94.67 ± 6.84	74.98 ± 4.23	23.85 ± 4.62	0.20 ± 0.03	0.90 ± 0.47	23.56 ± 2.44%
Wangdu2016	118.16 ± 8.43	44.66 ± 2.41	10.15 ± 1.20	0.22 ± 0.02	0.90 ± 0.18	21.00 ± 1.45%

315

Table S12 Sampling information and results of each [HONO] field measurement

Sample name	Latitude	Longitude	Sampling duration (time resolution)	[HONO] (pptv)	Reference
Mt Tai summit, Tai'an* Peking University, Beijing [#]	36.18 °N	117.11 °E	2018/07/19-2018/07/31 (1 hour) 2023/12/22-2024/04/02 (1 hour)	185 ± 163 654 ± 604	(46) This study

* Mt Tai summit observation is conducted inside a meteorological observatory (1534 m a.s.l.) at the eastern part of the summit of Mt. Tai and anthropogenic emissions are expected to be negligible.

[#] Peking University observation is conducted at a typical urban site which is located between the north fourth ring road and the north fifth ring road in Beijing.

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