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Supplement of

Measurement report: Variations and environmental impacts of atmospheric N_2O_5 concentrations in urban Beijing during the 2022 Winter Olympics

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Sect. S1 Technical details of CRDS

Sect. S1.1 Determination of the Limit of Detection (LOD)

The LOD of the CRDS analyzer for N_2O_5 was determined via a 4-hour zero-air injection experiment: zero air (free of target analytes) was continuously introduced into the instrument cavity (1 s time resolution), and Allan variance analysis was applied to evaluate system stability (Figure S1). The LOD was calculated using Eq. (S1) below, yielding a value of 2.9 pptv.

$$[A] = \frac{R_L}{c\sigma}\left(\frac{1}{\tau} - \frac{1}{\tau_0}\right) \tag{S1}$$

where [A] denotes the analyte concentration, "R_L" is the the ratio of the cavity length to the length over which the absorber is present, c is the speed of light, σ is the absorption cross-section, τ is the cavity ring-down time with sample gas, and τ_0 is the background ring-down time with zero air. During the zero-air experiment, the instrument background level (τ_0) was measured as 50 µs.

Sect. S1.2 Calibration

To ensure measurement accuracy, we performed regular calibrations using stable, calibrated NO_3 and N_2O_5 standard sources (generated via a dynamic standard gas system, NO_3 generated by the reaction of NO_2 and O_3, N_2O_5 generated by the equilibrium of NO_3 and NO_2, as referenced in our prior work: Zhang et al., 2026). These calibrations quantified two critical correction factors addressing sampling losses

• Tubing loss: Measured at 11.4 ± 1.3%.

• Filter membrane loss: Quantified as 4.5 ± 0.5%

The final concentrations of [NO_3 + N_2O_5] and derived NO_3 were obtained by dividing raw instrument measurements by the sum of these loss ratios (i.e., correcting for signal reduction during sample transport).

Sect. S1.3 Uncertainty

• Parameter uncertainties in concentration calculation: The absorption cross-section (σ) and effective absorption cavity length—key parameters in Eq. (1)—contribute 13% and 4% uncertainty, respectively.

• Data correction uncertainties: Corrections for membrane loss (4.5 ± 0.5%) and pipeline loss (11.4 ± 1.3%) during sample transport introduce an additional 1.4% uncertainty.

The total combined uncertainty was calculated following the method described in our prior work (Zhang et al., 2024), confirming the 13.7% value.

References:

Zhang, T., Zuo, P., Ma, J., Ye, C., Lin, W., and Zhu, T.: Characterization and Application of an Online Measurement System for NO_3 and N_2O_5 Based on Cavity Ring-Down Spectroscopy, Acta Sci. Nat. Univ. Pekin., 60, 563–574, https://doi.org/10.13209/j.0479-8023.2024.030, 2024

Zhang, T., Ma, J., Liu, T., Lin, W., Zuo, P., and Ye, C.: A dynamic generation system for NO_3 and N_2O_5 standard gases, Environ. Chem., 45, 1–7, https://doi.org/10.7524/j.issn.0254-6108.2024091302, 2026.

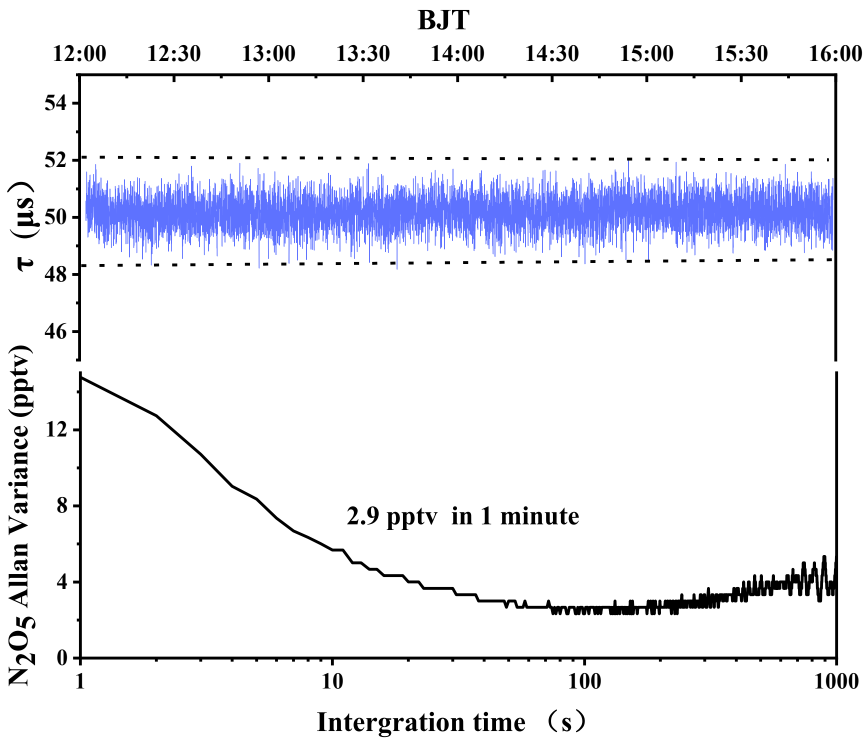

Figure S1. Limit of detection (LOD) and background signal of the instrument (blue line).

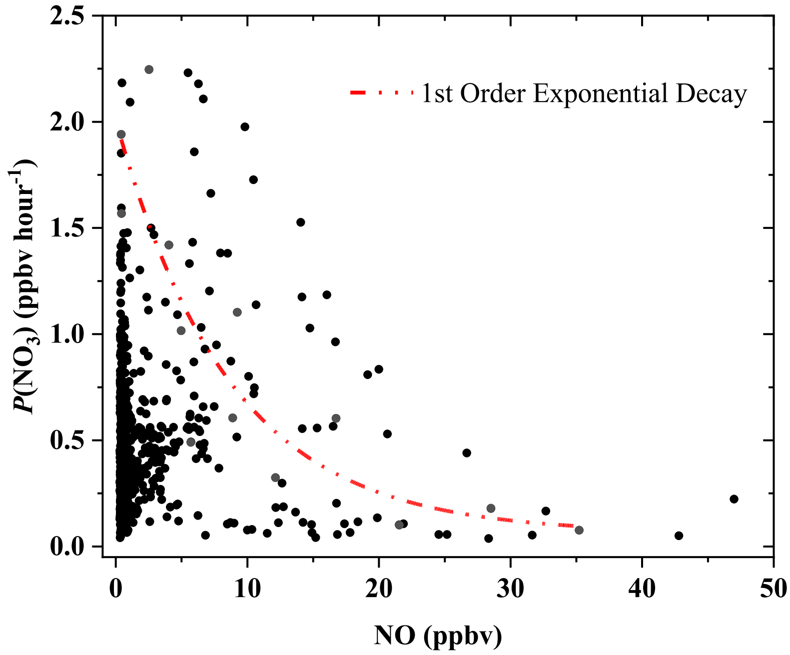

Figure S2. Schematic diagram of the correlation between NO and *P*(NO_3).

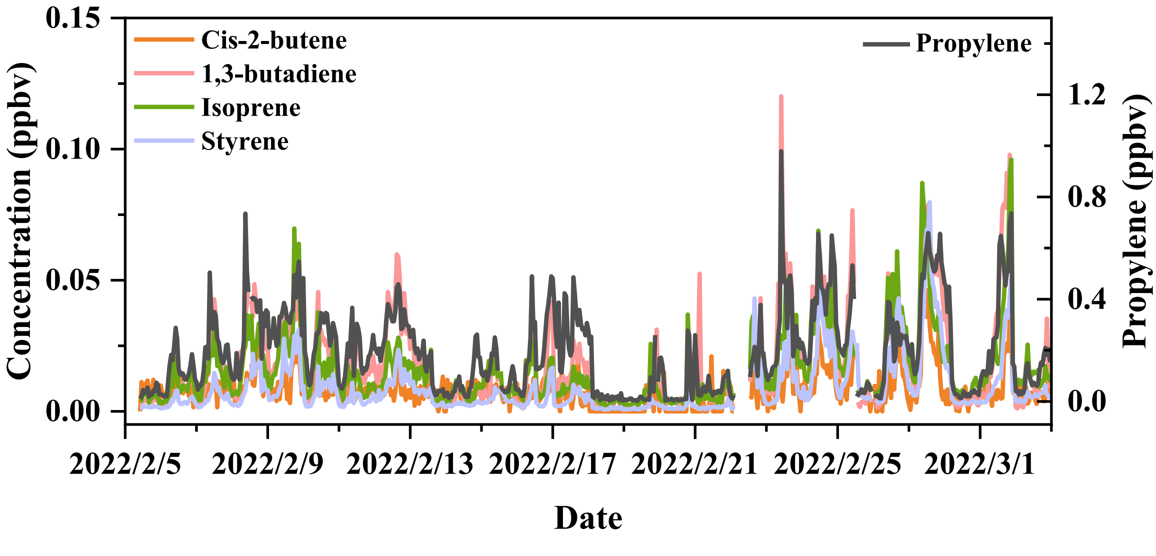

Figure S3. Temporal trends of highly reactive VOC concentrations during the observation period.

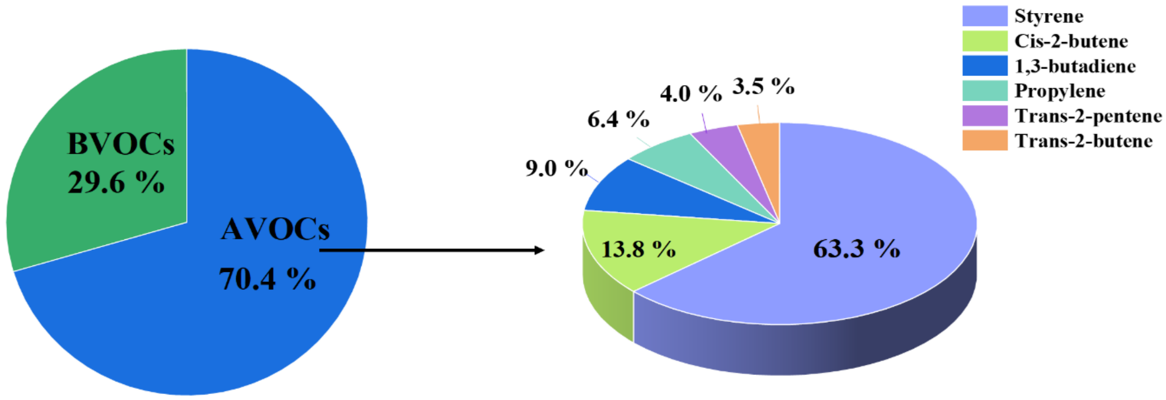

Figure S4. The proportion of reaction activity of NO_3 with different VOCs.

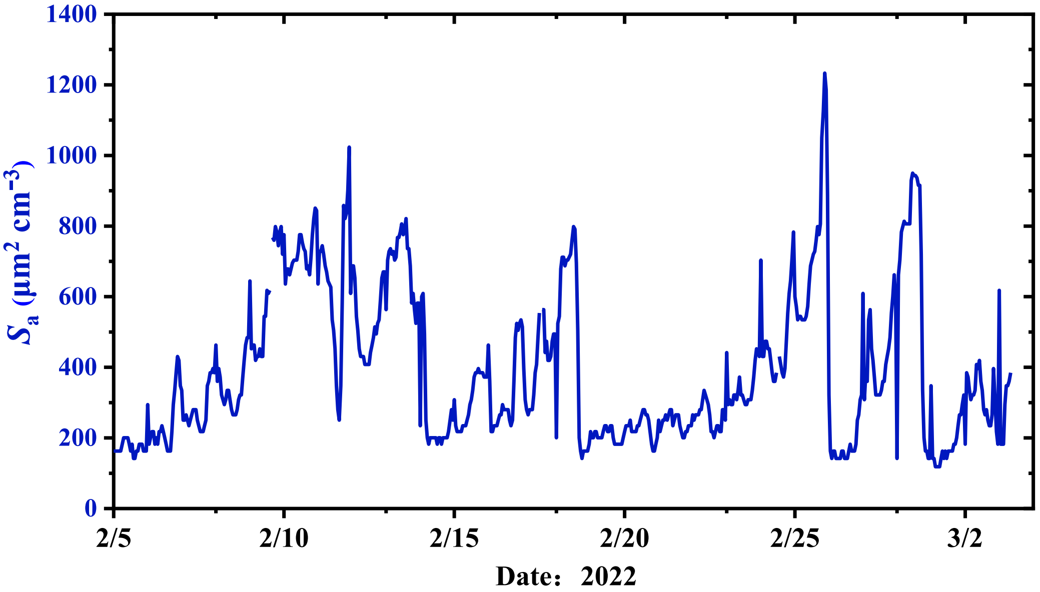

Figure S5. Time-series variations in 1h-mean S_a.

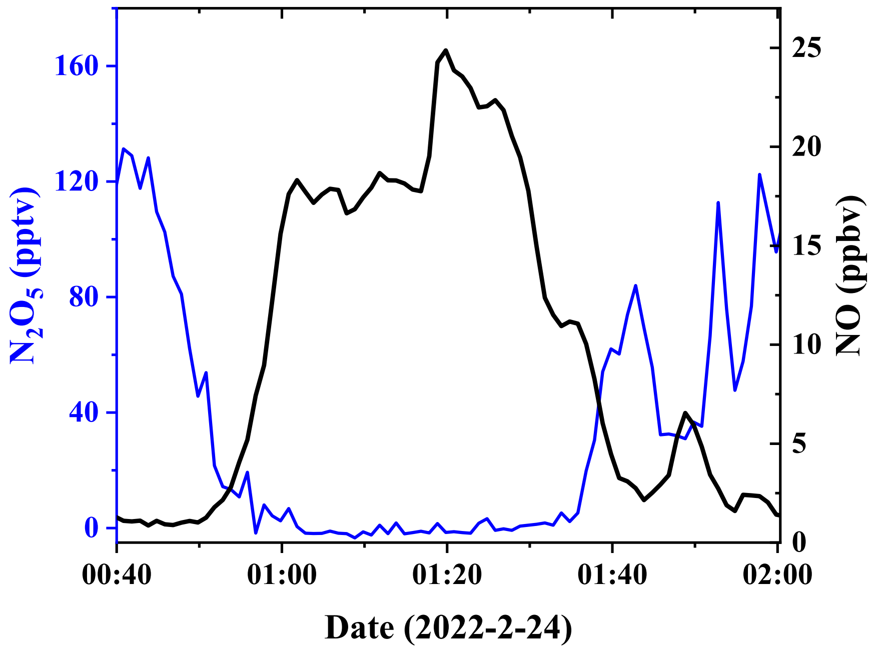

Figure S6. Variations in NO and N_2O_5 mixing ratios on Feb. 24, 2022.

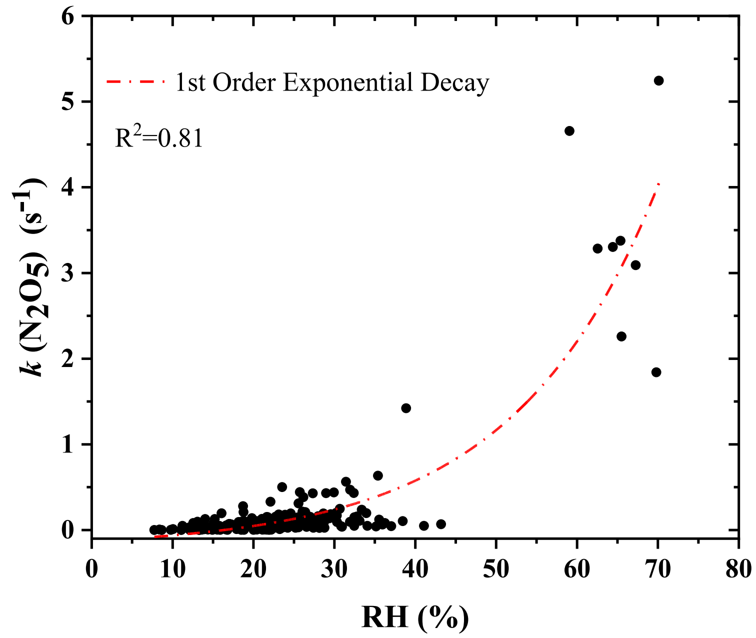

Figure S7. Schematic diagram of the correlation between RH and $k_{N_2O_5}$.

Table S1. Reaction rate coefficients of VOCs with respect to NO_3.

VOCs	OGP Concentration (ppbv)	POP Concentration (ppbv)	*k* (298K) (10^{-15} cm^3 molecule^{-1} s^{-1})
Ethane	3.61±1.55	4.03±2.12	0.01
Propane	1.91±0.97	2.46±1.67	＜0.07
Acetylene	1.41±1.04	1.61±1.09	0.21
Acetone	1.27±0.43	1.55±0.71	＜0.03
Ethylene	1.27±1.08	1.44±1.22	0.0049
Styrene	0.006±0.01	0.01±0.01	1500
Cis-2-butene	0.007±0.01	0.01±0.01	352
1,3-butadiene	0.02±0.01	0.02±0.02	100
Propylene	0.18±0.15	0.22±0.19	9.49
Isoprene (BVOC)	0.01±0.01	0.02±0.02	696

Table S2. N_2O_5 uptake coefficients and NO_3 loss rate coefficients from a nightly steady state analysis.

Start Time-End Time	$\gamma(N_2O_5)$	$k(NO_3)(s^{-1})$	Start Time-End Time	$\gamma(N_2O_5)$	$k(NO_3)$ (s^{-1})
2/06 0:00 - 2/06 05:40	0.0325	0.0713	2/19 20:40 - 2/20 06:00	0.0222	0.1214
2/06 19:00 - 2/07 05:40	0.0216	0.0999	2/20 19:20 - 2/21 06:20	0.011	0.1395
2/07 19:00 - 2/08 06:40	0.0198	0.0868	2/21 20:20 - 2/22 06:00	0.0285	0.1368
2/08 19:20 - 2/09 05:20	0.0296	0.2163	2/22 19:40 - 2/23 06:40	0.0108	0.1847
2/09 18:40 - 2/10 04:00	0.0042	0.3108	2/23 19:00 - 2/24 00:20	0.0053	0.2358
2/10 19:40 - 2/11 04:40	0.0108	0.0384	2/25 19:00 - 2/26 06:40	0.0101	0.062
2/11 18:40 - 2/12 06:40	0.0155	0.0097	2/26 18:20 - 2/27 02:40	0.024	0.1655
2/13 19:00 - 2/14 07:00	0.2244	0.7001	2/27 18:40 - 2/28 20:20	0.0345	0.2158
2/14 18:40 - 2/15 06:20	0.0162	0.3441	2/28 22:00 - 3/01 06:40	0.1232	0.0111
2/15 19:20 - 2/16 05:40	0.0125	0.1554	3/01 18:20 - 3/02 03:00	0.0395	0.0887
2/16 18:20 - 2/17 06:20	0.0043	0.1996	3/02 18:40 - 3/03 04:40	0.0014	0.1186
2/18 19:20 - 2/19 06:40	0.0402	0.1112			