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Supplement of

Characteristics, sources, and reactions of nitrous acid during winter at an urban site in the Central Plains Economic Region in China

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Supplement:

1. This AIM method and its details.

HONO was hygroscopically grown in the parallel plate denuder and collected as an aqueous solution in a cyclone assembly. The aqueous sample aliquots from both channels were transported to the ion chromatographic systems housed inside a ground container for hourly semicontinuous online analysis of HONO. The ion chromatographic system was calibrated for NO_2^- using mixed anion standard solutions of NO_2^- .

2. The concentration of OH radicals was calculated with the formulas of NO_2 , O_3 , and $J(\text{O}^1\text{D})$.

$$[\text{OH}] = \frac{k_{\text{HO}_2+\text{NO}} \tau_{\text{HC}} [\text{NO}_2] F_J}{k_{\text{NO}+\text{O}_3}} \times \sqrt{\frac{\alpha}{k_{\text{HO}_2+\text{HO}_2} [\text{O}_3]}} \times J(\text{O}^1\text{D}),$$

where $[\text{OH}]$ represents the concentration of OH radicals, $k_{\text{HO}_2+\text{NO}} = 8.56 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$, $\tau_{\text{HC}} = 0.3 \text{ s}$, $[\text{NO}_2]$ represents the NO_2 concentration, $F_J = 2 \text{ s}^{-0.5}$, $k_{\text{NO}+\text{O}_3} = 1.82 \times 10^{-14} \text{ cm}^3 \text{ s}^{-1}$, $\alpha = 0.075$, $k_{\text{HO}_2+\text{HO}_2} = 8.56 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$, $[\text{O}_3]$ represents the O_3 concentration, and $J(\text{O}^1\text{D})$ represents the O^1D efficiency of photolysis.

Figure Captions:

Fig. S1. The correlation study between HONO_{correct} and NO₂ in the nighttime.

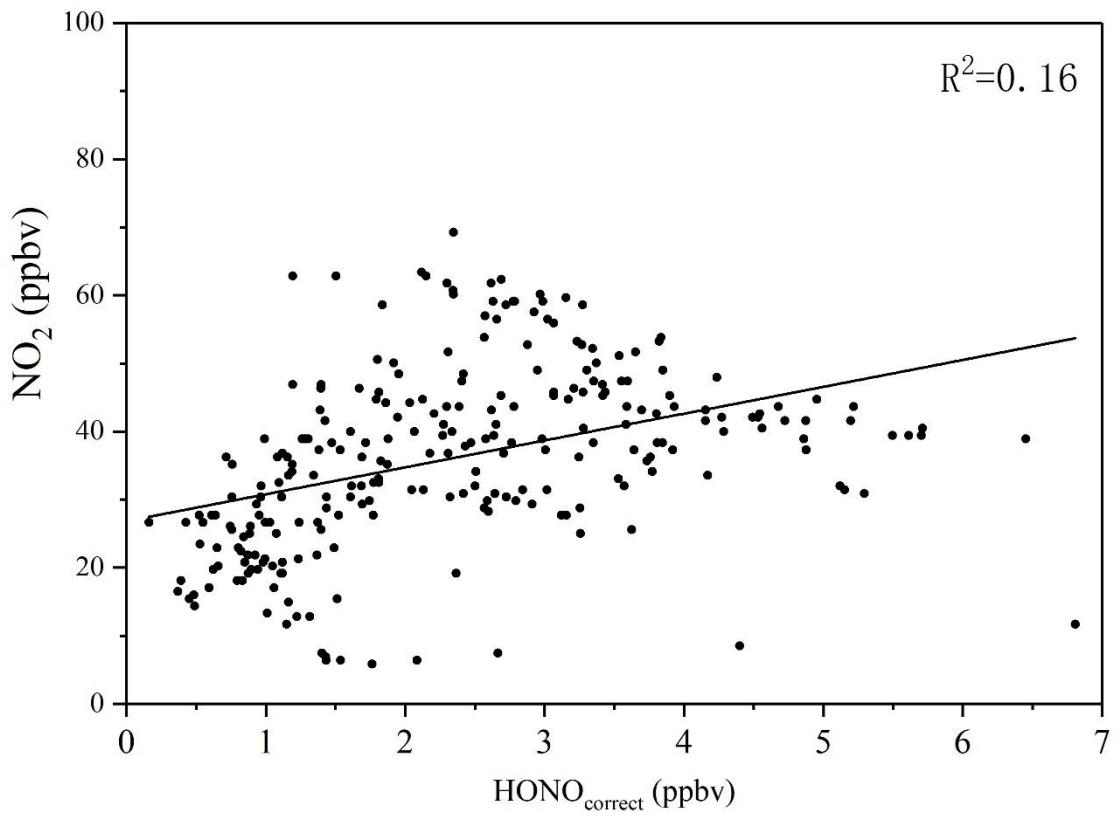


Fig. S1. The correlation study between HONO_{correct} and NO₂ in the nighttime.

Table Captions:

Table S1. Measured species and performance of the instruments.

Table S2 The error bars of Fig. 4. (The units of all species except HONO/NO₂ and HONO/NO_x are ppbv. The units of HONO/NO₂ and HONO/NO_x are %.)

Table S3 The error bars of Fig. 5. (The units of all species except P_{OH+NO}^{net} are ppbv. The unit of P_{OH+NO}^{net} is ppbv/h.)

Table S4 The error bars of Fig. 8. (The units of all species except HONO_{correct}/NO₂ are ppbv. The unit of HONO_{correct}/NO₂ is %.)

Table S1. Measured species and performance of the instruments.

Species	Measurement technique	Detection limit	Accuracy
PM _{2.5}	Tapered Element Oscillating Microbalance	1.5 $\mu\text{g m}^{-3}$	\pm 5%
HONO	Ion Chromatography	4 pptv	\pm 20%
CO	Absorbs Infrared Radiation	40 ppbv	\pm 5%
NO	Chemiluminescence	60 pptv	\pm 20%
NO ₂	Chemiluminescence	300 pptv	\pm 20%
O ₃	UV Photometry	0.5 ppbv	\pm 5%

The results came from instrument manufacturers.

Table S2-1 The error bars of Fig. 4. (The units of all species except HONO/NO₂ and HONO/NO_x are ppbv. The units of HONO/NO₂ and HONO/NO_x are %.)

Species-period	Local Time (hh:mm)									
	00:00	01:00	02:00	03:00	04:00	05:00	06:00	07:00	08:00	09:00
HONO-CD	1.7 ± 1.3	1.4 ± 0.6	1.3 ± 0.4	1.2 ± 0.3	1.2 ± 0.2	1.2 ± 0.2	1.4 ± 0.3	1.5 ± 0.6	1.7 ± 0.9	1.6 ± 0.9
HONO-PD	3.2 ± 1.5	3.1 ± 1.3	3 ± 1.1	3.3 ± 1.2	3.5 ± 1.3	3.5 ± 1.2	3.6 ± 1.1	3.3 ± 0.9	3.7 ± 1.6	4.1 ± 2.8
HONO-SPD	3.7 ± 0.9	4 ± 0.8	4.2 ± 0.6	4.4 ± 0.8	4.6 ± 1	4.6 ± 1.2	4.6 ± 1.5	4.4 ± 1.3	4.4 ± 1.1	5.7 ± 3
NO-CD	14.3 ± 17	9 ± 9.7	8.5 ± 12.7	10.1 ± 22.4	10.6 ± 21.1	21.9 ± 29	27.8 ± 33	40.1 ± 51	52.6 ± 79	55.5 ± 84
NO-PD	57.3 ± 48	62.7 ± 55.9	49.6 ± 49	44 ± 47.8	47 ± 48.7	46.6 ± 30	41.4 ± 34	44.7 ± 33	48.9 ± 35	53.7 ± 44
NO-SPD	79.4 ± 103	100.1 ± 118	128.3 ± 133	129 ± 134	111 ± 119	117 ± 95	100 ± 94	88.4 ± 85	82.3 ± 70	85.4 ± 71
NO ₂ -CD	25.4 ± 8.2	25.6 ± 9.9	24.7 ± 10.5	22.9 ± 10.4	24 ± 11.4	20.7 ± 11	20.2 ± 9	23.6 ± 11	28.6 ± 18	28.6 ± 18
NO ₂ -PD	41.1 ± 10	40.8 ± 11.2	39.7 ± 10.7	37.9 ± 7.1	36.6 ± 5.4	35.9 ± 5	33.8 ± 6	34.4 ± 6	33.2 ± 5	30.7 ± 6
NO ₂ -SPD	45.3 ± 9.5	43.5 ± 9.2	42.8 ± 8.8	42.1 ± 8.2	42.2 ± 8.1	41 ± 7.1	40.6 ± 6.9	40.7 ± 6	40.1 ± 6	39.2 ± 7
O ₃ -CD	14.2 ± 10	13.6 ± 10.4	14.2 ± 10.1	14.9 ± 9.4	13.6 ± 9.1	11.7 ± 10	13.8 ± 10	12.9 ± 9	11.6 ± 8	12.1 ± 7
O ₃ -PD	6.6 ± 6.1	6.4 ± 5.2	7.1 ± 5.2	6.3 ± 3.3	4.7 ± 2.2	5.3 ± 3	7.7 ± 6.9	5.3 ± 2.8	5.5 ± 3	7.1 ± 4
O ₃ -SPD	7.8 ± 6.4	7.7 ± 6.2	7.3 ± 5	6 ± 2.9	5.3 ± 2.3	5 ± 2.1	5.6 ± 2.5	5.2 ± 2.2	5.6 ± 2.6	6 ± 2.6
HONO/NO ₂ -CD	3.8 ± 1.5	4.4 ± 1	4.4 ± 1.1	4.9 ± 1	5.1 ± 0.8	8.3 ± 6	6.9 ± 2.1	6.2 ± 1.4	5.1 ± 0.8	4.3 ± 1.1
HONO/NO ₂ -PD	8 ± 3.6	7.8 ± 3.4	8 ± 3.3	9 ± 3.7	10 ± 4.5	10.1 ± 4	11.2 ± 4.6	10.3 ± 4	12.1 ± 7	14.3 ± 11
HONO/NO ₂ -SPD	8.3 ± 1.9	9.3 ± 1.4	10 ± 1.5	10.7 ± 1.9	11 ± 2.2	11.3 ± 3	11.5 ± 3.9	10.9 ± 3	11.1 ± 2	15 ± 8.3
HONO/NO _x -CD	2.7 ± 1.4	3.7 ± 1.5	4.2 ± 1.4	4.9 ± 1.1	4.9 ± 1	5.3 ± 2.5	5.1 ± 2.9	4.5 ± 2.4	3.6 ± 1.5	2.8 ± 1.4
HONO/NO _x -PD	4.4 ± 1.4	4.3 ± 1.7	4.6 ± 1.5	5.3 ± 1.3	5.3 ± 1	5.3 ± 1.1	6.6 ± 2.7	5.9 ± 2.3	6.5 ± 3.8	6.6 ± 4.3
HONO/NO _x -SPD	5.1 ± 2	5.3 ± 2.4	5.4 ± 3.4	5.8 ± 3.9	6.1 ± 3.9	5.7 ± 3.7	5.9 ± 3.6	5.7 ± 3	5.8 ± 2.9	6.7 ± 3.1

Table S2-2 The error bars of Fig. 4. (The units of all species except HONO/NO₂ and HONO/NO_x are ppbv. The units of HONO/NO₂ and HONO/NO_x are %.)

Species-period	Local Time (hh:mm)									
	10:00	11:00	12:00	13:00	14:00	15:00	16:00	17:00	18:00	19:00
HONO-CD	1.1 ± 0.6	0.6 ± 0.3	0.5 ± 0.3	0.6 ± 0.4	0.6 ± 0.5	0.7 ± 0.5	0.6 ± 0.5	0.7 ± 0.4	1 ± 0.5	1.2 ± 0.5
HONO-PD	2.9 ± 1.9	1.9 ± 1.3	1.3 ± 0.7	1 ± 0.3	0.9 ± 0.3	0.9 ± 0.3	0.9 ± 0.3	1.1 ± 0.4	1.4 ± 0.3	1.7 ± 0.3
HONO-SPD	6.9 ± 4.3	5.2 ± 3.8	3 ± 1.3	2.1 ± 0.7	1.8 ± 0.7	1.7 ± 0.6	1.8 ± 0.7	2 ± 0.5	2.7 ± 0.7	2.8 ± 0.8
NO-CD	43.9 ± 69.8	27.9 ± 40.8	14.9 ± 17.1	10.3 ± 7.8	7.3 ± 3	6 ± 4.5	6.4 ± 5.6	3.6 ± 3.4	2.6 ± 3.2	5.9 ± 7.7
NO-PD	49.3 ± 45.2	30 ± 26.2	21 ± 20.7	12.7 ± 14.7	9.4 ± 12.3	8.4 ± 9.5	5.7 ± 4.7	6.3 ± 6.8	9 ± 9	10 ± 10.3
NO-SPD	90.8 ± 73.4	79.3 ± 69.3	57.1 ± 52.3	34.8 ± 36.4	24.5 ± 28.7	19 ± 24.7	15 ± 18.8	11.8 ± 11	11.8 ± 7.9	22.4 ± 21
NO ₂ -CD	26.8 ± 15.7	22.7 ± 9.2	17.6 ± 7.1	17.1 ± 9	19.6 ± 9.6	21 ± 10.7	20.5 ± 9	21.4 ± 9	26 ± 12.5	30 ± 13.7
NO ₂ -PD	30 ± 6.9	28.8 ± 7.7	27.4 ± 9.6	24.8 ± 9.4	22.5 ± 10.6	25 ± 9.9	25.7 ± 9.3	27.1 ± 9	35 ± 8.7	36.2 ± 9.2
NO ₂ -SPD	39.8 ± 7.8	41.5 ± 8.3	42.3 ± 10.1	39.5 ± 12.6	38.5 ± 14.3	38 ± 14.7	38 ± 13.9	42 ± 15.4	45 ± 11.5	47 ± 10.8
O ₃ -CD	15.9 ± 8.8	19.5 ± 9.7	22.6 ± 8.3	25.5 ± 8.5	28.1 ± 9.1	29 ± 10.8	28 ± 10.8	29 ± 10.2	23.6 ± 10	17 ± 8.9
O ₃ -PD	9.6 ± 6.1	12.8 ± 6.2	18.7 ± 8.3	24.1 ± 8.4	28.2 ± 9.7	27 ± 10.8	28 ± 10.4	26 ± 10.5	17.4 ± 8.6	15 ± 11.6
O ₃ -SPD	6.3 ± 2.4	8.7 ± 4.5	12.8 ± 8.5	19.4 ± 12.9	24.1 ± 14.7	28 ± 16.6	29 ± 17.6	25 ± 16.1	17 ± 11.1	10.6 ± 9.7
HONO/NO ₂ -CD	4.1 ± 2.3	3.1 ± 1.9	3.3 ± 1.9	3.3 ± 1.3	3.1 ± 1.3	3.1 ± 1.3	2.9 ± 1.4	3.1 ± 1.4	3.9 ± 1.4	4.5 ± 2.2
HONO/NO ₂ -PD	9.4 ± 5.6	6.2 ± 3	4.7 ± 1.5	4.2 ± 1.2	4.7 ± 2.2	3.9 ± 0.7	3.7 ± 0.4	4.1 ± 1.2	4.3 ± 0.9	5 ± 1.5
HONO/NO ₂ -SPD	18.9 ± 13.7	13.7 ± 12	7.3 ± 3.5	5.6 ± 2.6	4.9 ± 2.1	4.8 ± 2.4	4.9 ± 1.6	5 ± 1	6.3 ± 1.8	6.2 ± 1.5
HONO/NO _x -CD	2.9 ± 2.1	2.2 ± 1.5	2.4 ± 1.5	2.5 ± 1.1	2.5 ± 1	2.6 ± 0.9	2.5 ± 0.9	2.8 ± 1	3.7 ± 1.1	4.1 ± 1.9
HONO/NO _x -PD	4.8 ± 2.4	3.8 ± 1.3	3.5 ± 1.2	3.5 ± 1.5	4 ± 2.1	3.4 ± 0.9	3.3 ± 0.5	3.7 ± 1.2	3.8 ± 0.7	4.3 ± 1.5
HONO/NO _x -SPD	8.2 ± 5.8	6.9 ± 5.7	4.3 ± 2	4 ± 2	3.8 ± 1.6	3.9 ± 1.9	4.3 ± 1.6	4.5 ± 1.2	5.5 ± 1.5	4.9 ± 1.3

Table S2-3 The error bars of Fig. 4. (The units of all species except HONO/NO₂ and HONO/NO_x are ppbv. The units of HONO/NO₂ and HONO/NO_x are %.)

Species-period	Local Time (hh:mm)			
	20:00	21:00	22:00	23:00
HONO-CD	1.3 ± 0.6	1.6 ± 0.9	2 ± 0.9	2.1 ± 0.9
HONO-PD	1.7 ± 0.7	1.8 ± 0.8	2 ± 0.9	2.1 ± 0.9
HONO-SPD	3.1 ± 0.9	3.2 ± 0.9	3.7 ± 0.8	4.6 ± 1.2
NO-CD	11.1 ± 16.9	14.5 ± 22.5	35.5 ± 68.9	50.8 ± 99.2
NO-PD	15 ± 14.1	15.3 ± 14.7	27.4 ± 28.5	33.9 ± 28.9
NO-SPD	29.4 ± 24.2	37.3 ± 26.6	38.5 ± 23.1	51.4 ± 31.4
NO ₂ -CD	31 ± 13.8	30.3 ± 14.5	31.6 ± 13.6	31 ± 14.3
NO ₂ -PD	37.3 ± 10.5	38.5 ± 13.9	38.3 ± 13.5	37.1 ± 13.2
NO ₂ -SPD	44.5 ± 11	43.5 ± 11.5	43.5 ± 11.1	42.1 ± 13.1
O ₃ -CD	13.3 ± 10.1	14 ± 11	12.2 ± 8.7	12.7 ± 8.8
O ₃ -PD	13.7 ± 10.3	10.9 ± 8.5	10.9 ± 7.7	12.2 ± 10.4
O ₃ -SPD	9.9 ± 8.6	10.8 ± 9.2	9.7 ± 8.7	9.6 ± 9.6
HONO/NO ₂ -CD	4.6 ± 2.2	5.7 ± 2.6	6.5 ± 2.6	6.8 ± 2.7
HONO/NO ₂ -PD	4.7 ± 1.9	4.6 ± 1.2	4.9 ± 0.8	5.3 ± 0.8
HONO/NO ₂ -SPD	7 ± 1.5	7.5 ± 1.4	8.9 ± 2.3	9.4 ± 2.4
HONO/NO _x -CD	4 ± 1.9	4.8 ± 2.2	4.9 ± 2.8	5 ± 3
HONO/NO _x -PD	3.9 ± 2.1	3.9 ± 1.3	3.8 ± 1	3.8 ± 0.9
HONO/NO _x -SPD	5.1 ± 1.5	5.2 ± 2	5.8 ± 2	5 ± 1.4

Table S3-1 The error bars of Fig. 5. (The units of all species except $P_{\text{OH+NO}}^{\text{net}}$ are ppbv. The unit of $P_{\text{OH+NO}}^{\text{net}}$ is ppbv/h.)

Species-period	Local Time (hh:mm)									
	19:00	20:00	21:00	22:00	23:00	00:00	01:00	02:00	03:00	04:00
$P_{\text{OH+NO}}^{\text{net}}\text{-CD}$	0.04 ± 0.06	0.08 ± 0.12	0.11 ± 0.17	0.33 ± 0.54	0.47 ± 0.79	0.12 ± 0.13	0.07 ± 0.08	0.03 ± 0.03	0.01 ± 0.1	0.02 ± 0.1
HONO-CD	1.18 ± 0.48	1.32 ± 0.62	1.62 ± 0.9	2.02 ± 0.94	2.09 ± 0.9	1.67 ± 1.34	1.43 ± 0.63	1.26 ± 0.44	1.2 ± 0.3	1.2 ± 0.22
NO-CD	5.4 ± 6.5	10.2 ± 14.4	13.3 ± 19.2	38.2 ± 62.2	54.9 ± 89.7	15 ± 14.8	8.8 ± 8.6	3.7 ± 4.2	1.5 ± 2.3	2.5 ± 2.6
$P_{\text{OH+NO}}^{\text{net}}\text{-HD}$	0.07 ± 0.07	0.1 ± 0.1	0.1 ± 0.1	0.19 ± 0.2	0.23 ± 0.2	0.4 ± 0.34	0.44 ± 0.4	0.34 ± 0.35	0.3 ± 0.34	0.3 ± 0.34
HONO-HD	1.7 ± 0.27	1.71 ± 0.68	1.82 ± 0.78	1.98 ± 0.89	2.06 ± 0.93	3.21 ± 1.54	3.05 ± 1.27	3.01 ± 1.08	3.3 ± 1.17	3.5 ± 1.34
NO-HD	8.5 ± 8.4	12.2 ± 11.5	12.5 ± 12	22.4 ± 23.3	27.7 ± 23.6	46.8 ± 39.5	51.2 ± 45.6	40.5 ± 40	35.9 ± 39	38 ± 39.7
$P_{\text{OH+NO}}^{\text{net}}\text{-SHD}$	0.15 ± 0.15	0.2 ± 0.17	0.25 ± 0.18	0.26 ± 0.16	0.35 ± 0.23	0.55 ± 0.75	0.7 ± 0.85	0.9 ± 0.96	0.9 ± 1.0	0.8 ± 0.86
HONO-SHD	2.8 ± 0.8	3.1 ± 0.9	3.2 ± 0.9	3.7 ± 0.8	4.6 ± 1.2	3.7 ± 0.9	4 ± 0.8	4.2 ± 0.6	4.4 ± 0.8	4.6 ± 1
NO-SHD	18 ± 17	24 ± 20	30 ± 21	31 ± 19	42 ± 25	64 ± 84	81 ± 96	104 ± 108	105 ± 110	90 ± 97

Table S3-2 The error bars of Fig. 5. (The units of all species except $P_{\text{OH+NO}}^{\text{net}}$ are ppbv. The unit of $P_{\text{OH+NO}}^{\text{net}}$ is ppbv/h.)

Species-period	Local Time (hh:mm)	
	05:00	06:00
$P_{\text{OH+NO}}^{\text{net}}$ -CD	0.12 ± 0.18	0.17 ± 0.22
HONO-CD	1.25 ± 0.21	1.36 ± 0.35
NO-CD	13.7 ± 20.9	19.5 ± 25.1
$P_{\text{OH+NO}}^{\text{net}}$ -HD	0.32 ± 0.22	0.28 ± 0.25
HONO-HD	3.5 ± 1.16	3.56 ± 1.09
NO-HD	38 ± 25.2	33.8 ± 28.5
$P_{\text{OH+NO}}^{\text{net}}$ -SHD	0.82 ± 0.87	0.7 ± 0.68
HONO-SHD	4.6 ± 1.2	4.6 ± 1.5
NO-SHD	95.6 ± 99	81.8 ± 77.1

Table S4-1 The error bars of Fig. 8. (The units of all species except $\text{HONO}_{\text{correct}}/\text{NO}_2$ are ppbv. The unit of $\text{HONO}_{\text{correct}}/\text{NO}_2$ is %.)

Species-period	Local Time (hh:mm)									
	19:00	20:00	21:00	22:00	23:00	00:00	01:00	02:00	03:00	04:00
$\text{HONO}_{\text{correct}}\text{-CD}$	1.0 ± 0.4	1.1 ± 0.6	1.4 ± 0.8	1.6 ± 0.7	1.6 ± 0.6	1.4 ± 1.4	1.2 ± 0.7	1.1 ± 0.5	1.1 ± 0.4	1.1 ± 0.2
$\text{NO}_2\text{-CD}$	30 ± 15	31 ± 15	30 ± 15	34 ± 15	34 ± 15	25 ± 9	24 ± 8	22 ± 8	20 ± 8	20 ± 8
$\text{HONO}_{\text{correct}}/\text{NO}_2\text{-CD}$	3.7 ± 2.2	3.9 ± 2.2	4.9 ± 2.6	5.5 ± 2.7	5.7 ± 2.9	11 ± 18.2	8.9 ± 12	8.6 ± 10.8	8.5 ± 9.7	7.7 ± 7.4
$\text{HONO}_{\text{correct}}\text{-HD}$	1.4 ± 0.3	1.4 ± 0.7	1.5 ± 0.7	1.6 ± 0.8	1.7 ± 0.8	2.7 ± 1.3	2.5 ± 1	2.5 ± 0.8	2.9 ± 0.9	3.1 ± 1.1
$\text{NO}_2\text{-HD}$	36 ± 9	37 ± 10	39 ± 14	38 ± 13	37 ± 13	41 ± 10	41 ± 11	40 ± 11	38 ± 7	37 ± 5
$\text{HONO}_{\text{correct}}/\text{NO}_2\text{-HD}$	4.2 ± 1.5	3.8 ± 2	3.8 ± 1.2	4 ± 0.8	4.4 ± 0.7	6.7 ± 3.1	6.5 ± 2.8	6.7 ± 2.8	7.8 ± 3.1	8.7 ± 3.8
$\text{HONO}_{\text{correct}}\text{-SHD}$	2.4 ± 0.6	2.6 ± 0.7	2.7 ± 0.7	3.2 ± 0.7	4.1 ± 1.3	3.1 ± 0.8	3.3 ± 0.6	3.4 ± 0.7	3.6 ± 1	3.9 ± 1.1
$\text{NO}_2\text{-SHD}$	47 ± 11	44 ± 11	43 ± 11	44 ± 11	42 ± 13	45 ± 9	43 ± 9	43 ± 9	42 ± 8	42 ± 8
$\text{HONO}_{\text{correct}}/\text{NO}_2\text{-SHD}$	5.4 ± 1.4	6.1 ± 1.4	6.5 ± 1.4	7.8 ± 2.2	14.4 ± 16.7	7 ± 1.9	7.8 ± 1.6	8.1 ± 2.2	8.8 ± 2.8	9.3 ± 2.9

Table S4-2 The error bars of Fig. 8. (The units of all species except $\text{HONO}_{\text{correct}}/\text{NO}_2$ are ppbv. The unit of $\text{HONO}_{\text{correct}}/\text{NO}_2$ is %.)

Species-period	Local Time (hh:mm)	
	05:00	06:00
$\text{HONO}_{\text{correct}}\text{-CD}$	1.0 ± 0.4	1.1 ± 0.6
$\text{NO}_2\text{-CD}$	30 ± 15	31 ± 15
$\text{HONO}_{\text{correct}}/\text{NO}_2\text{-CD}$	3.7 ± 2.2	3.9 ± 2.2
$\text{HONO}_{\text{correct}}\text{-HD}$	1.4 ± 0.3	1.4 ± 0.7
$\text{NO}_2\text{-HD}$	36 ± 9	37 ± 10
$\text{HONO}_{\text{correct}}/\text{NO}_2\text{-HD}$	4.2 ± 1.5	3.8 ± 2
$\text{HONO}_{\text{correct}}\text{-SHD}$	2.4 ± 0.6	2.6 ± 0.7
$\text{NO}_2\text{-SHD}$	47 ± 11	44 ± 11
$\text{HONO}_{\text{correct}}/\text{NO}_2\text{-SHD}$	5.4 ± 1.4	6.1 ± 1.4