Observation of nitrous acid (HONO) in Beijing, China: Seasonal variation, nocturnal formation and daytime budget

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HIGHLIGHTS

- Atmospheric HONO has been observed in Beijing over four different seasons.
- Seasonality of HONO conversion frequencies was closely related to RH levels.
- Daytime HONO formation was mainly controlled by the additional HONO source.
- Correlation studies evidenced the key role of JNO₂ for HONO formation.
- Photolysis of adsorbed HNO₃ and NO₃⁻ could be potential HONO source in autumn.

GRAPHICAL ABSTRACT

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ABSTRACT

Seasonal characteristics of atmospheric nitrous acid (HONO) were investigated with high time-resolution field measurements at an urban site of Beijing in four select months (representing four different seasons) from September 2015 to July 2016. The HONO concentrations displayed a pronounced seasonal profile with a maximum in autumn (2.27 ± 1.82 ppb) and a minimum in winter (1.05 ± 0.89 ppb). Significant diurnal cycles were also observed during the whole campaign. We found that the nighttime build-up of HONO was attributed to the heterogeneous conversion of NO₂ on wet surface. The calculated NO₂ to HONO conversion frequencies varied from 0.005 h^{-1} in spring to 0.010 h^{-1} in summer, with an average value of 0.008 h^{-1} . The seasonality of these conversion frequencies was closely related to the RH levels in different seasons. During daytime, large additional HONO sources were calculated. The noontime additional source was the highest in autumn 3.82 ppb h^{-1} , followed by summer 3.05 ppb h^{-1} , spring 2.63 ppb h^{-1} and winter 1.30 ppb h^{-1} . Correlation studies between the additional HONO source and related parameters demonstrated that the controlling processes responsible for HONO daytime formation varied in different seasons, and that the photo-enhanced formation on wet surface or the photolysis of adsorbed nitric acid and nitrate could be potential HONO sources in Beijing.

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1. Introduction

Nitrous Acid (HONO) is a key nitrogen-containing species in the atmosphere due to its contribution to the atmospheric oxidizing capacity.

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The photolysis of HONO (R1) is appreciated as a significant daytime source of hydroxyl radicals (OH) (Aumont et al., 2003; Kleffmann et al., 2005; Su et al., 2011; Villena et al., 2011), which acts as a dominant atmospheric oxidant and initiates the formation of ozone and secondary organic aerosol (SOA) (Hofzumahaus et al., 2009).

The photochemistry of HONO has been and is still widely discussed in the world. Apart from the direct emissions from combustion processes and the homogeneous reaction between nitric oxide (NO) and OH (R2), the heterogeneous conversion of NO₂ on wet surface (R3) was considered to be a dominant source of HONO, especially during nighttime (Finlayson-Pitts et al., 2003). To further sustain the observed HONO concentration during daytime, other formation mechanisms have been proposed, such as photosensitized conversion of nitrogen dioxide (NO₂) on soot (Monge et al., 2010) or humic acid surface (R4) (Han et al., 2016a; Han et al., 2016b; Stemmler et al., 2006; Stemmler et al., 2007), soil nitrite emission (R5) (Su et al., 2011), photolysis of adsorbed nitric acid (HNO₃) and nitrate (NO₃[−]) (R6) (Ye et al., 2016; Zhou et al., 2011; Zhou et al., 2003), homogeneous nucleation of NO₂, H₂O and NH₃ (R7) (Zhang and Tao, 2010), and the reaction between electronically excited nitrogen dioxide (NO₂^{*}) and a molecule of water (H₂O) (R8) (Li et al., 2008). However, the dominant mechanism responsible for HONO daytime formation remains unclear. More field observations in varieties of environments are still necessary for improving our understanding of HONO formation mechanisms.

Compared with HONO production, the loss of HONO is well understood. During daytime, except for the photolysis process (R1), HONO can also be removed through reaction with OH:

The main loss process during nighttime is dry deposition due to the absence of solar radiation and the low OH concentration. During the first half of the night, the HONO sink is weak. With the accumulation of HONO concentration, the strength of HONO dry deposition dominates. Then the concentration of HONO can reach a steady state when production, vertical mixing and dry deposition balance each other.

Due to the important role of HONO in atmospheric chemistry, numerous HONO measurements have been carried out in the world during the last three decades (Acker and Moellera, 2007; Elshorbany et al., 2009; Legrand et al., 2014; Perner and Platt, 1979; Pusede et al., 2015). With the fast economic growth, Beijing has been suffering from severe air pollution problems. In recent years, high levels of atmospheric HONO have been observed (up to 9.71 ppb) in urban areas of Beijing in winter (Spataro et al., 2013). The unknown HONO noontime source observed can reach up to 5 ppb h^{−1} (Liu et al., 2014). However, the existing HONO measurements mostly carried out over short periods

during summer or winter, and the on-line long-term HONO observations over different seasons were still rare in Beijing.

Hereby, we conducted continuous HONO measurements in four select months (covering four different seasons) from September 2015 to July 2016 in Beijing urban area with the Ambient Ion Monitor-Ion Chromatography (AIM-IC) analysis system. In addition, other water-soluble compounds, such as gaseous HNO₃ and particulate nitrate (NO₃[−]), trace gases (NO_x, CO and O₃), BC, PM_{2.5}, aerosol optical properties (total light scattering and absorption coefficients) and meteorological parameters were also measured simultaneously. The main objectives of this work were to investigate the seasonal characteristics of HONO concentrations, nocturnal formation and daytime budget, and to examine the relative importance of different HONO sources to daytime budget.

2. Experimental

2.1. Site description

The measurements were conducted in the campus of Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, which was located in the northwestern urban area of Beijing (40°00′28″N, 116°20′15″E) and outside the fourth ring road. The sampling site was located on the roof of a fifth-floor building (18 m above the ground level).

2.2. Instruments

Ambient concentrations of gaseous nitrous acid (HONO), nitric acid (HNO₃) and particulate nitrate (NO₃[−]) were measured by the AIM-IC analysis system (URG Corp., Chapel Hill, NC). The time resolution of this system was 1 h. A detailed description of this inlet design and the operation characteristics can be found in VandenBoer et al. (2014) and Markovic et al. (2012). Briefly, the ambient air was drawn at 3 L min^{−1} through a 2.5 μm particulate matter (PM_{2.5}) cyclone before being directed into two parallel liquid diffusion denuders. As the ambient air flow passed through the denuders, the water-soluble gases were scrubbed into deionized water containing 5 mM H₂O₂. The remaining water-soluble particles were transported into the aerosol supersaturation chamber and collected as aqueous solution in a cyclone assembly. Finally, these aqueous samples from both channels were analyzed continuously via anion and cation IC units. The system detection limits of HONO, HNO₃ and NO₃[−] were 65 ppt, 65 ppt and 45 ng m^{−3}, respectively. Previous works have demonstrated that the HONO observations measured with this AIM-IC system consisted well with those by the Stripping Coil-UV/Vis Absorption Photometer (SC-AP) system (VandenBoer et al., 2014), which utilized coil scrubbers, azo-dye derivatization and absorption detection.

Trace gases of NO–NO₂–NO_x, CO and O₃ were measured by NO–NO₂–NO_x analyzer (42i, Thermo, USA), CO analyzer (48i, Thermo, USA) and O₃ analyzer (49i, Thermo, USA), respectively, with a time resolutions of 1 min. Measurements of the total light scattering coefficient and absorption coefficient (Wu et al., 2009) were carried out by a nephelometer (Aurora-1000; Ecotech) and a seven-channel (370–940 nm) aethalometer (Model AE33; Magee Scientific, USA) with the time resolutions of 5 min. The PM_{2.5} mass concentration and meteorological parameters, including ambient temperature (T) and relative humidity (RH), were given by TEOM (1405-DF). Daily maintenance and routinely calibration have been carried out to ensure the accuracy of these data.

2.3. Simulations of photolysis rates

Direct measurements of the photolysis rates of HONO, NO₂ and O (¹D) were unavailable in this work. The NCAR Tropospheric Ultraviolet and Visible (TUV) transfer model was used to calculate J_{HONO}, J_{NO₂} and J_{O¹D} (Hendrick et al., 2014; Hou et al., 2016; Soergel et al., 2011; Su

et al., 2008b; VandenBoer et al., 2014). To reflect the effect of aerosols on the values of photolysis rates, aerosol optical depth (AOD), single scattering albedo (SSA) and Angstrom exponent values were used as input data in the TUV model. The AOD and Angstrom exponent values were measured by Moderate Resolution Imaging Spectroradiometer (MODIS) satellite (Remer et al., 2005). The SSA value was determined by an aethalometer and a nephelometer (Coen et al., 2004). The TUV model was run every hour from 9:00 to 15:00 during the whole campaign. Su et al. (2008b) have showed that under high AOD conditions, the uncertainties of J_{HONO} , J_{NO_2} and $J_{\text{O}^1\text{D}}$ simulated by the TUV model were 18%, 18% and 27%, respectively.

3. Results and discussions

3.1. General results

We performed HONO observations in four non-consecutive months: September 22 to October 21, 2015 (autumn); January 3 to January 27, 2016 (winter); April 1 to May 14, 2016 (spring) and June 20 to July 25, 2016 (summer) (Fig. 1). Table 1 documents the statistics of HONO, NO_2 , gaseous HNO_3 , particulate NO_3^- , HONO/ NO_2 and meteorological parameters in four seasons. A marked seasonality of HONO concentration was observed in Beijing. The highest concentration of HONO was found in autumn (2.27 ± 1.82 ppb), followed by summer (1.38 ± 0.90 ppb), spring (1.05 ± 0.95 ppb) and winter (1.05 ± 0.89 ppb). Such seasonal variation in Beijing was different from that in Shanghai (Wang et al., 2013), where weak seasonality was found. In autumn, our sampling site had experienced two severe haze periods with extremely high concentrations of $\text{PM}_{2.5}$, particulate nitrate and associated gaseous pollutants, such as NO_x , CO and O_3 (Fig. 1). During the haze periods, with the accumulation of other pollutants, HONO concentration increased and reached up to 9.00 ppb. In summer, in spite of the efficient solar radiation, the HONO concentration was still much higher comparing with that observed in winter. On average, the HONO concentrations in Beijing were comparable with the measurements performed in polluted cities, such as Kathmandu and Shanghai, while significantly higher than the observations in rural sites, such as Ontario and Alaska (Table 2).

Comparing with the individual HONO concentration, HONO/ NO_2 has the advantage of being less influenced by dilution during transport process and can be used to evaluate the level of HONO formed from the heterogeneous conversion of NO_2 (Kleffmann et al., 2003; Li et al., 2012; Liu et al., 2014; Spataro et al., 2013; Xu et al., 2015; Yu et al., 2009). When

the observed air mass was freshly emitted, the value of HONO/ NO_2 would be the lowest (ranging from 0.1 to 0.8%) (Kirchstetter et al., 1996). If the air mass got aged (experiencing the conversion from NO_2 to HONO), this ratio will increase. In Table 1, we found that the HONO/ NO_2 value also demonstrated a distinct seasonality, ranging from 4.08% in spring to 7.89% in summer, with the mean value of around 5.97%. The higher value in summer indicates more efficient heterogeneous conversion from NO_2 to HONO in this season. The average HONO/ NO_2 value during the whole campaign was in the same magnitude as the observations previously reported in Shanghai and Back Garden (Table 2) but much higher than those observed in vehicle exhaust, which suggests that the HONO production in Beijing was mainly controlled by secondary mechanisms.

3.2. Diurnal variation of HONO

The diurnal profiles of HONO, NO_2 , O_3 and HONO/ NO_2 averaged every hour during the whole campaign were demonstrated in Fig. 2. Ozone showed a typical bell shaped profile with an average maximum around 16:00 in each season. It should be noted that the peak in summer (80 ppb) was more significant than those in other seasons, especially in winter (25 ppb). The diurnal cycle of NO_2 reflects the balance between direct emissions and photochemical sinks. In four seasons, the diurnal cycles of NO_2 were overall similar, characterized by two peaks occurring in the morning and evening rush hours and a continuous decrease during the daytime due to the strong photochemical reaction with OH radicals.

HONO concentrations showed pronounced diurnal cycles in four seasons. The nighttime variation pattern of HONO concentration presented two types: in autumn and winter, it increased rapidly in the first half of night and then gradually dropped to the low point at around 3:00; in spring and summer, after sunset the concentration gradually climbed to this maximum in the morning rush hour. The accumulation during nighttime indicates the presence of significant HONO source surpassing the dry deposition sink of HONO. The daytime HONO concentrations showed similar variation patterns in different seasons: it dropped rapidly after sunrise and remained relatively constant from local noon until 16:00. The morning decrease was due to the onset of photolysis and the vertical mixing of HONO. It is evident that this drop point varied seasonally according to different sunrise time. In winter, the HONO concentration began to decrease at around 8:00; whereas it began to decrease at around 7:00 in autumn and around 6:00 in summer/spring.

Fig. 1. Temporal trends of HONO, HNO_3 , particulate NO_3^- , NO , NO_2 , O_3 , CO, $\text{PM}_{2.5}$, relative humidity (RH) and temperature (T) in four seasons (autumn, winter, spring and summer).

Table 1Statistics of HONO, NO₂, gaseous HNO₃, particulate NO₃⁻, HONO/NO₂ and meteorological parameters, such as temperature (T) and relative humidity (RH), in four seasons.

	Entire study		Autumn		Winter		Spring		Summer	
	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD
NO ₂ (ppb)	25.60	16.85	32.91	20.44	19.96	16.28	25.97	15.80	19.21	11.25
HONO (ppb)	1.44	1.33	2.27	1.82	1.05	0.89	1.05	0.95	1.38	0.90
HONO/NO ₂ (%)	5.97	5.50	7.04	3.32	4.63	2.38	4.08	2.33	7.89	4.14
HNO ₃ (ppb)	0.39	0.25	0.26	0.16	0.29	0.18	0.46	0.20	0.48	0.33
NO ₃ ⁻ (μg m ⁻³)	6.64	12.32	14.83	21.88	5.61	7.06	4.11	5.06	2.95	2.93
RH (%)	43.34	23.09	51.11	22.54	30.48	13.78	34.73	20.83	55.30	21.97
T (°C)	16.01	12.26	17.33	4.78	-3.57	4.53	18.44	5.18	28.11	4.45

The nighttime values (between sunset and sunrise) ranged from 1.26 ppb in spring to 2.78 ppb in autumn, with the mean value of 1.74 ppb. The average HONO concentration at daytime (± 3 h around local noon) over the whole measurement period varied from 0.75 ppb in winter to 1.66 ppb in autumn, with the average value of 0.95 ppb. Our observed HONO values were comparable to those in Guangzhou (Qin et al., 2009) and Santiago (Elshorbany et al., 2009), while much higher than the observations in other places, such as California (VandenBoer et al., 2014), Milan (Alicke et al., 2002) and Seoul (Song et al., 2009). Given the short lifetime of HONO against photolysis, the high HONO concentration during daytime indicates the presence of large HONO production sources.

The HONO to NO₂ ratio also showed marked diurnal cycle with a maximum in the early morning and a minimum around 18:00. Of note, the daytime decrease was weak. In summer, this ratio almost kept stable; in spring and winter, a noontime peak can even be observed. This phenomenon can be attributed to the enhanced conversion of NO₂ to HONO by solar shortwave radiation (Liu et al., 2014) or some other photo-induced processes, which were not related to NO₂, such as the photolysis of HNO₃ (Li et al., 2012).

3.3. HONO formation during nighttime

3.3.1. The relationship between HONO and NO₂

In previous works, NO₂ was considered as the dominant precursor for HONO formation. To further investigate the potential role of NO₂ for HONO formation during nighttime, the correlation analyses between HONO and NO₂ were conducted in four different seasons. The scatter plots in Fig. 3 demonstrated positive relationships between HONO and NO₂. In addition, we found that the increase of HONO/NO₂ was accompanied by the simultaneous increase of RH. The RH values in winter and spring were relatively low (about 35%), and the corresponding ratios of HONO/NO₂ were mainly around 5%. On the contrary, given the appropriate RH values in autumn and summer (about 60%), the ratios of HONO/NO₂ were much higher, mostly falling between the dashed lines corresponding to the HONO/NO₂ values of 5% and 10%, respectively. In autumn, the maximum HONO/NO₂ value can even reach 30% (shown with the red dash line in Fig. 3). Therefore, we concluded that water was necessary for HONO formation and the accumulation of HONO at night was most likely resulted from heterogeneous conversion of NO₂ on wet surfaces.

Table 2

Overview on HONO measurements performed in Beijing and other cities.

Location	Date	HONO (ppb)	HONO/NO ₂ (%)	NO ₂ (ppb)	Ref.
Beijing/China ^a	Jul 2008–Apr 2009	0.19 (Spring) 0.18 (Summer) 0.46 (Autumn) 0.48 (Winter)	1.5% (Spring) 0.8% (Summer) 2.0% (Autumn) 1.5% (Winter)		1
Xianghe/China ^a	Mar 2010–Dec 2012	0.16 (Spring) 0.09 (Summer) 0.38 (Autumn) 0.34 (Winter)	2.4% (Spring) 1.7% (Summer) 1.8% (Autumn) 2.0% (Winter)		
Beijing/China	Aug 2007; Jan–Feb 2007	1.45 (Summer) 1.04 (Winter)	5.0% (summer) 3.0% (winter)	31.70 (summer) 38.76 (winter)	2
Shanghai/China	Aug 2010–Jun 2012	0.92	4.9%		3
Back Garden/China	Jun 2006	0.24 (Day) 0.95 (Night)	7.1%		4
Xinken/China	Oct–Nov 2004	1.20		46.74	5
Hong Kong/China	Aug 2011–May 2012	0.35 (Spring) 0.66 (Summer) 0.93 (Autumn) 0.91 (Winter)		15.50 (Spring) 19.80 (Summer) 26.80 (Autumn) 24.70 (Winter)	6
Seoul/Korea	May–July 2005	0.36	0.7%	56.16	7
Kathmandu/Nepal	Jan–Feb 2003	1.55		14.14	8
Ontario/Canada	Jun–Jul 2007	0.06 (Day) 0.10 (Night)	1.6%		9
Paris/France ^b	Jul 2009; Jan–Feb 2010	0.10–0.21 (Summer) 0.40–0.5 (Winter)			10
Milan/Italy	Mar 1998	0.14 (Day) 0.92 (Night)	0.8% (Day) 2.8% (Night)	18.30 (Day) 33.20 (Night)	11
Barrow/Alaska	Mar–Apr 2009	0.03		0.51	12
Beijing/China	Sep 2015–Jul 2016	1.44	5.97%	25.60	(This work)

1: (Hendrick et al., 2014); 2: (Spataro et al., 2013); 3: (Wang et al., 2013); 4: (Li et al., 2012); 5: (Su et al., 2008b); 6: (Xu et al., 2015); 7: (Song et al., 2009); 8: (Yu et al., 2009); 9: (Wentzell et al., 2010); 10: (Michoud et al., 2014); 11: (Alicke et al., 2002); 12: (Villena et al., 2011).

^a Only daytime data available.

^b 14 km southwest of Paris in a semi-urban environment.

Fig. 2. Mean diurnal cycles of HONO, NO₂, O₃ and HONO/NO₂ in Beijing in four seasons.

As illustrated in Fig. 4, we found a particular case on the night of January 20, 2016 (21:00–02:00): the HONO formation rate or the ratio of HONO/NO₂ increased with the concurrent decrease of other pollutants, such as PM_{2.5}, CO, NO and O₃. This indicates that this increasing formation rate of HONO was not driven by the gas-phase reaction between nitric oxide (NO) and OH (related to O₃ concentration (Kanaya et al., 2007)) or the decrease of boundary layer height (BLH). Interestingly, we found that within these 4 h, the value of RH increased from 40% to

60%. This phenomenon strengthened the conclusion we proposed before: water vapor level was essential for nocturnal HONO formation.

3.3.2. HONO conversion frequency

In order to reduce the uncertainties resulted from diffusion processes, we adopted a combined scaling method proposed by Su et al. (2008a) to calculate the HONO conversion frequency C_{HONO} (h⁻¹). In this work, we only took the night with wind speed lower than

Fig. 3. Correlation of HONO against NO₂. The nighttime data are in the time period from 18:00 to 6:00 and color coded by the relative humidity (RH). The dashed lines correspond to the HONO/NO₂ values of 1%, 5%, 10% and 30%. Symbol “N” represents the number of data points in each season.

Fig. 4. Temporal variation of HONO and other parameters from January 20 to January 21, 2016.

4 m s⁻¹ into consideration. Because of the increasing role of HONO sink in the second half of night, we restricted this analysis to the time frame from 18:00 to 24:00. Here we adopted CO and NO₂ as the reference gases, and the C_{HONO} can be expressed as:

$$C_{\text{HONO}}^x = \frac{2 \left(\frac{[\text{HONO}]_{t1}}{[x]_{t1}} \times [\bar{x}] - \frac{[\text{HONO}]_{t2}}{[x]_{t2}} \times [\bar{x}] \right)}{(t_1 - t_2) \left(\frac{[\text{NO}_2]_{t1}}{[x]_{t1}} \times [\bar{x}] + \frac{[\text{NO}_2]_{t2}}{[x]_{t2}} \times [\bar{x}] \right)} = \frac{2 \left(\frac{[\text{HONO}]_{t1}}{[x]_{t1}} - \frac{[\text{HONO}]_{t2}}{[x]_{t2}} \right)}{(t_1 - t_2) \left(\frac{[\text{NO}_2]_{t1}}{[x]_{t1}} + \frac{[\text{NO}_2]_{t2}}{[x]_{t2}} \right)} \quad (1)$$

$$C_{\text{HONO}} = \frac{1}{3} (C_{\text{HONO}}^0 + C_{\text{HONO}}^{\text{CO}} + C_{\text{HONO}}^{\text{NO}_2}) \quad (2)$$

where [HONO]_t, [NO₂]_t and [x]_t represent the mixing ratios of HONO, NO₂ and reference gases at the sampling time *t*, $\bar{x}$ is the mean mixing ratio of reference gas during the time interval of (t₁ – t₂), and C_{HONO}^x stands for the conversion frequency scaled with X reference gas (C_{HONO}⁰ indicates the conversion frequency that is not scaled).

Table 3 summarized the C_{HONO} derived during the nighttime period over four different seasons. The calculated C_{HONO} varied from 0.005 h⁻¹ in spring to 0.010 h⁻¹ in summer, with an average value of 0.008 h⁻¹, which was in line with the observations conducted by Wang et al. (2013) in Shanghai (0.007 h⁻¹), while lower than the values in other places, such as Back Garden (0.024 h⁻¹) (Li et al., 2012), Milan (0.012 h⁻¹) (Alicke et al., 2002) and Kathmandu (0.014 h⁻¹) (Yu et al., 2009). It is interesting to note that the variation pattern of C_{HONO} followed well with the seasonality of RH. In order to further test the influence of RH on the conversion reaction from NO₂ to HONO, we studied the relationship between C_{HONO} and RH values in each individual night over different seasons. In Fig. 5, HONO conversion frequency was plotted against RH. It can be found that when RH was

Fig. 5. Relationship between C_{HONO} and RH. The black square represents the C_{HONO} value averaged over 10% RH intervals.

lower than 65%, the C_{HONO} value tended to increase along with RH; however, when RH was higher than 65%, C_{HONO} depended inversely on RH. This phenomenon consisted well with the work carried out by Yu et al. (2009) in Kathmandu.

This negative dependence (RH > 65%) was probably attributed to the efficient HONO uptake by the rapidly growing aqueous layer on the ground or aerosol surface. It has been reported that the dependence of water coverage (number of monolayers of water) on RH values was different upon various material surfaces (Sumner et al., 2004). In the case of soil and stone, the increase of water coverage from one monolayer to 3–5 monolayers was accompanied by the increase of RH from 20% to 80%. Above 80%, the monolayers rapidly increased (Stutz et al., 2004). As for the glass, the turning point of this dependence was 70% (Saliba et al., 2001). Considering the complex structure of natural surface, this dependence was uncertain in the field. Through our in-situ observation, we can conclude that the turning point in Beijing city center was 65%. When RH was above 65%, the number of monolayers formed upon atmospheric surface would increase rapidly. Besides, we found that this dependence was consistent for different seasons, which indicates that the responsible surface for HONO conversion changed little under varying environments. The seasonality of HONO conversion frequencies during the whole campaign was determined by RH levels.

3.4. Daytime HONO budget

Given the short lifetime of HONO against photolysis, the gas phase reaction between OH and NO was not sufficient to explain the high HONO concentration observed during daytime (Fig. 2). Therefore, the presence of additional HONO daytime source (R_{unknown}) was needed. The magnitude of this additional source was estimated from the measured constraints on the HONO concentration observed during the day via (i) reaction of OH with NO (R_{OH+NO}), (ii) photolysis of HONO

Table 3
HONO conversion frequencies (C_{HONO}) derived during the nighttime period.

Season	N (day)	C _{HONO} (h ⁻¹)	RH (%)	HONO (ppb)	NO ₂ (ppb)	PM _{2.5} (μg m ⁻³)	NO (ppb)	T̄ (°C)
Autumn	18	0.009	51.32	3.63	58.77	99.28	38.79	16.84
Winter	17	0.006	44.39	2.25	43.78	95.75	65.65	−5.84
Spring	20	0.005	41.24	1.72	37.02	56.60	21.39	16.14
Summer	19	0.010	62.36	1.83	26.71	49.55	3.08	25.39

(R_{phot}), and (iii) reaction of OH with HONO ($R_{\text{OH}+\text{HONO}}$):

$$\partial[\text{HONO}]/\partial t = (R_{\text{OH}+\text{NO}} + R_{\text{unknown}}) - (R_{\text{OH}+\text{HONO}} + R_{\text{phot}}) \quad (3)$$

Such that,

$$R_{\text{unknown}} = \Delta[\text{HONO}]/\Delta t + J_{\text{HONO}}[\text{HONO}] + k_{\text{OH}+\text{HONO}}[\text{OH}] \times [\text{HONO}] - k_{\text{OH}+\text{NO}}[\text{OH}][\text{NO}] \quad (4)$$

where $\Delta[\text{HONO}]/\Delta t$ indicates the observed variation of HONO concentration (ppb s^{-1}), J_{HONO} means the photolysis rate of HONO (s^{-1}). The rate constants of $k_{\text{OH}+\text{NO}}$ and $k_{\text{OH}+\text{HONO}}$ are 9.8×10^{-12} and $6.0 \times 10^{-12} \text{ cm}^3 \text{ molecules}^{-1} \text{ s}^{-1}$, respectively, at 298 K and 1010 hPa (Atkinson et al., 2004). Considering the larger uncertainty in estimates of the photolysis rates at sunrise and sunset, we only investigated the HONO budget from 9:00 to 15:00. Here we ignored the influence of HONO direct emission source, dry deposition and transport processes, because these terms were several orders smaller than R_{phot} (Li et al., 2012; Su et al., 2008b). Since OH measurements were not available in this work, an estimate was made. The daytime OH concentrations can be estimated by a simple empirical model (Lu et al., 2013; Lu et al., 2012; Spataro et al., 2013) developed based on the relationship proposed by Rohrer and Berresheim (2006), representing that OH concentration scales well with $\text{O}(^1\text{D})$ production. During winter and summer, the average noontime OH concentrations were $1.56 \times 10^6 \text{ cm}^{-3}$ and $1.14 \times 10^7 \text{ cm}^{-3}$, respectively. These results were within the OH ranges obtained in highly polluted cities, varying from 0.5×10^6 to $4 \times 10^6 \text{ cm}^{-3}$ in winter (Emmerson et al., 2005) and from 4×10^6 to $17 \times 10^6 \text{ cm}^{-3}$ in summer (Lu et al., 2013), respectively.

The contributions of the terms of Eq. (3) to HONO budgets in four seasons were shown in Fig. 6. The photolysis of HONO (R_{phot}) in autumn was the highest and about 1–2 times larger than that in winter. Comparing with R_{phot} , the reaction between OH and HONO ($R_{\text{OH}+\text{HONO}}$) had little contribution to HONO sinks during the whole campaign. The HONO sources through gas phase reaction between OH and NO ($R_{\text{OH}+\text{NO}}$) all peaked in the morning and then gradually decreased. Comparing with $R_{\text{OH}+\text{NO}}$, HONO formation was mainly controlled by the unknown

source (R_{unknown}). Only a minor part of the HONO sources came from $R_{\text{OH}+\text{NO}}$, especially in summer, with R_{unknown} accounting for 89.45% of the total HONO daytime source. Of note, we found that R_{unknown} all climbed to the maximum at noon in four seasons. The highest noontime R_{unknown} was 3.82 ppb h^{-1} in autumn, followed by 3.05 ppb h^{-1} in summer, 2.63 ppb h^{-1} in spring and 1.30 ppb h^{-1} in winter. The magnitude of these additional sources were comparable to the observations conducted by Su et al. (2008b) in XinKen (around 2 ppb h^{-1}) and by Liu et al. (2014) in Beijing (up to 5 ppb h^{-1}), but much higher than those by Wong et al. (2012) in Houston (around 0.6 ppb h^{-1}) and Michoud et al. (2014) in Paris (0.7 and 0.25 ppb h^{-1} in summer and winter, respectively).

As NO_2 was thought to be the dominant precursor of HONO daytime formation, here we normalized R_{unknown} by NO_2 mixing ratios (Fig. 7). The normalized R_{unknown} has the same unit (h^{-1}) as the nocturnal HONO conversion frequency, and can be referred to as the daytime HONO conversion frequency from NO_2 (Soergel et al., 2011). We found that the normalized R_{unknown} was much larger than the nighttime conversion frequency calculated before. For example, in summer, the average normalized R_{unknown} was 0.305 h^{-1} , which was about 30 times faster than the nighttime conversion (0.010 h^{-1}). If this nighttime conversion reaction continued at daytime, its contribution to R_{unknown} would be small. Besides, we noticed that the normalized R_{unknown} showed a typical bell shaped profile with the maximum around noon; the peak of the normalized R_{unknown} coincided with the maximum solar radiation. Therefore, we assumed that the heterogeneous conversion from NO_2 to HONO during daytime should be light-induced, or some other sources which were independent of NO_2 , such as the photolysis of adsorbed nitrate, were responsible for the observed R_{unknown} .

In order to identify the reactions responsible for the additional HONO source, correlations of R_{unknown} with various parameters were investigated (Table 4). Here, we focused on the parameters that were related to the processes identified as HONO sources in the literature.

During the whole campaign, the correlations of R_{unknown} against NO_2 , $\text{PM}_{2.5}$, BC, J_{NO_2} and RH did not show any clear relationships. The weak dependence of R_{unknown} on BC, $\text{PM}_{2.5}$, $\text{PM}_{2.5} \times [\text{NO}_2]$ or $\text{BC} \times [\text{NO}_2]$ suggests that the aerosol or the soot surface might not be the place

Fig. 6. Mean diurnal individual sources (positive values) and sinks (negative values) of HONO for different seasons.

Fig. 7. Mean diurnal variation of R_{unknown} normalized by NO_2 mixing ratios during the whole campaign. The orange open circle represents the mean photolysis frequency of NO_2 (J_{NO_2}). The upper and lower ends of the bar reflect the 75% and 25% percentiles; the line and square in between are the median and mean values, respectively. The upper whisker refers to the maximum and the lower one represents the minimum. The red line indicates the average nocturnal HONO conversion frequency (C_{HONO}) calculated in each season.

where unknown HONO production took place. When we multiplied J_{NO_2} to RH instead of considering J_{NO_2} or RH alone, the correlation significantly increased, especially in summer, with R^2 value of 0.68. This improvement indicates that the calculated R_{unknown} may be photolytic and heterogeneous occurring upon wet surface. Besides, we found that the significance of this relationship in different seasons was in line with the seasonality of RH values (Table 1).

Li et al. (2012) have provided evidence that the photolysis of adsorbed nitric acid (HNO_3) and nitrate (NO_3^-) contributed to the HONO formation in the Pearl River Delta region. In this work, we also found significant correlation between R_{unknown} and $J_{\text{NO}_2} \times [\text{THNO}_3]$ in autumn ($R^2 = 0.48$). Comparing with other seasons, the ambient THNO_3 (the sum of particulate nitrate and gaseous HNO_3) concentration in autumn was the highest, with the value of 5.62 ppb. The production

rate of HONO through this mechanism can be calculated by the following equation (Li et al., 2012; Spataro et al., 2013; Zhou et al., 2007):

$$P_{\text{HNO}_3 \rightarrow \text{HONO}} = \frac{f \times [\text{THNO}_3] \times v_{\text{HNO}_3} \times t_d \times j_{\text{HNO}_3 \rightarrow \text{HONO}}}{H} \quad (5)$$

where f is the fraction of noontime full sun to which the surface was exposed (0.25), H means the boundary mixing height (m), v_{HNO_3} is the dry deposition velocity of HNO_3 ($5 \times 10^{-2} \text{ m s}^{-1}$) over t_d (h) period, and $j_{\text{HNO}_3 \rightarrow \text{HONO}}$ is the photolysis frequency of HNO_3 via HONO pathway. Here, we assumed an accumulation time of 24 h and a mixing height of 250 m. The photolysis frequency $j_{\text{HNO}_3 \rightarrow \text{HONO}}$ derived from Eq. (5) was $3.56 \times 10^{-5} \text{ s}^{-1}$, which was in line with the measurement by Zhou et al. (2003) ($(1.2 \pm 2) \times 10^{-5} \text{ s}^{-1}$). Therefore, we concluded that the photolysis of adsorbed nitric acid or nitrate on ground surface could be one likely source for daytime HONO formation in autumn. However, the correlations were comparably weaker in other seasons. This difference could be explained by the seasonal variation of ambient THNO_3 concentrations levels. In other seasons, the ambient THNO_3 concentrations were much lower. Large part of the additional HONO source could be explained by the photo-enhanced production upon wet surface or some other sources we have not taken into account, such as the ground deposited HONO during nighttime, which may form a nitrite reservoir in the following day (VandenBoer et al., 2013; VandenBoer et al., 2014; VandenBoer et al., 2015), and the direct HONO emission from soil (Su et al., 2011).

4. Conclusion

The measurements of nitrous acid (HONO) have been taken over four select months in different seasons in Beijing, China. The observed HONO concentration levels were comparable to those in heavily polluted regions. During nighttime, the correlation analyses and case study suggest that the accumulation of HONO was most likely attributed to the conversion of NO_2 on wet surfaces. The calculated HONO conversion frequency was closely related to RH levels. Of note, the turning point of this dependence was 65% and consistent over four different seasons.

Table 4

Correlations of R_{unknown} against various parameters.

Seasons	Parameters	Correlation coefficient (R^2)	Seasons	Parameters	Correlation coefficient (R^2)
Autumn ($N = 161$)	NO_2	0.04	Winter ($N = 113$)	NO_2	0.08
	$\text{PM}_{2.5}$	0.18		$\text{PM}_{2.5}$	0.11
	RH	0.13		RH	0.10
	BC	0.13		BC	0.10
	J_{NO_2}	0.02		J_{NO_2}	0.24
	$\text{NO}_2^* \text{BC}$	0.06		$\text{NO}_2^* \text{BC}$	0.09
	$\text{NO}_2^* \text{PM}_{2.5}$	0.10		$\text{NO}_2^* \text{PM}_{2.5}$	0.10
	$J_{\text{NO}_2^* \text{RH}}$	0.32		$J_{\text{NO}_2^* \text{RH}}$	0.19
	$J_{\text{NO}_2^* \text{THNO}_3^a}$	0.48		$J_{\text{NO}_2^* \text{THNO}_3^a}$	0.04
Spring ($N = 199$)	NO_2	0.18	Summer ($N = 153$)	NO_2	0.05
	$\text{PM}_{2.5}$	0.28		$\text{PM}_{2.5}$	0.08
	RH	0.12		RH	0.02
	BC	0.25		BC	0.11
	J_{NO_2}	0.00		J_{NO_2}	0.10
	$\text{NO}_2^* \text{BC}$	0.17		$\text{NO}_2^* \text{BC}$	0.07
	$\text{NO}_2^* \text{PM}_{2.5}$	0.27		$\text{NO}_2^* \text{PM}_{2.5}$	0.09
	$J_{\text{NO}_2^* \text{RH}}$	0.24		$J_{\text{NO}_2^* \text{RH}}$	0.68
	$J_{\text{NO}_2^* \text{THNO}_3^a}$	0.27		$J_{\text{NO}_2^* \text{THNO}_3^a}$	0.18

^a Sum of particulate nitrate and gaseous HNO_3 .

This result may help to improve the operation of air-quality models to simulate nocturnal HONO conversion frequency in Beijing urban area. During daytime, we found that HONO formation was different from that dominated in the nighttime and was mainly controlled by the additional HONO source in all seasons. The correlation studies demonstrated that the photo-enhanced production upon wet surface or the photolysis of adsorbed nitric acid and nitrate can be potential candidates to explain the unknown HONO daytime source; however, the contributions of these sources varied in different seasons. Our results suggest that the photochemical models should consider this seasonal variability to better simulate realistic HONO concentrations in the future.

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