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Influence of biomass burning plumes on HONO chemistry in eastern China

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Abstract. Nitrous acid (HONO) plays a key role in atmospheric chemistry by influencing the budget of hydroxyl radical (OH). In this study, a two-month measurement of HONO and related quantities were analyzed during a biomass burning season in 2012 at a suburban site in the western Yangtze River delta, eastern China. An overall high HONO concentration with the mean value of 0.76 ppbv (0.01 ppbv to 5.95 ppbv) was observed. During biomass burning (BB) periods, both HONO concentration and HONO/NO₂ ratio were enhanced significantly (more than a factor of 2, p<0.01) compared with non-biomass burning (non-BB) periods. A correlation analysis showed that the HONO in BB plumes was more correlated with nitrogen dioxide (NO₂) than that with potassium (a tracer of BB). Estimation by the method of potassium tracing suggests a maximum contribution of 17±12 % from BB emission to the observed HONO concentrations, and the other over 80 % of the observed nighttime HONO concentrations during BB periods were secondarily produced by the heterogeneous conversion of NO₂. The NO₂-to-HONO conversion rate (C_HONO) in BB plumes was almost twice as that in non-BB plumes (0.0062 hr⁻¹ vs. 0.0032 hr⁻¹). Given that the residence time of the BB air masses was lower than that of non-BB air masses, these results suggest BB aerosols have higher NO₂ conversion potentials to form HONO than non-BB aerosols. A further analysis based on comparing the surface area at similar particle mass levels and HONO/NO₂ ratios at similar surface area levels suggested larger specific surface areas and higher NO₂ conversion efficiencies of BB aerosols. A mixed plume of BB and anthropogenic fossil fuel (FF) emissions was observed on 10 June with even higher HONO concentrations and HONO/NO₂ ratios. The strong HONO production potential (high HONO/NO₂ to PM₂.5 ratio) was accompanied with a high sulfate concentration in this plume, suggesting a promotion of mixed aerosols to the HONO formation. In summary, our study suggests an important role of BB in atmospheric chemistry by affecting the HONO budget. This can be especially important in eastern China, where agricultural burning plumes are inevitably mixed with urban and industrial pollution.

1 Introduction

Nitrous acid (HONO) is an important constituent in the troposphere due to its role in hydrogen oxide (HOₓ) cycling (Platt et al., 1980; Kleffmann, 2007; Hofzumahaus et al., 2009; Elshorbany et al., 2012). The photolysis of HONO provides a daytime source of hydroxyl radical (OH), which controls the daytime oxidation capacity and consequently influences the ozone (O₃) chemistry and secondary organic aerosol (SOA) formation. This process is especially impor-
tant in the early morning when contributions from other OH
sources, like O₃ photolysis, are still small (Alicke et al.,
2002; Kleffmann et al., 2005; Elshorbany et al., 2010).

The sources of atmospheric HONO, including direct emis-
sion from fossil fuel combustion (Kurtenbach et al., 2001)
and soil (Su et al., 2011), homogeneous gas phase reac-
tions and heterogeneous processes on the surface of atmo-
spheric aerosols and the ground (Harrison and Collins,
1998; Longfellow et al., 1999; Stutz et al., 2002; VandenBoer et
al., 2013), are hitherto not well understood. Among these
sources, heterogeneous processes are commonly accepted as
the least understood pathway to the production of HONO.
For example, nitrogen dioxide (NO₂) can be converted to
HONO on the ground (Harrison and Kito, 1994), wet sur-
faces (Finlayson-Pitts et al., 2003), soot particles (Ammann
et al., 1998; Kalberer et al., 1999; Kleffmann and Wiesen,
2005), and organic substrates (Bröské et al., 2003; Am-
mann et al., 2005). These processes have been considered
the primary contributor to nocturnal HONO formation, but
they cannot sustain the frequently observed elevated daytime
HONO concentration levels (Kleffmann, 2007; Sörgel et al.,
2011; Li et al., 2012, and references therein). Recently, sev-
eral heterogeneous and possibly photo-enhanced processes
have been demonstrated that might play an important role in
daytime HONO formation (George et al., 2005; Stemmler et
al., 2006; Ndour et al., 2008; Nie et al., 2012; Langridge et
al., 2009; Bedjanian and El Zein, 2012). However, although
these studies have drawn a clearer picture of HONO chem-
istry, there are still large knowledge gaps in HONO sources.
The heterogeneous production of HONO in the atmosphere
by a variety of mechanisms is still under debate.

Biomass burning is a major source of atmospheric aerosol
particles (Janhäll et al., 2010) and trace gases (Andreae and
Merlet, 2001; Burling et al., 2010), consequently influen-
cing climate and air quality. Recent studies have connected
HONO chemistry to biomass burning (BB) via both direct
HONO emissions and emissions of soot particles (Roberts
et al., 2010; Veres et al., 2010). Although high emission ra-
tios of HONO have been detected in laboratory fires (Burling
et al., 2010; Veres et al., 2010), the mixing ratio of HONO in
aged BB plumes is expected to be relatively independent of
its direct emissions due to the rapid dilution and photol-
ysis for primary HONO during atmospheric transport. Soot
particles, as one major component in BB plumes, have been
demonstrated to be an effective media to convert NO₂ to
HONO (Kleffmann et al., 1999; Aumont et al., 1999; Prince
et al., 2002; Kleffmann and Wiesen, 2005; Aubin and Ab-
batt, 2007), especially in the case that aged soot particles
can be re-activated in the present of light (Monge et al., 2010)
and play a continuous role in the HONO chemistry. These
processes may significantly influence the HONO chemistry
during a BB period, but their exact roles are rarely demon-
strated in the real atmosphere, especially when BB aerosols
are mixed with anthropogenic pollutants.

In this study, a two-month measurement campaign was
conducted during the intensive BB (burning of wheat straw)
period (April–June 2012) at the SORPES station (Station
for Observing Regional Processes of the Earth System) in
the western Yangtze River delta (YRD) of East China (Ding
et al., 2013c). Several HONO-related quantities were mea-
sured, with the aim to investigate the HONO chemistry in
the YRD, a region undergoing rapid urbanization and indus-
trialization. Special attention was paid to the impact of BB
plumes and mixed plumes of agricultural burning and foss-
il fuel (FF) emissions on HONO formation after long-range
transport. In the following, the general features related to
HONO during the campaign were first described. The differ-
cees in HONO formation between the BB events and non-
BB events were then investigated. Finally, the influences of
mixed plumes of intensive BB and FF emission (Ding et al.,
2013b) on HONO formation were discussed.

2 Experimental methodologies
2.1 Field campaign

The field campaign was conducted from late April–June
2012 at the SORPES “flagship” central site in Xianlin of
Nanjing (Ding et al., 2013c). It is a regional background
site, located on top of a hill (118°57′10″E, 32°07′14″N; 40 m a.s.l.) in the Xianlin campus of Nanjing University and
about 20 km east of the suburban Nanjing city (see Fig. 1 in
Ding et al., 2013c). A suite of trace gases, aerosols and me-
teorological quantities were measured, with more detailed
descriptions found in Ding et al. (2013b, c). The present study
is focused on HONO and related quantities, including NO₂,
NO₃, CO, SO₂, PM₂.₅ mass, total water-soluble ions (WSIs),
potassium ions (K⁺), sulfate (SO₄²⁻), and particle surface-
area size distribution over the size range of 6–800 nm.

Figure 1. Temporal variation of the concentrations of HONO, NO₂, PM₂.₅ mass and potassium, at the SORPES station during late April–June 2012. BB episodes mostly occurred during May and early June (shaded in the figure).

2.2 Measurement techniques

The HONO concentration was measured with a Monitor for Aerosols and Gases in Air (MARGA, Metrohm Co.), which includes a wet rotating denuder (WRD) (Spindler et al., 2003; Su et al., 2008; Makkonen et al., 2012) connected to an ion chromatograph (IC, Metrohm USA, Inc., Riverview, FL). The time resolution of this measurement is 1 h. There were 1608 hourly samples during the campaign. The WRD consists of two concentric glass cylinders whose wall is coated with 10 ppm H$_2$O$_2$ solution to absorb HONO and other gases. The liquid sample streams from the WRD are drawn into 25 mL syringes before being injected into the IC system. The residence time of sampling air is about 4.5 s in the sampling tubes and about 0.2 s in WRD.

Other measurement techniques are described briefly as follows. The fine particle mass concentration (PM$_{2.5}$) was continuously measured with a combined technique of light scattering photometry and beta radiation attenuation (Thermo Scientific SHARP Monitor Model 5030). Sulfate (SO$_4^{2-}$) and potassium ions (K$^+$) concentrations in PM$_{2.5}$ were measured with the MARGA system (Ding et al., 2013b). NO$_2$ was converted to nitric oxide (NO) with a molybdenum oxide (MoO) catalytic converter inside the instrument and measured with a chemiluminescence analyzer (TEI model 42i). It should be noted that the technique of using a molybdenum converter to measure NO$_2$ may overestimate its ambient concentrations during daytime due to the potential conversion of species other than NO$_2$ (e.g., peroxyacetyl nitrate (PAN)) to NO (Xu et al., 2013). However, the interference is much lower at nighttime without photochemical reaction. Total reactive nitrogen oxides (NO$_x$) was measured with an externally placed molybdenum converter and a NO analyzer. The sulfur dioxide (SO$_2$) concentration was measured with a pulsed UV fluorescence analyzer (TEI model 43i). Detailed information can be found in Ding et al. (2013c).

2.3 Sampling artifacts and data correction

The sampling artifacts of HONO measurement with the WRD method are mainly caused by the NO$_2$ conversion on the surface of the sampling tube and the WRD (interference 1) and the reaction of NO$_2$ with S (IV) in the absorption solution in WRD (interference 2) (Spindler et al., 2003; Barnes and Rudziński, 2012). In this study, 10 ppm of H$_2$O$_2$ was used as the absorption solution for the MARGA system, which can oxidize the S (IV) very quickly to form H$_2$SO$_4$, and thus can avoid the interference 2 induced by the reaction of NO$_2$ with S (IV) (Genfa et al., 2003). In addition, the formation of H$_2$SO$_4$ can acidify the absorption solution, which will reduce the interference 1 in WRD by suppressing the absorption and reaction of NO$_2$ on the surface of the absorption solution (Kleffmann et al., 2002). Therefore, in this study, the interference of HONO measurement should be mainly from the NO$_2$ conversion on the surface of the sampling tube (part of interference 1). Here, to avoid the possible overestimation, we corrected the data set with the following formula recommended by an inter-comparison study on the HONO measurement between a WRD and a LOPAP system conducted in a similar atmospheric environment in China (Su, 2008):

$$\text{HONO}_{\text{LOPAP}} = 0.833 \times \text{HONO}_{\text{WRD}} - 0.17.$$  \hspace{1cm} (1)

It should be noted that the data set corrected by this formula is expected to underestimate the HONO concentration because the absorption solution deployed by Su (2008) was Na$_2$CO$_3$, which can induce additional interference in WRD (interference 2 and part of interference 1). Given that we probably underestimated the HONO concentrations and overestimated the NO$_2$ concentrations (Xu et al., 2013), the values of HONO/NO$_2$ and HONO/NO$_x$ calculated in Sect. 3 are actually lower limits for these ratios.

Several studies (Appel et al., 1990; Muller et al., 1999; Genfa et al., 2003) have demonstrated that the overestimation of HONO concentrations measured by WRD mainly occur during daytime, so we used only nighttime data (except in the case of 10 June, when the solar radiation was significantly decreased to a very low level (Ding et al., 2013b) in Sects. 3.2 and 3.3.

2.4 Calculation of the nocturnal HONO lifetime

Generally the nocturnal boundary layer is low and stable, the observed plumes during the nighttime were assumed to always be transported inside the planetary boundary layer (PBL) and probably make contact with the ground surface. In this case, there are three major pathways for the loss of HONO during nighttime, including deposition on ground surfaces (Path-A), heterogeneous loss on aerosol surfaces (Path-B) and reaction with the OH radical (Path-C) (Li et al., 2012). For Path-A, the HONO lifetime ($T_a$) is given by

$$T_a = \frac{1}{k_a} = \frac{H}{V_{\text{HONO}}},$$  \hspace{1cm} (2)

where $H$ is the mixing height (assumed as 100 m) and $V_{\text{HONO}}$ is the dry deposition velocity of HONO, assumed to be equal to 0.8 cm s$^{-1}$ (Li et al., 2012). For the loss Path-B, the corresponding lifetime ($T_b$) can be written as

$$T_b = \frac{1}{k_b} = \frac{1}{\frac{1}{4} \times \phi_{\text{HONO}} S_{\text{aerosol}} \times \frac{1}{V_{\text{HONO}}}}.$$  \hspace{1cm} (3)

There is no modern literature reporting the HONO uptake coefficient on aerosols, but an uptake coefficient of HONO on the ground ranging from $10^{-5}$ to $10^{-4}$ was reported in recent studies (VandenBoer et al., 2013; Donaldson et al., 2013). Considering the lower surface area and pH of aerosols (Su et al., 2011), the uptake coefficient of HONO on aerosols may be less and was estimated as $10^{-5}$ or less. $S_{\text{aerosol}}$ is the aerosol surface during the observation with a mean value of about 1.5 x 10$^3$ μm$^2$ cm$^{-3}$ calculated from the particle size.
distribution, and $v_{\text{HONO}}$ is the mean molecular velocity of HONO (about 380 m s$^{-1}$). For the loss Path-C, the lifetime ($T_c$) is equal to

$$T_c = \frac{1}{k_c} = \frac{1}{k_\text{HONO} + \text{OH} \times \text{OH}}.$$  \hspace{1cm} (4)

The OH concentration was estimated as $10^6$ cm$^{-3}$ (Hofzumahaus et al., 2009). $k_{\text{HONO} + \text{OH}}$ is the reaction rate of HONO and OH. The value of $5.0 \times 10^{-12}$ cm$^3$ s$^{-1}$ at 298 K (Sander et al., 2006) was used. In these conditions, the overall lifetime, $t$, is obtained from the following formula:

$$\frac{1}{t} = \frac{1}{T_a} + \frac{1}{T_b} + \frac{1}{T_c}.$$  \hspace{1cm} (5)

The lifetime of HONO was calculated to be about 3.3 h. That means about 8–9 h are needed for the emitted HONO to be consumed within the nocturnal PBL.

2.5 Tracer of biomass burning plumes

Most BB tracers are organic compounds (Simoneit, 2002; Andreae and Merlet, 2001), which were not measured during this campaign. Carbon monoxide (CO) in the gas phase (Andreae and Merlet, 2001) and potassium ions (K$^+$) in the aerosol phase (Andreae, 1983; Ma et al., 2003; Reid et al., 2005; Li et al., 2007) are well recognized inorganic tracers of BB. In this study, the observation site is located in the YRD, one of the most developed, and most polluted, regions in China (Ding et al., 2013c). Many CO sources other than BB, such as industry and traffic, can contribute significantly to the CO loading, even during the BB season. Otherwise, there are no other significant sources of K$^+$ in this region. Therefore, K$^+$ is a suitable tracer of BB for regions with heavy air pollution. In this study, the samples with K$^+$ concentrations higher than 2 µg m$^{-3}$ and a ratio of K$^+$ to PM$_{2.5}$ larger than 0.02 were defined as BB samples (203 samples). The samples with K$^+$ concentrations lower than 2 µg m$^{-3}$ and a ratio of K$^+$ to PM$_{2.5}$ smaller than 0.02 were categorized as non-BB samples (1122 samples). The defined samples, including BB and non-BB, account for 82.4 % of the total. The other undefined samples account for 17.6 %.

3 Results and discussion

3.1 Observation overview

Figure 1 shows the temporal variations of concentrations of HONO, NO$_2$, PM$_{2.5}$ mass and K$^+$ observed at the Xianlin SORPES central site during the time period of April–June 2012. The average concentration of HONO was 0.76 ± 0.79 ppbv, which was lower than the concentrations measured at a polluted rural site in the Pearl River delta region (Su et al., 2008) and an urban site in Shanghai (Wang et al., 2013), but much higher than those measured in Europe (Acker and Möller, 2007). Both HONO concentrations (Fig. 2a) and ratios of HONO to NO$_2$ (HONO/NO$_2$) (Fig. 2b) exhibited distinct diurnal cycles, with a diurnal maximum during night/early morning and a minimum around noon.

During the campaign, and especially from late May to early June, several BB episodes were observed and revealed by elevated concentrations of PM$_{2.5}$ (up to 426 µg m$^{-3}$) and K$^+$ (up to 22 µg m$^{-3}$) (Fig. 1) (Ding et al., 2013b; Ding et al., 2013c). HONO concentrations were also enhanced during the BB episodes. In order to investigate the relation between BB and HONO chemistry, we compared the HONO concentrations, HONO/NO$_2$ ratios and HONO/NO$_x$ ratios between the BB and non-BB periods. On average, all three parameters were significantly enhanced during BB periods compared to non-BB periods (Fig. 3d, e, f). HONO concentrations increased by 156 % (1.56 ± 1.43 ppbv vs. 0.61 ± 0.54 ppbv, $p<0.01$); HONO/NO$_2$ ratios increased by 134 % (0.066 ± 0.043 vs. 0.028 ± 0.020, $p<0.01$); and HONO/NO$_x$ ratios increased by 134 % (0.055 ± 0.031 vs. 0.023 ± 0.016, $p<0.01$). These results indicate a positive impact of BB plumes on the ambient mixing ratio of HONO.

The enhanced HONO production in BB plumes would impact the atmospheric oxidation capacity, and influence the formation of secondary aerosols (Li et al., 2010; Gonçalves et al., 2012; Elshorbany et al., 2014). In this study, the average values of HONO to NO$_x$ ratios (0.028 ± 0.021), especially during the BB periods (0.062 ± 0.031) (see Fig. 3f) were considerably higher than 0.02, the assumed global aver-
3.2 Influence of BB on HONO formation

3.2.1 Contribution of direct emission

Several laboratory studies have demonstrated BB as an effective HONO source via direct emissions (Burling et al., 2010; Veres et al., 2010), so HONO might play an important role in the atmospheric chemistry over BB source regions. However, HONO is easily consumed by chemical sinks during its atmospheric transport (the estimated lifetime was about 3.3 h in the nighttime, and emitted HONO can be consumed in about 8 hours, see Sect. 2.4). In this study, the main BB source area is located in the northern part of Anhui province, several hundred kilometers from the SORPES station (Fig. 4). As shown in Fig. 4a, in addition to some individual fire points, distributed in the 8 h backward retroplume, the air masses from the major source regions cannot influence the SORPES station in 8 h transport, suggesting that direct emission from BB may have an influence on the observed enhancement of the HONO but should not be the major contributor. The correlations of HONO with K$^+$ (BB tracer) and NO$_2$ for the nighttime BB samples were illustrated in Figs. 5.
and 10. The results showed that the HONO was positively correlated to both K$^+$ and NO$_2$, but the correlation efficiency ($R$) for HONO and NO$_2$ was higher than that for HONO and K$^+$. These results indicate that despite of some contribution from direction emission, the secondary production of HONO should play the key role.

As few publications reported the emission factors of both K$^+$ and HONO from the burning of wheat straw, to estimate the contribution of BB direct emission to HONO here we first calculated the contribution of BB emission to observed CO concentrations. The ratio of emission factors of K$^+$ and CO was assumed to be identical for the BB events observed during this campaign. Here we took the minimum molar ratio of non-background CO to K$^+$ for nighttime BB samples (the value was 67) as the ratio of the emission factors of these two species because of the additional strong CO sources other than BB emission in the YRD. The background concentrations of CO around the SORPES station were estimated as the intercept of the linear regression fit for the whole samples of CO and NO$_y$ during the campaign (the value was 480 ppb, figure not shown) (Wang et al., 2004). In this case, the CO concentration contributed from BB emission was calculated to be 260 ± 189 ppbv.

We then estimated the contribution of BB emission to observed HONO concentrations by taking account of the emission ratio of HONO to CO from the burning of wheat straw and the loss of emitted HONO during transport. Noting that the deposition of CO and K$^+$ in fine particles was slow, their losses during transport were assumed to be negligible. The averaged emission ratio of HONO to CO from the burning of wheat straw was taken as 0.0027 (Stockwell et al., 2014). The loss of HONO should be related to the transport time of BB plumes. However, the transport time was difficult to calculate as the exact source region (fire point on the map, Fig. 4) for each BB episode cannot be identified. Some episodes may be influenced by several source regions on the transport pathway, and the exact time and duration of the fires cannot be identified with the satellite fire count data. However, given that there were few fire points very close to the SORPES station (Fig. 4), and the air plumes of several episodes, such as 9–11 June and 12–13 June, have been demonstrated as being transported for several days before arriving at the station (Fig. 9d and e in Ding et al., 2013c), we therefore used 3.3 h (HONO nighttime lifetime, see Sect. 2.4) as the mean transport time, which is actually underestimated for most BB episodes to estimate HONO loss during transportation. In which case, although there may be large uncertainties, here our best estimate of the HONO contribution from direct emission of BB was 0.27 ± 0.19 ppbv, which accounted for 17 ± 12 % of the observed HONO concentrations. That means more than 80 % of the observed nighttime HONO during BB periods was secondarily formed.

3.2.2 Heterogeneous conversion and the possible influence of the ground surface

The reaction of NO and OH was one major source of daytime HONO, but its contribution to nighttime HONO is negligible due to the limitation of nighttime OH concentration. Therefore, over 80 % of the observed HONO in the nighttime BB plumes, which was secondary formed, should be produced from the heterogeneous conversation of NO$_2$. In which case, the enhancement of HONO during BB periods should be ascribed to either the increase in NO$_2$ concentrations or increased NO$_2$ to HONO conversion potentials. As shown in Figs. 1 and 3c, the concentration levels of NO$_2$ were comparable during the BB and non-BB periods ($p = 0.51$), so the higher HONO level during BB periods was probably due in large part to a higher NO$_2$ conversion potential (HONO/NO$_2$ ratio).

To further verify this point, in Fig. 6 we presented the changes of HONO to NO$_2$ ratios during nighttime for both BB and non-BB plumes. The NO$_2$-to-HONO conversion rate ($C_{\text{HONO}}$), which estimated by change rates of HONO/NO$_2$
ratios along the time (the slopes in Fig. 6, 19:00–03:00), in BB plumes almost two times higher than that in non-BB plumes (0.0062 hr⁻¹ vs. 0.0032 hr⁻¹), further suggesting a higher NO₂ conversion potential to produce HONO in BB plumes than that in non-BB plumes.

Both ground and aerosols are effective surfaces for converting NO₂ to HONO. Here, to estimate the possible role of the ground surface in the enhancement of HONO concentrations, we conducted backward Lagrangian dispersion modeling for the air masses arriving at the SORPES station using the HYSPLIT model, following the method developed by Ding et al. (2013a). Considering that the night-time HONO lifetime was estimated to be about 3.3 h, we ran the models for an 8 h backward period, during which the emitted HONO from BB could possibly be consumed. Figure 4a and b presents the “footprint” retroplumes, which represented the distribution of probability or residence time of the simulated air masses in their last 8 h transport time prior to arrival at the measurement site (Ding et al., 2013a). The residence time was calculated to be 10 % lower for BB air masses than for non-BB air masses, suggesting that the aerosol surface rather than the ground surface was the major contributor to the observed enhancement of HONO concentrations and HONO/NO₂ ratios during BB periods. It should be noted here that we cannot totally get rid of the influence of the ground surface as the exact role of varied land use and land cover in HONO chemistry was not clear. But the results tend to support the view that heterogeneous reaction of NO₂ on the surface of BB aerosols was the major contributor to the observed increase of HONO concentration during BB periods.

### 3.2.3 Role of BB aerosols in HONO chemistry

The surface area and chemical nature of aerosol particles are the two dominating factors that influence the heterogeneous conversion of NO₂ to produce HONO. In this study, the enhanced aerosol particle loadings associated with the BB plumes (Figs. 1 and 3a), providing large aerosol surface areas (Fig. 7a), should aid the conversion of NO₂ to HONO. Besides particle mass concentration, the particle specific surface area related to the particle size distribution and morphology also influences the total particle surface area concentration. In Fig. 7a, we present the relationship between the particle surface area and particle mass concentration (PM$_{2.5}$) for both the BB and non-BB samples. The slope of the data pairs for BB samples was almost twice as that of non-BB aerosols, suggesting a much higher specific surface area for BB aerosols than that for non-BB aerosols. To further verify this point and find out the causes, we selected the samples with the PM$_{2.5}$ mass in the overlap concentration range 100–150 µg m⁻³ during both BB and non-BB periods (Fig. 7a and b), and compared their surface area concentrations calculated by the size distribution (Fig. 7c). The results showed an evidently larger surface area concentration for BB aerosols compared with non-BB aerosols. These results clearly suggest that BB aerosols have a larger specific surface area than non-BB aerosols, which is caused by a much higher number of accumulation mode particles, and favor NO₂ to HONO conversion at similar levels of the PM mass concentration. To further investigate the influence of BB aerosols on the particle specific surface area, we plotted the ratios of particle surface area to PM$_{2.5}$ against the abundance of potassium in PM$_{2.5}$ (Fig. 8) during BB periods. The result showed a positively linear correlation between the two metrics, suggesting a strong enhancement of BB aerosols on the particle specific area concentrations. Besides the surface area concentrations, the chemical nature of aerosols, which control the NO₂ conversion efficiency, is also a candidate influencing the transformation of NO₂ to HONO.

The NO₂ conversion efficiency refers to the ability of the interface to convert NO₂ to HONO. In the ambient air, both aerosol and ground surface contribute to the HONO/NO₂ ratio. Therefore, the NO₂ conversion efficiency can be represented by (HONO/NO₂)/(particle surface area + ground surface area) when the NO₂ and HONO reach a steady state (02:00–05:59, see Fig. 6). Here, we assume the related ground surface areas for each BB or non-BB sample are the same. In which case, the ratios of (HONO/NO₂)/(ground...
surface + aerosol surface) can only be compared when the aerosol surface areas of BB and non-BB aerosols are the same. Therefore, we selected the samples at HONO and NO$_2$ steady state with the surface area concentrations in the overlapped range 1.5–2.2 × 10$^{-9}$ m$^2$ cm$^{-3}$, and compared the ratios of (HONO/NO$_2$)/(aerosol surface) instead to the comparison of (HONO/NO$_2$)/(ground surface + aerosol surface). As shown in Fig. 9, the values of this ratio were 67% higher for BB samples than those for non-BB samples, further suggesting the NO$_2$ conversion efficiency of BB aerosols was higher than that of non-BB aerosols.

In summary, the elevated HONO formation observed in BB plumes was caused by the combined effects of enhanced particle loadings, higher specific aerosol surface areas, and more efficient conversion of NO$_2$ to HONO on particle surfaces. It is well known that high particle loadings associated with BB are caused by both primary particle emissions and secondary aerosol formation during atmospheric transport (Andreae and Merlet, 2001; Li et al., 2003; Capes et al., 2008). Large aerosol specific surface areas are probably due to the extremely high number concentrations of accumulation mode particles during BB (Jahnäll et al., 2010), and possibly the irregular shape of soot particles (Dobbins and Megaridis, 1987; Cai et al., 1993), which is one major product of BB. The higher NO$_2$ to HONO conversion efficiency on particle surfaces in BB plumes compared with non-BB air is a complex issue. One possible reason is the high abundance of organic (e.g., humic-like substances) and soot particles (Reid et al., 2005), which are high-performance media for converting NO$_2$ to HONO. This is supported by the much higher concentrations of organics and black carbon, estimated as the differences of PM$_{2.5}$ and the water-soluble ions, in BB periods compared to those in non-BB periods (see Fig. 3b).

### 3.3 Influence of mixed plumes of biomass burning and fossil fuel emissions on HONO chemistry

An intense BB episode mixed with FF emissions that significantly influenced everyday weather was observed on 10 June 2012 (from 18:00 on 9 June to 05:00 on 11 June) (Ding et al., 2013b). Interestingly, the highest mixing ratios of HONO, exceeding 5 ppbv, occurred during this episode (Fig. 1). The solar radiation intensity was significantly decreased in the daytime of this episode due to the extremely high particle loading (see Fig. 3 in Ding et al., 2013b), and HONO concentrations during the daytime were at a similar level to those during the nighttime. Again, we investigated the relation between HONO and potassium. The result showed no correlation (slope = −0.08, $R = 0.24$, figure not shown), suggesting that the enhanced HONO concentrations during the case of 10 June were secondarily produced. Although a high particle loading should be a contributor to the high HONO levels, it was unlikely to be the most predominant factor because the PM concentrations during this event were comparable to the peak concentrations during the other BB episodes (Fig. 1). Another possible reason is that the plumes on 10 June were more aged than the other BB plumes, which would enhance the HONO production with a longer NO$_2$ contact time with the aerosol and ground surface. However, as shown in Fig. 6, HONO and NO$_2$ can reach a steady state in 8 hours. The steady values of HONO/NO$_2$ ratios were 0.083 ± 0.014 (the value for 03:00) for other BB plumes, which were still much lower than those in the 10 June case (0.17 ± 0.046), suggesting some other factors other than the plume age enhanced the HONO concentrations during 10 June.

Figure 10 shows the scatter plot between HONO and NO$_2$ concentrations during the BB periods. The data set was separated into two groups: the first 5 h of the 10 June case (red squares, 18:00–22:00 on 9 June) combined with other BB
Figure 10. Scatter plot between HONO and NO\textsubscript{2} concentration during the BB periods (without the case of 10 June, blue solid squares), the beginning (red solid diamonds) and latter (green dots) state of the 10 June episode.

episodes (blue squares) and the later stage of the 10 June case (green circle dots). Both groups revealed a strong relation between HONO and NO\textsubscript{2} with a correlation coefficient higher than 0.8. The slope of the regression of the latter stage of the 10 June case was almost twice that of the other group (0.12 vs. 0.07), indicating a higher NO\textsubscript{2} to HONO conversion potential of the aerosols in the later stage of the 10 June case compared with other BB episodes.

To further verify this point and exclude the influence of particle loading, samples with PM\textsubscript{2.5} concentrations in the range 190–300 µg m\textsuperscript{-3} (the overlapping parts) were selected from both groups. Although the selected samples had similar PM concentration levels (Fig. 11a), the HONO/NO\textsubscript{2} ratios (Fig. 11b) and ratios between HONO/NO\textsubscript{2} and PM\textsubscript{2.5} (Fig. 11c) were much higher on the 10 June than those during the other BB episodes, indicating a higher potential for the aerosols on the 10 June to convert NO\textsubscript{2} to HONO. It should be noted that particle surface area data were not available for the 10 June case because the extremely high particle loading influenced the sample inlet of the differential mobility particle sizer (DMPS). The exact contributors to the enhancement of NO\textsubscript{2} conversion potentials, which was either higher specific aerosol surface areas or stronger conversion efficiency, are therefore not clear.

Our previous study demonstrated that the episode on the 10 June was caused not only by BB but a mixture of intense BB and anthropogenic FF emissions (Ding et al., 2013b). As shown in Fig. 12, the SO\textsubscript{2} concentration was low at the beginning of this episode and then gradually increased, suggesting the mixing of anthropogenic pollution rich in SO\textsubscript{2} with the BB particles several hours after the invasion of the BB plume. This is why the chemical features (HONO/NO\textsubscript{2}) in the plume at the beginning stage of the 10 June case was similar to that in other BB episodes, yet very different from the later stage of the 10 June case (Fig. 10).

The mix of BB plumes and FF emissions will promote the formation of secondary aerosols (e.g. sulfate and secondary organic aerosols (SOA)) on BB particles, and thus modify their morphology and surface chemical nature (Li et al., 2003; Capes et al., 2008). As shown in Fig. 11d, the abundance of sulfate in PM\textsubscript{2.5} was significantly enhanced in the 10 June case compared with other BB episodes. This coincided with the high NO\textsubscript{2} to HONO conversion efficiency (Fig. 11c), indicating a promotion of secondary aerosol formation on BB particles to HONO formation.

Figure 11. Whisker plots of (a) PM\textsubscript{2.5} mass, (b) ratios of HONO to NO\textsubscript{2}, (c) ratios of HONO/NO\textsubscript{2} to PM\textsubscript{2.5} mass, (d) ratios of sulfate to PM\textsubscript{2.5}, in the selected PM\textsubscript{2.5} mass concentration range (190–300µg m\textsuperscript{-3}) in the BB plume (10 samples) and the mixed plume (27 samples).
As discussed above, the specific surface area and chemical nature of aerosol particles are the key factors in determining their potential to convert NO$_2$ to HONO. Therefore, changes in the morphology and size distribution caused by secondary aerosol formation may have enhanced the specific surface area and led to increased HONO production in the mixed plumes. Besides, the enhanced aerosol water content (Fig. 12) caused by the production of hydrophilic species, e.g., sulfate, may also play a role in accelerating the NO$_2$ conversion (Stutz et al., 2004). Another factor that might have enhanced HONO production could be the formation of some specific secondary material on BB particles, e.g., sulfate (Kleffmann et al., 1998) and secondary organic aerosols (Bröske et al., 2003).

4 Conclusions and implications

In this study, we analyzed a two-month measurement of atmospheric HONO during the BB season of 2012 (May and June) at the SORPES station in the western YRD of eastern China, and demonstrated an important role of BB in the HONO chemistry in the ambient atmosphere. Direct emissions from BB have been estimated to contribute 17% ± 12% of the observed HONO concentrations during nighttime BB episodes. The other over 80 % was produced by the heterogeneous conversion of NO$_2$. The NO$_2$-to-HONO ($C_{HONO}$) conversion rates were detected to be significantly elevated during the BB periods due to the combined effect of enhanced particle loadings, larger specific surface areas of particles and higher NO$_2$ conversion efficiency on BB aerosols. An episode of mixed plumes of intense BB and anthropogenic FF emissions was observed on the 10 June, during which the HONO production potentials from the conversion of NO$_2$ was further promoted by the formation of secondary particulate matter on BB particles.

Given that BB plumes are easily mixed with other anthropogenic pollutants in eastern China, their influence on the atmospheric chemistry is expected to be important via affecting the HONO budget and thus the radical pool. Furthermore, considering the potential re-activation of BB particles (e.g., soot) during their atmospheric transport, the HONO chemistry associated with BB plumes may affect atmospheric chemistry for long distances downwind of BB areas, even in the marine boundary layer. Therefore, more studies are encouraged on BB related chemistry in eastern China, which is a unique “laboratory” with frequent mixed plumes of BB and anthropogenic pollution.

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