Impacts of an unknown daytime HONO source on the mixing ratio and budget of HONO, and hydroxyl, hydroperoxyl and organic peroxy radicals, in the coastal regions of China

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Abstract

Many field experiments have found high nitrous acid (HONO) mixing ratios in both urban and rural areas during daytime, but these high daytime HONO mixing ratios cannot be explained well by gas-phase production, HONO emissions, and nighttime hydrolysis conversion of nitrogen dioxide (NO_2) on aerosols, suggesting that an unknown daytime HONO source ($P_{unknown}$) could exist. The formula $P_{unknown} \approx 19.60[NO_2] \cdot J(NO_2)$ was obtained using observed data from 13 field experiments across the globe. The three additional HONO sources (i.e., the $P_{unknown}$, nighttime hydrolysis conversion of NO_2 on aerosols, and HONO emissions) were coupled into the WRF-Chem model (Weather Research and Forecasting model coupled with Chemistry) to assess the $P_{unknown}$ impacts on the concentrations and budgets of HONO and peroxy (hydroxyl, hydroperoxyl, and organic peroxy) radicals

(RO_x) (= OH + HO_2 + RO_2) in the coastal regions of China. Results indicated that the additional HONO sources produced a significant improvement in HONO and OH simulations, particularly in the daytime. High daytime average $P_{unknown}$ values were found in the coastal regions of China, with a maximum of 2.5 ppb h^{-1} in the Beijing–Tianjin–Hebei region. The $P_{unknown}$ produced a 60%–250% increase of OH, HO_2 and RO_2 near the ground in the major cities of the coastal regions of China, and a 5%–48% increase of OH, HO_2 and RO_2 in the daytime meridional-mean mixing ratios within 1000 m above the ground. When the three additional HONO sources were included, the photolysis of HONO was the second most important source in the OH production rate in Beijing, Shanghai and Guangzhou before 10:00 LST with a maximum of 3.72 ppb h^{-1} and a corresponding $P_{unknown}$ contribution of 3.06 ppb h^{-1} in Beijing, whereas the reaction of HO_2 + NO (nitric oxide) was dominant after 10:00 LST with a maximum of 9.38 ppb h^{-1} and a corresponding $P_{unknown}$ contribution of 7.23 ppb h^{-1} in Beijing. The whole RO_x cycle was accelerated by the three additional HONO sources, especially the $P_{unknown}$. The daytime average OH production rate was enhanced by 0.67 due to the three additional HONO sources [0.64 due to the $P_{unknown}$] to 4.32 [3.86] ppb h^{-1} via the reaction of HO_2 + NO, and by 0.49 [0.47] to 1.86 [1.86] ppb h^{-1} via the photolysis of HONO, and the OH daytime average loss rate was enhanced by 0.58 [0.55] to 2.03 [1.92] ppb h^{-1} via the reaction of OH + NO_2 and by 0.31 [0.28] to 1.78 [1.64] ppb h^{-1} via the reaction of OH + CO (carbon monoxide) in Beijing, Shanghai and Guangzhou. Similarly, the three additional HONO sources produced an increase of 0.31 [corresponding $P_{unknown}$

contribution of 0.28] to 1.78 [1.64] ppb h^{-1} via the reaction of OH + CO and 0.10 [0.09] to 0.63 [0.59] ppb h^{-1} via the reaction of CH_3O_2 [methylperoxy radical] + NO in the daytime average HO_2 production rate, and 0.67 [0.61] to 4.32 [4.27] ppb h^{-1} via the reaction of HO_2 + NO in the daytime average HO_2 loss rate in Beijing, Shanghai and Guangzhou. The above results suggest that the $P_{unknown}$ considerably enhanced the RO_x concentrations and accelerated RO_x cycles in the coastal regions of China, and could produce significant increases in concentrations of inorganic aerosols and secondary organic aerosols and further aggravate haze events in these regions.

1. Introduction

The hydroxyl radical (OH) is the dominant oxidant in the troposphere, initiating daytime photochemistry, removing the majority of reactive gases, and leading to the formation of secondary products [e.g. ozone (O_3), PANs (peroxyacyl nitrates) and aerosols] that can affect air quality, climate, and human health (Stone et al., 2012). OH is formed primarily through the photolysis of O_3, nitrous acid (HONO), hydrogen peroxide (H_2O_2), the reactions of O_3 with alkenes, and the hydroperoxyl radical (HO_2) to OH conversion process (HO_2+NO) (Platt et al., 1980; Crutzen and Zimmermann, 1991; Atkinson and Aschmann, 1993; Fried et al., 1997; Paulson et al., 1997). Recent field experiments have found that the contribution of the photolysis of HONO to daytime OH production can reach up to 56%, 42% and 33% in urban, rural and forest areas, respectively (Ren et al., 2003; Kleffmann et al., 2005; Acker et al., 2006), more than that of the photolysis of O_3. However, most current air quality models fail to predict observed HONO concentrations, underestimating daytime HONO in particular (Czader et al., 2012; Gonçalves et al., 2012; Li et al., 2011), due to the incomplete knowledge of HONO sources.

It is generally accepted that the photolysis of HONO [Reaction (R2)] in the early morning could be a major source of OH. After sunrise, HONO mixing ratios are usually in low concentrations due to the strong photolysis of HONO. However, many field experiments have found daytime HONO mixing ratios that are unexpectedly higher than the theoretical steady value (~10 ppt), in both urban and rural areas: e.g., 0.15–1.50 ppb in Asia (Su et al., 2008; Wu et al., 2013; Spataro et al., 2013), 0.01–0.43 ppb in Europe (Kleffmann et al., 2005; Acker et al., 2007; Sörgel et al., 2011; Michoud et al., 2014), 0.02–0.81 ppb in North America (Zhou et al., 2002a,b; Ren et al., 2010; Villena et al., 2011; N. Zhang et al., 2012; Wong et al., 2012; VanderBoer et al., 2013), 2.00 ppb (maximum) in South America (Elshorbany et al., 2009), and 0.015–0.02 ppb in Antarctica (Kerbrat et al., 2012) (Fig. 1). These high HONO mixing ratios, particularly in the daytime, cannot be explained well by gas-phase production [Reaction (R1)], HONO emissions, and nighttime hydrolysis conversion of NO_2 on aerosols, suggesting that an unknown daytime HONO source ($P_{unknown}$) could exist.

$$OH + NO \rightarrow HONO \tag{R1}$$

$$HONO + h\nu \rightarrow OH + NO \tag{R2}$$

$$HONO + OH \rightarrow NO_2 + H_2O \tag{R3}$$

The $P_{unknown}$ was calculated by Su et al. (2008) at Xinken (Guangzhou, China), with a maximum of 4.90 ppb h^{-1}. Spataro et al. (2013) proposed a $P_{unknown}$ value of 2.58 ppb h^{-1} in Beijing. In fact, $P_{unknown}$ values, ranging from 0.06 to 4.90 ppb h^{-1} have been obtained from many field studies across the globe, as shown in Fig. 1, suggesting $P_{unknown}$ could contribute greatly to the daytime production of OH and HO_2.

The most important formation pathway for nocturnal HONO could be the hydrolysis reaction of nitrogen dioxide (NO_2) on humid surfaces [Reaction (R4)] (Kleffmann et al., 1999; Alicke et al., 2002; Finlayson-Pitts et al., 2003):

$$2NO_2 + H_2O \rightarrow HONO + HNO_3 \qquad (R4)$$

Ammann et al. (1998) found HONO formation via the heterogeneous reduction of NO_2 on the surface of soot [Reaction (R5)], and Reaction (R5) can be enhanced by irradiation (Monge et al., 2010):

$$NO_2 + red_{ads} \rightarrow HONO + ox_{ads} \qquad (R5)$$

George et al. (2005) and Stemmler et al. (2006, 2007) showed the heterogeneous reduction of NO_2 on organic surfaces [Reaction (R6)] (e.g. humic acid) to produce HONO:

$$NO_2 + HC_{red} \rightarrow HONO + HC_{ox} \qquad (R6)$$

Li et al. (2008) proposed a homogeneous reaction of photolytically excited NO_2 with H_2O [Reaction (R7)], but this reaction has been proven to be unimportant in the real atmosphere (Carr et al., 2009; Wong et al., 2011; Amedro et al., 2011). Zhang and Tao (2010) suggested the homogeneous nucleation of NO_2, H_2O and ammonia (NH_3)

for the production of HONO [Reaction (R8)], but Reaction (R8) has not yet been tested in laboratory studies, nor observed in field experiments:

$NO_2 + h\upsilon\ (\lambda > 420\ nm) \rightarrow NO_2^*$

$NO_2^* + H_2O \rightarrow HONO + OH$ (R7)

$NO_2^* + M \rightarrow NO_2 + M$

$2NO_2 + H_2O(g) + NH_3 \rightarrow HONO + NH_4NO_3(s)$ (R8)

Zhou et al. (2002b, 2003, 2011) demonstrated that the photolysis of adsorbed nitric acid (HNO_3) and nitrate (NO_3^-) at ultraviolet wavelengths (~300 nm) [Reaction (R9)] can produce HONO:

$HNO_3/NO_3^- + h\upsilon \rightarrow HONO/\ NO_2^- + O$ (R9)

Additionally, HONO could be emitted from soils (Su et al., 2011; Oswald et al., 2013), and may be important in farmland and forest areas.

Based on these mechanisms outlined above, some modeling studies have been carried out to simulate HONO concentrations (e.g. An et al., 2011; Czader et al., 2012; Gonçalves et al., 2012). Sarwar et al. (2008) incorporated Reactions (R4), (R9) and HONO emissions into the Community Multiscale Air Quality (CMAQ) model, but still underestimated HONO mixing ratios during daytime. Li et al. (2010) considered both aerosol and ground surface reactions, and HONO emissions, in the WRF-Chem model (Weather Research and Forecasting model coupled with Chemistry), and found that HONO simulations were significantly improved. However, Li et al. (2010) used a relatively high emissions ratio of 2.3% for $HONO/NO_2$ to compute the direct emissions of HONO, which could have overestimated the HONO concentrations in the air (An et al., 2013). Czader et al. (2012) added Reactions (R6), (R7) and HONO emissions into the CMAQ model. The HONO simulations matched well with observations at night, but were significantly lower than observations at noon. Wong et al. (2013) reported good agreement between simulated and observed daytime HONO when HONO emissions, photolytically enhanced daytime formation mechanisms on both aerosols and the ground, and Reaction (R7), were included. However, according to our recent studies (Tang et al., 2014), this result depended heavily on the selection of uptake coefficients of NO_2 heterogeneous chemistry. Overall, the topic of HONO sources remains under discussion today, and so it is a challenge for modelers to decide which mechanism(s) to be coupled into an air quality model.

To investigate the importance of the mechanisms described above, correlation tests between the $P_{unknown}$ and NO_2, HNO_3, irradiation or the photolysis frequency of NO_2 [$J(NO_2)$] were conducted in field experiments (Acker et al., 2007; Sörgel et al., 2011; Villena et al., 2011; Wong et al., 2012). Many of these studies demonstrated that there is a clear dependency of the $P_{unknown}$ on irradiation/$J(NO_2)$ during daytime, particularly at noon. Rohrer et al. (2005) proposed that the photolytic HONO source at the surface of the chamber strongly depended on light intensity. Acker et al. (2007) summarized field experiments in several European countries and showed a strong correlation (R^2=0.81) between the $P_{unknown}$ and $J(NO_2)$. Wong et al. (2012) also indicated that the $P_{unknown}$ showed a clear symmetrical diurnal variation with a maximum around noontime, closely correlated with actinic flux (NO_2 photolysis frequency) and solar irradiance; the correlation coefficient was over 0.70.

Besides irradiation/J(NO_2), good correlations between the $P_{unknown}$ and NO_2 mixing ratios have been found from both field and laboratory studies, supporting the viewpoint that NO_2 is the primary precursor of HONO. Through estimating the $P_{unknown}$, Acker et al. (2007) speculated that the daytime HONO levels might be explained by a fast electron transfer onto adsorbed NO_2. Sörgel et al. (2011) indicated that the conversion of NO_2 most likely accounted for light-induced HONO formation, about an order of magnitude stronger than HONO formation during nighttime. High correlations between the $P_{unknown}$ and NO_2 mixing ratios have also been found [e.g., $R^2 = 0.77$ in Qin et al. (2006), $R^2 = 0.80$ in Villena et al. (2011), and $R^2 = 0.62$ in Elshorbany et al. (2009)], indicating that the photosensitized conversion of NO_2 is more likely to be the daytime HONO source. This is the reason why the recent CalNex 2010 (California Research at the Nexus of Air Quality and Climate Change) study found a very strong positive correlation ($R^2= 0.985$) between HONO flux and the product of NO_2 concentration and solar radiation at the Bakersfield site (Ren et al., 2011).

Based on the studies introduced above, the $P_{unknown}$ calculated from field experiments may be a practical method to help quantify the daytime HONO source. In this study, field experiment data from 13 different field campaigns across the globe were used to express the $P_{unknown}$ as a function of NO_2 mixing ratios and J(NO_2) (see Sect. 2.2). We then added the $P_{unknown}$ into the WRF-Chem model to assess the impacts of the $P_{unknown}$ on the concentrations and production and loss rates of HONO, OH, HO_2, and organic peroxy radicals (RO_2).

2. Data and methods

2.1 Observed data

Anthropogenic emissions were based on the year 2006/2007. Limited measurements of HONO, OH, and HO_2 in the coastal regions of China were made in the summers of 2006/2007, so these limited measurements were used for model evaluation. Observed air temperature (TA), relative humidity (RH), wind speed (WS) and direction (WD) near the ground were obtained from the National Climatic Data Center, China Meteorological Administration (H. Zhang et al., 2012). Surface mixing ratios of O_3 and NO_2 in Beijing were obtained from the Beijing Atmospheric Environmental Monitoring Action, carried out by the Chinese Academy of Sciences (Li et al., 2011; Wang et al., 2014), except those in Guangzhou, which were sourced from Qin et al. (2009). HONO observations were conducted using two annular denuders at the campus of Peking University (39°59′N, 116°18′E) in Beijing on 17–20 August 2007 (Spataro et al., 2013) and a long path absorption photometer at the Backgarden (BG) supersite (23°30′N, 113°10′E), about 60 km northwest of Guangzhou on 3–31 July 2006 (X. Li et al., 2012). The measurement systems are described in detail in Spataro et al. (2013) and X. Li et al. (2012). OH and HO_2 were measured by laser induced fluorescence at the BG supersite on 3–30 July 2006 (Lu et al., 2012).

2.2 Parameterization of HONO sources

Besides HONO gas-phase production from Reaction (R1), three additional HONO sources [HONO emissions, Reaction (R4) (nighttime), and the $P_{unknown}$] were coupled into the WRF-Chem model in this work.

HONO emissions were calculated using $[0.023 \times f_{DV} + 0.008 \times (1 - f_{DV})] \times f_{TS}$, where f_{DV} denotes the nitrogen oxides (NO_x) emissions ratio of diesel vehicles to total vehicles, and f_{TS} is the NO_x emissions ratio of the traffic source to all anthropogenic sources (Li et al., 2011; An et al., 2013; Tang et al., 2014). Reaction (R4) was inserted into the Carbon-Bond Mechanism Z (CBM-Z) during nighttime only. The heterogeneous reaction rate was parameterized by $k = \left(\frac{a}{D_g} + \frac{4}{v\gamma}\right)^{-1} A_s$ (Jacob, 2000), where a is the radius of aerosols, v is the mean molecular speed of NO_2, D_g is a gas-phase molecular diffusion coefficient taken as 10^{-5} m^2 s^{-1}(Dentener and Crutzen, 1993), and A_s is the aerosol surface area per unit volume of air, calculated from aerosol mass concentrations and number density in each bin set by the Model for Simulating Aerosol Interactions and Chemistry (MOSAIC). Hygroscopic growth of aerosols was considered (Li et al., 2011).

Previous studies (Sörgel et al., 2010; Villena et al., 2011; Wong et al., 2012) have shown $P_{unknown} \propto [NO_2] \cdot J(NO_2)$. To quantify the relationship between the $P_{unknown}$ and NO_2 mixing ratios and irradiation, daytime $P_{unknown}$, NO_2 mixing ratios and $J(NO_2)$, based on all the available data sets from 13 different field campaigns across the globe (Table S1), were plotted in Fig. 2. As expected, good correlation (R^2 = 0.75) between the $P_{unknown}$ and NO_2 mixing ratios was obtained (Fig. 2a). Furthermore, the correlation between the $P_{unknown}$ and $[NO_2] \cdot J(NO_2)$ was increased to 0.80, with a linear regression slope of 19.60 (Fig. 2b). For the coastal regions of China (mainly including Laoning, Beijing, Tianjin, Hebei, Shandong, Jiangsu, Anhui, Shanghai, Zhejiang, Jiangxi, Fujian, and Guangdong), the correlation between the $P_{unknown}$ and $[NO_2]\cdot J(NO_2)$ was 0.48, with a linear regression slope of 17.37 (Fig. S2b), which is within the maximum $P_{unknown}$ uncertainty range of 25% (Table S1). The $P_{unknown}$ cloud be expressed as a function of NO_2 mixing ratios and $J(NO_2)$, i.e., $P_{unknown} \approx 19.60[NO_2]\cdot J(NO_2)$. This formula is very similar to $P_{unknown} \approx \alpha \cdot J(NO_2)\cdot[NO_2]\cdot[H_2O]\cdot(S/V_g + S/V_a)$ proposed by Su et al. (2008), and $P_{unknown} \approx 3.3\times10^{-8}[NO_2]\cdot Q_s$ suggested by Wong et al. (2012) as an additional daytime source of HONO through analysis of observed data, where S/V_a is the aerosol surface area-to-volume ratio, S/V_g is the ground surface area-to-volume ratio, α is a fitting parameter, and Q_s is solar visible irradiance.

2.3 Model setup

Used in this study was the WRF-Chem model version 3.2.1 (Grell et al., 2005; Fast et al., 2006), with the CBM-Z (Zaveri and Peters, 1999) and the MOSAIC (Zaveri et al., 2008). The detailed physical and chemical schemes for the simulations can be found in Tang et al. (2014). Two domains with a horizontal resolution of 27 km were employed in this study: domain 1 covered East Asia, whereas domain 2 covered the coastal regions of China, including the Beijing–Tianjin–Hebei region (BTH), the Yangtze River delta (YRD), and the Pearl River delta (PRD) (Fig. 3), which are the three most rapidly-developing economic growth regions of China. The rapid economic development and urbanization has led to a serious deterioration in air quality in these three regions. Beijing, Shanghai, and Guangzhou are three representative cities of the three regions, so this study focuses on the three regions, including the three representative cities. There were 28 vertical model layers from the ground to 50 hPa, and the first model layer was ~28 m above the ground. Meteorological initial and boundary conditions were obtained from the NCEP (National Centers for Environmental Prediction) 1 °×1 ° reanalysis dataset. Chemical initial and boundary conditions were constrained with the output of MOZART-4 (Model for Ozone and Related chemical Tracers, version 4) (Emmons et al., 2010), every 6 h. Monthly anthropogenic emissions in 2006/2007 and biogenic emissions were the same as those used by Li et al. (2011) and An et al. (2013).

Six simulations (cases R, R_{wop}, and R_p, performed for the entire months of August 2007 and July 2006), with a spin-up period of seven days, were conducted to assess the $P_{unknown}$ effects on the concentrations and budgets of HONO, OH, HO_2, and RO_2. Case R only considered Reaction (R1) as a reference; Case R_{wop} included case R with HONO emissions, and Reaction (R4) only at night; case R_p contained case R_{wop} with the $P_{unknown}$ [$\approx 19.60[NO_2] \cdot J(NO_2)$]. The $P_{unknown}$ and Reaction (R4) were added to the CBM-Z, and diagnostic variables (i.e., production and loss rates of HONO, OH, HO_2, RO_2, O_3, and other species) were inserted into the CBM-Z to quantify the $P_{unknown}$ impacts on the budgets of HONO, OH, HO_2, and RO_2 (Wang et al., 2014).

3. Results and discussion

3.1 Comparison of simulations and observations

The statistical metrics of mean bias (MB), mean error (ME), root-mean-square error (RMSE), normalized mean bias (NMB), normalized mean error (NME), index of agreement (IOA), and correlation coefficient (CC), were used. The MB, ME, and RMSE are given in the same units as the measurements (absolute metrics). The MB quantifies the tendency of the model to over- or underestimate values, while the ME and RMSE measure the magnitude of the difference between modeled and observed values regardless of whether the modeled values are higher or lower than observations. One disadvantage of absolute metrics is that they make intercomparisons of model performance in clean and polluted environments or across different pollutants difficult to interpret. Consequently, a range of relative metrics are often used. These metrics are presented either in fractional or percentage units. The NMB and NME all normalize by observed values. The IOA and CC provide a sense of the strength of the relationship between model estimates and observations that have been paired in time and space. Perfect agreement for any metric alone may not be indicative of good model performance, so multiple metrics must be considered when evaluating model performance. Simulations of TA, RH, WS and WD were compared with observations, as shown in Wang et al. (2014). The MB, ME, RMSE, NMB, NME, IOA, and CC were comparable with those of Wang et al. (2010) and L. Li et al. (2012) using MM5 (the fifth-generation Pennsylvania State University/National Center for Atmospheric Research Mesoscale Model), and H. Zhang et al. (2012) using the WRF model. For O_3 in Beijing of the BTH region and Guangzhou of the PRD region, the NMB, NME and IOA were −22.80%, 58.70% and 0.79, respectively (Table 1 for case R), comparable to the values of 30.2% for

NMB, 55.8% for NME and 0.91 for IOA reported in L. Li et al. (2012) using the CMAQ model. When HONO emissions, Reaction (R4) and the $P_{unknown}$ were included, the NMB, NME and IOA increased to −2.20%, 66.10% and 0.80, respectively (Table 1 for case R_p). The NO_2 fluctuations were generally captured (Fig. 4) but the simulated amplitude of NO_2 was underestimated in some cases (Fig. 4). This underestimation could be related with the uncertainty of NO_x emissions. For NO_2 in case R, the NMB, NME and IOA were −13.50%, 42.10% and 0.57, respectively (Table 1), similar to the results of Wang et al. (2010) using the CMAQ model (NMB of −33.0%, NME of 50.0%, and IOA of 0.61). Compared with case R, NO_2 simulations (Table 1 for case R_p) were further underestimated for case R_p due to the underestimation of NO_x emissions in Guangzhou.

HONO simulations only with the gas-phase production (case R) were always substantially underestimated compared with observations (Fig. 5), similar to the results of Sarwar et al. (2008), Li et al. (2011) and An et al. (2013). When HONO emissions and Reaction (R4) were included, HONO simulations were significantly improved, especially at night (Fig. 5 and Table 2 for case R_{wop}). For Beijing, the nighttime RMSE and NME were reduced by 0.90×10^6 molecules cm^{-3} and 44.70%, whereas the NMB and IOA were increased by 50.00% and 0.29, respectively (Table 2). For Guangzhou, the nighttime RMSE and NME were reduced by 0.44×10^6 molecules cm^{-3} and 32.90%, and the NMB and IOA were enhanced by 58.80% and 0.18, respectively. When the $P_{unknown}$ was included, daytime HONO simulations were considerably improved (Fig. 5 and Table 2 for case R_p). Compared with case R_{wop}, the daytime NME in Beijing was reduced by 19.60%, and the NMB and IOA in Beijing were increased to −24.30% from −62.00% and 0.73 from 0.64, respectively (Table 2); the daytime NME in Guangzhou was reduced by 8.10%, and the NMB in Guangzhou was increased to −61.20% from −76.50% (Table 2).

Simulated diurnal variations of OH and HO_2 showed consistent patterns with the observed data (Fig. 6). When HONO emissions and Reaction (R4) were considered (case R_{wop}), OH and HO_2 enhancements were ≤ ~6% in most cases compared with case R (Fig. 6 and Table 3), but the $P_{unknown}$ led to 10%–150% improvements in OH simulations on 5–12 July 2006 (Fig. 6). The 20%–90% overestimation of OH mixing ratios on 20–25 July 2006 (Fig. 6) needs further investigation. Compared with case R, the NME was reduced by 79.60% (=136.60% − 57.00%), whereas the NMB was increased by 105.40% (123.00% − 17.60%), and the IOA was improved to 0.84 from 0.79 (Table 3). When the $P_{unknown}$ was considered, HO_2 simulations were substantially improved (Fig. 6), the IOA was improved to 0.61 from 0.54 and the CC was improved to 0.66 from 0.57 (Table 3). However, HO_2 simulations were still substantially underestimated (Fig. 6). One of the major reasons for the HO_2 underestimation could be related to the considerable underestimation of anthropogenic volatile organic compounds (VOCs) (Wang et al., 2014).

3.2 $P_{unknown}$ simulations and its impacts on production and loss rates of HONO

High $P_{unknown}$ values were found in the coastal regions of China (Fig. 7), especially in the BTH, YRD and PRD regions due to elevated emissions of NO_x

(Zhang et al., 2009). The largest daytime average $P_{unknown}$ value reached 2.5 ppb h^{-1} in Tianjin of the BTH region (Fig. 7a), whereas it was 2.0 ppb h^{-1} in Shanghai of the YRD region (Fig. 7b). The largest daytime average $P_{unknown}$ value reached 1.2 ppb h^{-1} in Guangzhou and Shenzhen of the PRD (Fig. 7c), lower than the values of 2.5 ppb h^{-1} and 2.0 ppb h^{-1}. One major reason is the underestimation of daytime NO_2 mixing ratios in the PRD (Fig. 4b).

For case R, daytime HONO production was primarily from the reaction of OH and nitric oxide (NO) [Reaction (R1)], with a maximum production rate of 0.69 ppb h^{-1} in Beijing, 1.20 ppb h^{-1} in Shanghai, and 0.72 ppb h^{-1} in Guangzhou near noon due to high OH mixing ratios (Fig. 8a, c, e). The loss rate of HONO was 0.62 ppb h^{-1} in Beijing, 1.09 ppb h^{-1} in Shanghai, and 0.65 ppb h^{-1} in Guangzhou via Reaction (R2), much higher than the 0.01–0.02 ppb h^{-1} in Beijing, Shanghai and Guangzhou via Reaction (R3) (Fig. 8b, d, f), indicating that Reaction (R2) accounted for approximately 99% of the total loss rate of HONO.

When the additional HONO sources [HONO emissions, Reaction (R4), and the $P_{unknown}$] were coupled into the WRF-Chem model, nighttime HONO was formed mainly via Reaction (R4) (0.30–1.42 ppb h^{-1} in Beijing, 0.20–0.45 ppb h^{-1} in Shanghai, and 0.25–0.84 ppb h^{-1} in Guangzhou) (Fig. 8a, c, e). HONO emissions contributed 0.04–0.62 ppb h^{-1} to HONO production (Fig. 8a, c, e). Simulated $P_{unknown}$ values ranged from 0.42 to 2.98 ppb h^{-1} in Beijing, from 0.18 to 2.58 ppb h^{-1} in Shanghai, and from 0.06 to 1.66 ppb h^{-1} in Guangzhou (Fig. 8a, c, e). The simulated $P_{unknown}$ values in Beijing (Fig. 8a) were in good agreement with the results of Spataro et al. (2013), with an average unknown daytime HONO production rate of 2.58 ppb h^{-1} in the studied summer period. However, the simulated $P_{unknown}$ values in Guangzhou (Fig. 8e) were lower than the 2.36–4.90 ppb h^{-1} reported by Su et al (2008), due mainly to the underestimation of the daytime NO_2 mixing ratios in the PRD region. The additional HONO sources produce more HONO, which subsequently photolyzes to yield more OH. Therefore, the formation of HONO through Reaction (R1) was greatly enhanced, with a maximum of 4.70 [1.44 due to the $P_{unknown}$] ppb h^{-1} in Beijing, 4.25 [3.13] ppb h^{-1} in Shanghai, and 1.58 [0.40] ppb h^{-1} in Guangzhou in the morning (Fig. 8a, c, e), much higher than the 0.69 ppb h^{-1} in Beijing, 1.20 ppb h^{-1} in Shanghai, and 0.72 ppb h^{-1} in Guangzhou, respectively, for case R (Fig. 8a, c, e). Meanwhile, the loss rate of HONO via Reaction (R2) was significantly enhanced, with a maximum enhancement of 5.20 (= 5.82 − 0.62) [1.97 due to the $P_{unknown}$] ppb h^{-1} in Beijing, 4.31 (= 5.40 − 1.09) [1.44] ppb h^{-1} in Shanghai, and 1.96 (= 2.61 − 0.65) [1.18] ppb h^{-1} in Guangzhou (Fig. 8b, d, f). The HONO loss rate via dry deposition ranged from 0.28 to 0.45 ppb h^{-1} (not shown), roughly equivalent to the contribution of HONO emissions, suggesting that dry deposition of HONO cannot be neglected in high NO_x emission areas. The maximum $P_{unknown}$ uncertainty range of 25% (Table S1), a 25% increase (decrease) in the slope factor (19.60) led to a 9.19%–18.62% increase (a 8.40%–14.32% decrease) in the maximum production and loss rate of HONO (Fig. S3).

3.3 $P_{unknown}$ impacts on concentrations of OH, HO_2 and RO_2

Incorporation of the $P_{unknown}$ into the WRF-Chem model led to substantial enhancements in the daytime average mixing ratios of OH in the coastal regions of China, e.g., 60%–190% in the BTH region, 60%–210% in the YRD region, and 60%–200% in the PRD region (Fig. 9a). The maximum enhancement of HO_2 reached 250% in the BTH region, 200% in the YRD region, and 140% in the PRD region (Fig. 9b). Similarly, a daytime average increase of 100%–180%, 60%–150% and 40%–80% in RO_2 [= CH_3O_2 (methylperoxy radical) + ETHP (ethylperoxy radical) + C_2O_3 (peroxyacyl radical) + others] were found in the BTH, YRD and PRD regions, respectively (Fig. 9c).

Vertically, the $P_{unknown}$ enhanced the monthly meridional-mean daytime (06:00–18:00 LST) mixing ratios of OH, HO_2 and RO_2 by 5%–38%, 5%–47% and 5%–48%, respectively, within 1000 m above the ground in the coastal regions of China (Fig. 10). Strong vertical mixing in the daytime in summer led to a roughly uniform vertical enhancement of OH, HO_2 and RO_2 within the 1000 m at the same latitude (Fig. 10). Different $P_{unknown}$ values in different latitudes produced distinct differences in the enhancements of OH, HO_2 and RO_2, with a maximum located near 35 °N (Fig. 10).

3.4 $P_{unknown}$ impacts on the budgets of OH, HO_2 and RO_2

OH radicals are produced mainly through the reaction of HO_2 + NO, the photolysis of O_3 and HONO, and the reactions between O_3 and alkenes (Fig. 11). For case R, the predominant contribution to P(OH) (production rate of OH) was the reaction of HO_2 + NO (Fig. S1a, c, e), and the photolysis of O_3 was the second most important source of OH (Fig. S1a, c, e). When the three additional HONO sources were added, the most important source was the reaction of HO_2 + NO, with a diurnal maximum conversion rate reaching 9.38 [7.23 due to the $P_{unknown}$] ppb h^{-1} in Beijing, 2.63 [1.15] ppb h^{-1} in Shanghai, and 4.88 [1.43] ppb h^{-1} in Guangzhou near noon (Fig. 11a, c, e). The photolysis of HONO became the second most important source of OH in Beijing and Guangzhou before 10:00 LST, and in Shanghai before 12:00 LST; the diurnal peaks were 3.72 [3.06] ppb h^{-1} in Beijing at 09:00 LST, 0.89 [0.62] ppb h^{-1} in Shanghai at 11:00 LST, and 0.97 [0.78] ppb h^{-1} in Guangzhou at 09:00 LST (Fig. 11a, c, e), which were comparable to or lower than the 3.10 ppb h^{-1} reported by Elshorbany et al. (2009). Kanaya et al. (2009), who also conducted similar studies at Mount Tai (located in a rural area) of China, using an observationally constrained box model, suggested that the reaction of HO_2 + NO was the predominant OH source, with a daytime average of 3.72 ppb h^{-1}, more than the 1.38 ppb h^{-1} of the photolysis of O_3. Using an observationally constrained box model, Hens et al. (2014) reported similar results in a boreal forest, in which the dominant contributor to OH was the reaction of HO_2 + NO, ranging from 0.23 to 1.02 ppb h^{-1} during daytime. The production rates of OH in our study were higher than in Kanaya et al. (2009) and Hens et al. (2014) due to higher NO_x emissions in urban areas than in rural areas.

The dominant loss rate of OH was the reaction of OH + NO_2 for both cases R and R_p (Figs. 11b, d, f and S1b, d, f). The diurnal maximum loss rates were 1.98 ppb h^{-1} in Beijing, 1.12 ppb h^{-1} in Shanghai, and 1.70 ppb h^{-1} in Guangzhou for case R (Fig. S1b, d, f), whereas these values were 5.61 [4.38 due to the $P_{unknown}$] ppb h^{-1} in

Beijing, 2.00 [1.00] ppb h^{-1} in Shanghai, and 2.65 [1.02] ppb h^{-1} in Guangzhou for case R_p (Fig. 11b, d, f). The reactions of OH + VOCs to form HO_2 and RO_2 were the second most important loss path of OH, with a diurnal maximum of 0.75–1.73 ppb h^{-1} for case R (Fig. S1b, d, f) and 1.57 [0.82 due to the $P_{unknown}$] to 5.37 [4.05] ppb h^{-1} for case R_p in Beijing, Shanghai and Guangzhou (Fig. 11b, d, f). The third most important OH loss path was the reaction of OH + CO to form HO_2; the diurnal maximum rates were 0.46–1.47 ppb h^{-1} for case R (Fig. S1b, d, f) and 0.93 [0.49 due to the $P_{unknown}$] to 3.58 [2.86] ppb h^{-1} for case R_p in Beijing, Shanghai and Guangzhou (Fig. 11b, d, f).

The averaged radical conversion rates in the daytime (06:00–18:00 LST) are illustrated in Fig. 12. OH radicals are produced mainly via the photolysis of O_3, HONO and hydrogen peroxide (H_2O_2), and the reactions between O_3 and alkenes, after which OH radicals enter the RO_x (= OH + HO_2 + RO_2) cycle (Fig. 12 and Tables 4, S2 and S3).

For case R, the reaction of HO_2 + NO was the major source of OH [2.78 ppb h^{-1} (81.73% of the total daytime average production rate of OH) in Beijing, 0.73 ppb h^{-1} (67.09%) in Shanghai, and 1.75 ppb h^{-1} (71.54%) in Guangzhou] (Fig. 12a and Table 4). The second largest source of OH was the photolysis of O_3 (Table 4). OH radicals were removed mainly through the reaction of OH + NO_2 [1.12 ppb h^{-1} (39.31% of the total daytime average loss rate of OH) in Beijing, 0.47 ppb h^{-1} (46.63%) in Shanghai, and 0.77 ppb h^{-1} (38.33%) in Guangzhou] (Table 4), whereas those were converted to HO_2 mainly via the reaction of OH + CO (Table 4). For HO_2, the predominant production pathways were the reactions of OH + CO and CH_3O_2 + NO and the photolysis of formaldehyde (HCHO) (Table S2). HO_2 radicals were consumed primarily via the reaction of HO_2 + NO [2.78 ppb h^{-1} (99.34%) in Beijing, 0.73 ppb h^{-1} (99.61%) in Shanghai, and 1.75 ppb h^{-1} (98.29%) in Guangzhou] (Table S2). RO_2 radicals were formed mainly from the reactions of OH + OLET (terminal olefin carbons)/OLEI (internal olefin carbons), OH + ETH (ethene), OH + methane (CH_4), and OH + AONE (acetone). RO_2 radicals were consumed primarily via the reaction of CH_3O_2 + NO [0.54 ppb h^{-1} (94.56%) in Beijing, 0.16 ppb h^{-1} (95.28%) in Shanghai, and 0.33 ppb h^{-1} (96.07%) in Guangzhou] (Table S3).

When the three additional HONO sources were inserted into the WRF-Chem model (case R_p), the daytime average OH production rate was enhanced by 4.32 (= 7.10 − 2.78) [3.86 due to the $P_{unknown}$] ppb h^{-1} in Beijing, 0.67 (= 1.40 − 0.73) [0.64] ppb h^{-1} in Shanghai, and 0.80 (= 2.55 − 1.75) [0.68] ppb h^{-1} in Guangzhou via the reaction of HO_2 + NO, and by 1.86 [1.86] ppb h^{-1} in Beijing, 0.50 [0.50] ppb h^{-1} in Shanghai, and 0.49 [0.47] ppb h^{-1} in Guangzhou via the photolysis of HONO, respectively (Table 4). The enhancements of the daytime average OH production rate due to the photolysis of HONO were comparable to or lower than the 2.20 ppb h^{-1} obtained by Liu et al. (2012). The daytime average OH loss rate was increased by 2.03 [1.92 due to the $P_{unknown}$] ppb h^{-1} in Beijing, 0.58 [0.55] ppb h^{-1} in Shanghai, and 0.65 [0.58] ppb h^{-1} in Guangzhou via the reaction of OH + NO_2, and by 1.78 [1.64] ppb h^{-1} in Beijing, 0.31 [0.28] ppb h^{-1} in Shanghai, and 0.42 [0.36] ppb h^{-1} in Guangzhou via the reaction of OH + CO, respectively (Table 4). Similarly, the daytime average HO_2 production rate was increased by 0.31 [0.28 due to the $P_{unknown}$] to 1.78 [1.64] ppb h^{-1} in Beijing, Shanghai and Guangzhou via the reaction of OH + CO, and by 0.63 [0.59] ppb h^{-1} in Beijing, 0.10 [0.09] ppb h^{-1} in Shanghai, and 0.19 [0.17] ppb h^{-1} in Guangzhou via the reaction of CH_3O_2 + NO; whereas, the daytime average HO_2 loss rate was enhanced by 0.67 [0.61 due to the $P_{unknown}$] to 4.32 [4.27] ppb h^{-1} in Beijing, Shanghai and Guangzhou via the reaction of HO_2 + NO (Table S2).

Overall, the net daytime production rate of RO_x was increased to 3.48 (= 2.56 + 0.71 + 0.21) [2.06 due to the $P_{unknown}$] from 1.20 (= 0.60 + 0.43 + 0.17) ppb h^{-1} in Beijing, 1.09 (= 0.86 + 0.19 + 0.04) [0.45] from 0.54 (= 0.36 + 0.14 + 0.04) ppb h^{-1} in Shanghai, and 1.52 (= 1.21 + 0.26 + 0.05) [0.58] from 0.92 (= 0.68 + 0.20 + 0.04) ppb h^{-1} in Guangzhou (Fig. 12) due to the three additional HONO sources, indicating that the RO_x source was mainly from OH production, especially via the photolysis of HONO (Tables 4, S2 and S3). This result is different from the conclusion of Liu et al. (2012) that the photolysis of HONO and oxygenated VOCs is the largest RO_x source. One of the primary reasons for this is the underestimation of anthropogenic VOCs (Wang et al., 2014). For Beijing, the net production rate of RO_x was 3.48 ppb h^{-1}, lower than the 6.60 ppb h^{-1} from the field studies of Liu et al. (2012). Our results reconfirmed the view of Ma et al. (2012) that the North China Plain acts as an oxidation pool. The additional HONO sources produced an increase of 2.03 [1.96 due to the $P_{unknown}$] ppb h^{-1} in Beijing, 0.56 [0.54] ppb h^{-1} in Shanghai, and 0.66 [0.59] ppb h^{-1} in Guangzhou in the net loss rate of RO_x (Fig. 12).

4. Conclusions

The relationship between the $P_{unknown}$, NO_2 mixing ratios and $J(NO_2)$ was investigated using available data from 13 field studies across the globe. The formula $P_{unknown} \approx 19.60[NO_2] \cdot J(NO_2)$ was obtained, and then the three additional HONO sources (i.e., the $P_{unknown}$, HONO emissions and nighttime hydrolysis conversion of NO_2 on aerosols) were inserted into the WRF-Chem model, to assess the $P_{unknown}$ impacts on the concentrations and budgets of HONO and RO_x in the coastal regions of China. The results showed that:

(1) The additional HONO sources led to significant improvements in the simulations of HONO and OH, especially in the daytime.

(2) Elevated daytime average $P_{unknown}$ values were found in the coastal regions of China, reaching 2.5 ppb h^{-1} in the BTH region, 2.0 ppb h^{-1} in the YRD region, and 1.2 ppb h^{-1} in the PRD region.

(3) The additional HONO sources substantially enhanced the production and loss rates of HONO. Dry deposition of HONO contributed 0.28–0.45 ppb h^{-1} to the loss rate of HONO, approximately equivalent to the contribution of HONO emissions, emphasizing the importance of dry deposition of HONO in high NO_x emissions areas.

(4) The $P_{unknown}$ produced a 60%–210% enhancement of OH, a 60%–250% enhancement of HO_2, and a 60%–180% enhancement of RO_2 near the ground in the major cities of the coastal regions of China. Vertically, the $P_{unknown}$ enhanced the daytime meridional-mean mixing ratios of OH, HO_2 and RO_2 by 5%–38%, 5%–47%

and 5%–48%, respectively, within 1000 m above the ground.

(5) When the three additional HONO sources were added, the photolysis of HONO became the second most important source of OH in Beijing and Guangzhou before 10:00 LST, and in Shanghai before 12:00 LST, with a maximum of 3.72 [3.06 due to the $P_{unknown}$] ppb h^{-1} in Beijing, 0.89 [0.62] ppb h^{-1} in Shanghai, and 0.97 [0.78] ppb h^{-1} in Guangzhou; whereas, the reaction of HO_2 + NO was the most important source of OH, dominated in Beijing and Guangzhou after 10:00 LST and in Shanghai after 12:00 LST, with a maximum of 9.38 [7.23] ppb h^{-1} in Beijing, 2.63 [1.15] ppb h^{-1} in Shanghai, and 4.88 [1.43] ppb h^{-1} in Guangzhou.

Overall, the above results suggest that the $P_{unknown}$ significantly enhances the atmospheric oxidation capacity in the coastal regions of China by increasing RO_x concentrations and accelerating RO_x cycles, and could lead to considerable increases in concentrations of inorganic aerosols and secondary organic aerosols and further aggravate haze events in these regions.

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Table 1. Model performance statistics for O_3 and NO_2 in Beijing in August 2007 and Guangzhou in July 2006.

Species	Case	MB (ppb)	ME (ppb)	RMSE (ppb)	NMB (%)	NME (%)	IOA
O_3	R_p	−0.65	19.40	25.44	−2.20	66.10	0.80
	R	−6.69	17.21	25.24	−22.80	58.70	0.79
NO_2	R_p	−9.50	17.31	21.40	−29.10	53.00	0.51
	R	−4.40	13.75	17.61	−13.50	42.10	0.57

MB: mean bias; ME: mean error; RMSE: root-mean-square error; NMB: normalized mean bias; NME: normalized mean error; IOA: index of agreement.

Table 2. Model performance statistics for daytime (06:00–18:00 LST) and nighttime (19:00–05:00 LST) HONO in Beijing in August 2007 and Guangzhou in July 2006.

Species	Case	MB (10^6 molec cm^{-3})	ME (10^6 molec cm^{-3})	RMSE (10^6 molec cm^{-3})	NMB (%)	NME (%)	IOA	CC
$\text{HONO}_{\text{daytime}}$ (Beijing)	R_p	−0.54	0.98	1.41	−24.30	44.50	0.73	0.57
	R_{wop}	−1.37	1.41	1.83	−62.00	64.10	0.64	0.63
	R	−2.07	2.07	2.58	−93.80	93.80	0.46	0.31
$\text{HONO}_{\text{nighttime}}$ (Beijing)	R_p	−0.73	0.84	1.09	−42.20	49.10	0.77	0.74
	R_{wop}	−0.82	0.91	1.16	−47.90	53.20	0.75	0.75
	R	−1.68	1.68	2.06	−97.90	97.90	0.46	0.76
$\text{HONO}_{\text{daytime}}$ (Guangzhou)	R_p	−0.38	0.43	0.58	−61.20	69.60	0.58	0.56
	R_{wop}	−0.48	0.49	0.65	−76.50	77.70	0.55	0.56
	R	−0.60	0.60	0.80	−95.60	96.20	0.43	-0.30
$\text{HONO}_{\text{nighttime}}$ (Guangzhou)	R_p	−0.42	0.75	1.05	−32.90	58.50	0.66	0.43
	R_{wop}	−0.49	0.83	1.15	−38.40	64.30	0.63	0.38
	R	−1.25	1.25	1.59	−97.20	97.20	0.45	-0.01

CC: correlation coefficient.

Table 3. Model performance statistics for OH and HO_2 in Guangzhou in July 2006.

Species	Case	MB (10^6 molec cm^{-3})	ME (10^6 molec cm^{-3})	RMSE (10^6 molec cm^{-3})	NMB (%)	NME (%)	IOA	CC
OH	R_p	−1.35	4.37	6.22	−17.60	57.00	0.84	0.75
	R_{wop}	−3.00	4.58	6.25	−112.20	126.50	0.81	0.72
	R	−3.36	4.85	6.55	−123.00	136.60	0.79	0.70
HO_2	R_p	−3.80	3.81	5.59	−78.50	78.60	0.61	0.66
	R_{wop}	−4.19	4.20	6.14	−86.60	86.70	0.54	0.59
	R	−4.22	4.23	6.16	−87.20	87.30	0.54	0.57

Table 4. Daytime (06:00–18:00 LST) average OH budgets in Beijing/Shanghai/Guangzhou in August 2007.

Reaction	Case R		Case R_{wop}		Case R_p	
	Rate (ppb h^{-1})	Contribution (%)	Rate (ppb h^{-1})	Contribution (%)	Rate (ppb h^{-1})	Contribution (%)
			OH production			
HO_2+NO	**2.778/0.732/1.748**	**81.73/67.09/71.54**	**3.242/0.760/1.871**	**83.74/68.00/72.02**	**7.101/1.402/2.553**	**73.34/61.95/67.55**
***$(HONO+hv)_{net}$**	**--/--/--**	**--/--/--**	**--/--/0.017**	**--/--/0.66**	**1.855/0.497/0.489**	**19.16/21.98/12.93**
O^1D+H_2O	**0.465/0.307/0.617**	**13.68/28.17/25.27**	**0.479/0.306/0.630**	**12.36/27.38/24.24**	**0.568/0.312/0.651**	**5.86/13.80/17.23**
O_3+OLET/OLEI	0.101/0.024/0.027	2.98/2.16/1.11	0.095/0.023/0.027	2.45/2.08/1.03	0.080/0.021/0.025	0.83/0.91/0. 65
*$(H_2O_2+hv)_{net}$	0.035/0.023/0.029	1.02/2.07/1.17	0.035/0.023/0.030	0.91/2.03/1.16	0.037/0.022/0.032	0.38/0.97/0.19
HO_2+O_3	0.009/0.001/0.014	0.28/0.07/0.59	0.010/0.001/0.015	0.26/0.06/0.58	0.026/0.001/0.019	0.27/0.05/0.51
*$(HNO_3+hv)_{net}$	0.005/0.001/0.002	0.15/0.06/0.10	0.005/0.001/0.002	0.13/0.06/0.09	0.007/0.001/0.003	0.07/0.04/0.07
ROOH+hv	0.003/0.004/0.005	0.09/0.36/0.19	0.003/0.004/0.005	0.09/0.38/0.19	0.007/0.007/0.007	0.07/0.29/0.19
O_3+ETH	0.002/<0.001/<0.001	0.05/0.02/0.01	0.002/<0.001/<0.001	0.04/0.02/0.01	0.001/<0.001/<0.001	0.02/0.01/0.01
HO_2+NO_3	<0.001/<0.001/<0.001	<0.01/<0.01/0.01	<0.001/<0.001/<0.001	<0.01/<0.01/<0.01	<0.001/<0.001/<0.001	<0.01/<0.01/<0.01
O_3+ISOP	<0.001/<0.001/<0.001	0.01/<0.01/<0.01	<0.001/<0.001/<0.001	0.01/<0.01/<0.01	<0.001/<0.001/<0.001	<0.01/<0.01/<0.01
Total	3.399/1.091/2.443	100/100/100	3.873/1.118/2.598	100/100/100	9.683/2.263/3.779	100/100/100
			OH loss			
OH+NO_2	**1.116/0.474/0.770**	**39.31/46.63/38.33**	**1.225/0.501/0.844**	**38.11/45.86/38.86**	**3.146/1.045/1.424**	**38.08/44.29/40.76**
OH+CO	**0.785/0.203/0.576**	**27.65/19.97/28.67**	**0.932/0.227/0.637**	**29.00/20.78/29.33**	**2.573/0.506/1.001**	**31.14/21.45/28.65**
OH+OLET/OLEI	**0.192/0.054/0.059**	**6.76/5.31/2.94**	**0.264/0.065/0.077**	**8.21/5.95/3.55**	**0.537/0.206/0.095**	**6.50/8.73/2.72**
OH+HCHO	**0.150/0.050/0.146**	**5.28/4.92/7.27**	**0.166/0.053/0.156**	**5.16/4.85/7.18**	**0.544/0.096/0.242**	**6.59/4.07/6.93**
OH+CH_4	0.103/0.057/0.135	3.63/5.61/6.72	0.109/0.059/0.142	3.39/5.40/6.54	0.260/0.115/0.223	3.15/4.87/6.38
OH+ALD2/MGLY/ ANOE	0.092/0.018/0.045	3.24/1.77/2.24	0.109/0.020/0.049	3.39/1.83/2.26	0.323/0.047/0.081	3.91/1.99/2.32

OH+SO$_2$	0.054/0.030/0.035	1.90/2.95/1.74	0.064/0.034/0.041	1.99/3.11/1.89	0.172/0.116/0.072	2.08/4.92/2.06
OH+XYL	0.052/0.022/0.023	1.83/2.16/1.14	0.066/0.026/0.029	2.05/2.38/1.34	0.141/0.078/0.045	1.71/3.31/1.29
OH+H$_2$	0.038/0.021/0.050	1.34/2.07/2.49	0.040/0.022/0.052	1.24/2.01/2.39	0.095/0.027/0.075	1.15/1.14/2.15
OH+TOL	0.027/0.007/0.011	0.95/0.69/0.55	0.034/0.008/0.014	1.06/0.73/0.64	0.086/0.025/0.024	1.04/1.06/0.69
OH+HONO	0.003/0.003/0.005	0.11/0.30/0.25	0.006/0.004/0.007	0.19/0.37/0.32	0.069/0.023/0.032	0.84/0.97/0.92
OH+HNO$_x$	0.005/0.001/0.005	0.18/0.10/0.25	0.005/0.001/0.005	0.16/0.09/0.23	0.015/0.002/0.008	0.18/0.08/0.23
OH+O$_3$	0.028/0.006/0.035	0.99/0.59/1.70	0.029/0.006/0.036	0.90/0.55/1.66	0.072/0.005/0.046	0.87/0.21/1.32
OH+H$_2$O$_2$	0.015/0.008/0.027	0.53/0.79/1.34	0.016/0.008/0.029	0.50/0.73/1.34	0.040/0.010/0.043	0.48/0.42/1.23
OH+ETH/OPEN	0.007/0.002/0.004	0.25/0.20/0.20	0.008/0.002/0.005	0.25/0.18/0.23	0.036/0.009/0.011	0.44/0.38/0.31
OH+CH$_3$OOH/ROOH	0.010/0.011/0.014	0.35/1.08/0.70	0.011/0.012/0.014	0.34/1.10/0.64	0.022/0.020/0.022	0.27/0.85/0.63
OH+ISOP	0.019/0.004/0.002	0.67/0.39/0.10	0.020/0.004/0.003	0.62/0.37/0.14	0.017/0.007/0.003	0.21/0.30/0.09
OH+PAR	0.005/0.002/0.004	0.18/0.20/0.20	0.007/0.003/0.005	0.22/0.27/0.23	0.015/0.005/0.007	0.18/0.21/0.20
OH+ONIT /ISOPRD	0.028/0.005/0.016	0.99/0.49/0.80	0.030/0.005/0.018	0.93/0.46/0.83	0.077/0.013/0.025	0.93/0.55/0.72
OH+C$_2$H$_6$	0.002/0.001/0.002	0.07/0.10/0.10	0.003/0.001/0.002	0.09/0.09/0.09	0.008/0.002/0.004	0.10/0.08/0.11
OH+CH$_3$OH/ANOL/CRES	0.002/0.001/0.002	0.07/0.10/0.10	0.002/0.001/0.002	0.06/0.09/0.09	0.007/0.002/0.003	0.08/0.08/0.09
OH+HO$_2$	0.001/<0.001/0.004	0.04/0.05/0.20	0.002/<0.001/0.005	0.06/0.05/0.23	0.006/<0.001/0.008	0.07/0.02/0.23
OH+NO	0.105/0.036/0.039	3.70/3.54/1.94	0.066/0.030/--	2.05/2.75/--	--/--/--	--/--/--
Total	2.839/1.017/2.009	100/100/100	3.214/1.093/2.172	100/100/100	8.261/2.360/3.495	100/100/100

OLET: internal olefin carbons (C=C); OLEI: terminal olefin carbons (C=C); ROOH: higher organic peroxide; ETH: ethene; ISOP: isoprene; ALD2: acetaldehyde; MGLY: methylglyoxal; ANOE: acetone; XYL: xylene; TOL: toluene; HNO$_x$: HNO$_3$ + HNO$_4$; OPEN: aromatic fragments; PAR: paraffin carbon –C–; ONIT: organic nitrate; ISOPRD: lumped intermediate species; ANOL: ethanol; CRES: cresol and higher molar weight phenols.

*The reactions of HONO+hv, H_2O_2+hv and HNO_3+hv are reversible, “net” in the subscript means subtracting the corresponding reverse reactions.

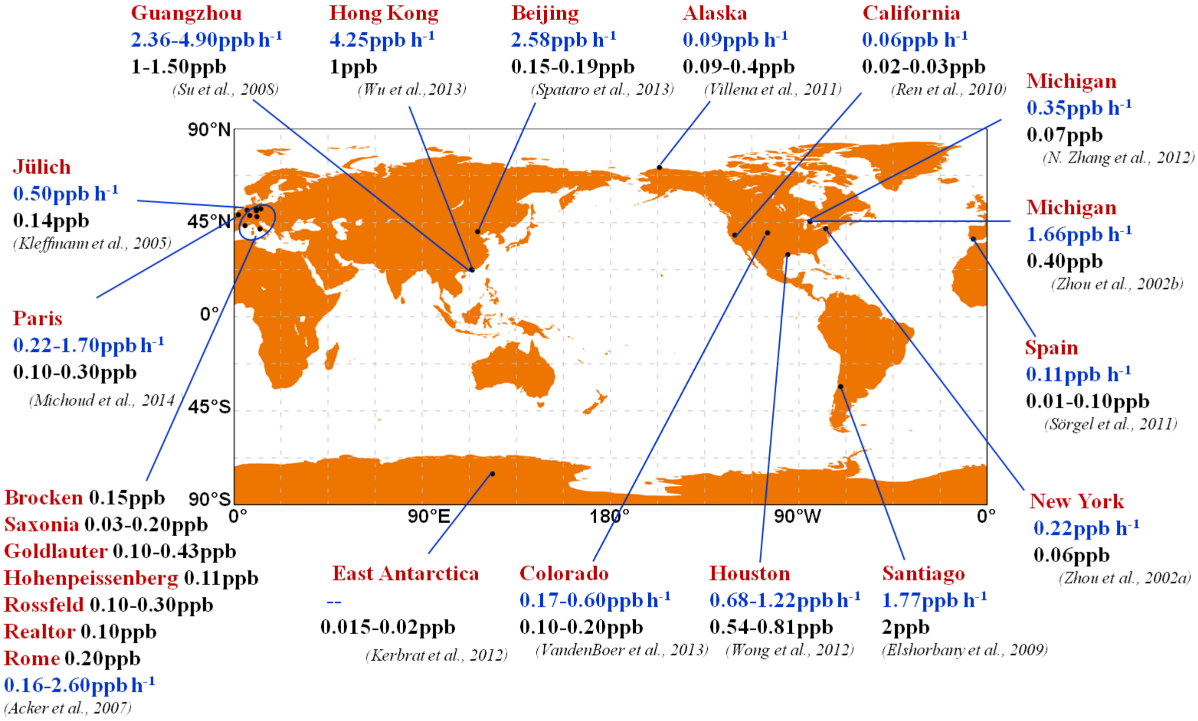

Fig. 1. Summary of observed HONO mixing ratios at noon (black font) and the calculated unknown daytime HONO source (blue font) from field studies.

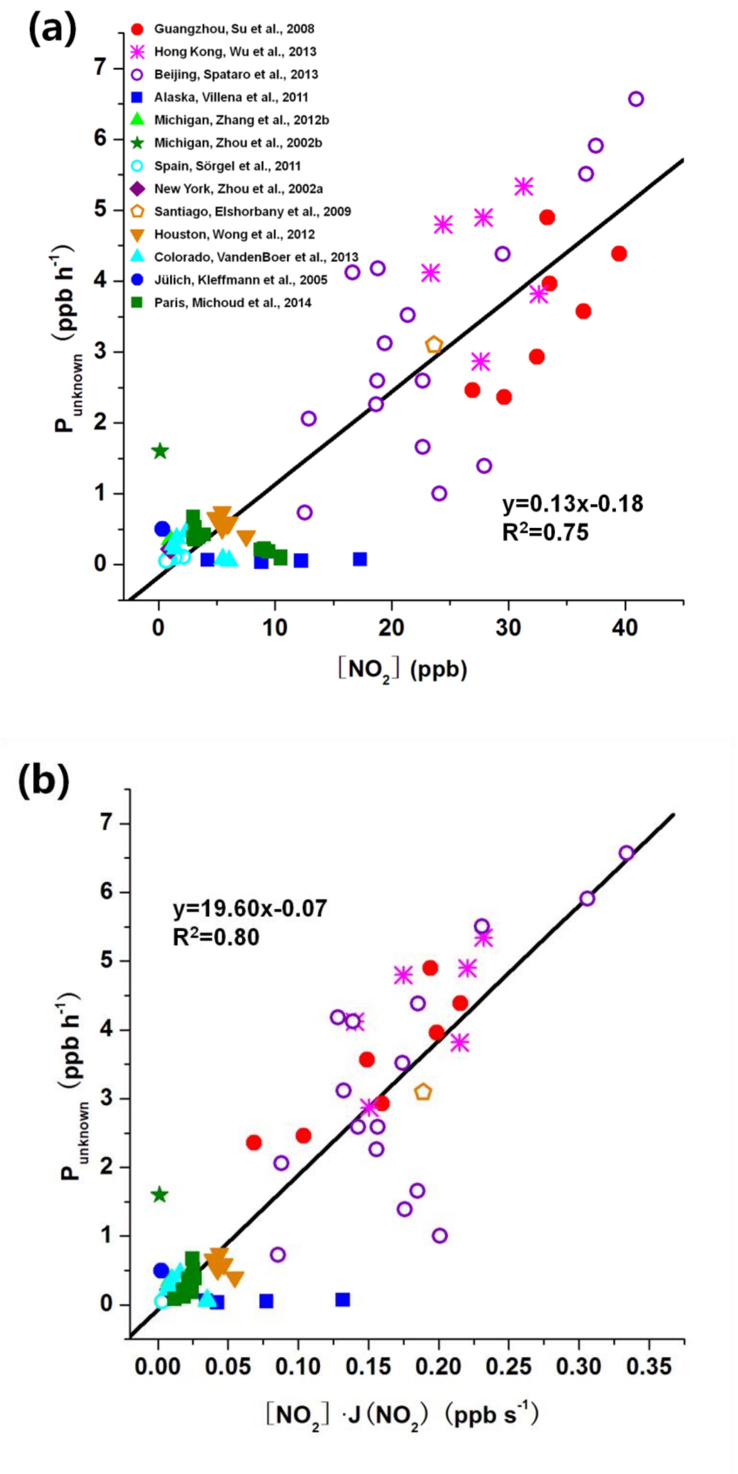

Fig. 2. Correlation of the unknown daytime HONO source ($P_{unknown}$) (ppb h^{-1}) with (a) [NO_2] (ppb) and (b) [NO_2] × J(NO_2) (ppb s^{-1}), based on the field experiment data shown in Fig. 1.

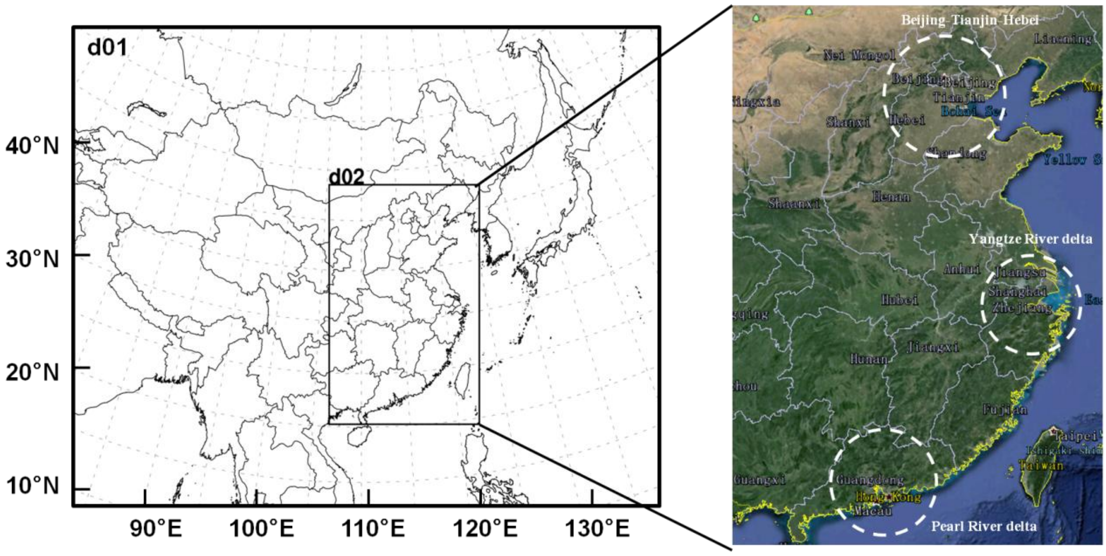

Fig. 3. Model domains used in this study. Domain 2 covers the Beijing–Tianjin–Hebei (BTH), Yangtze River delta (YRD), and Pearl River delta (PRD) regions.

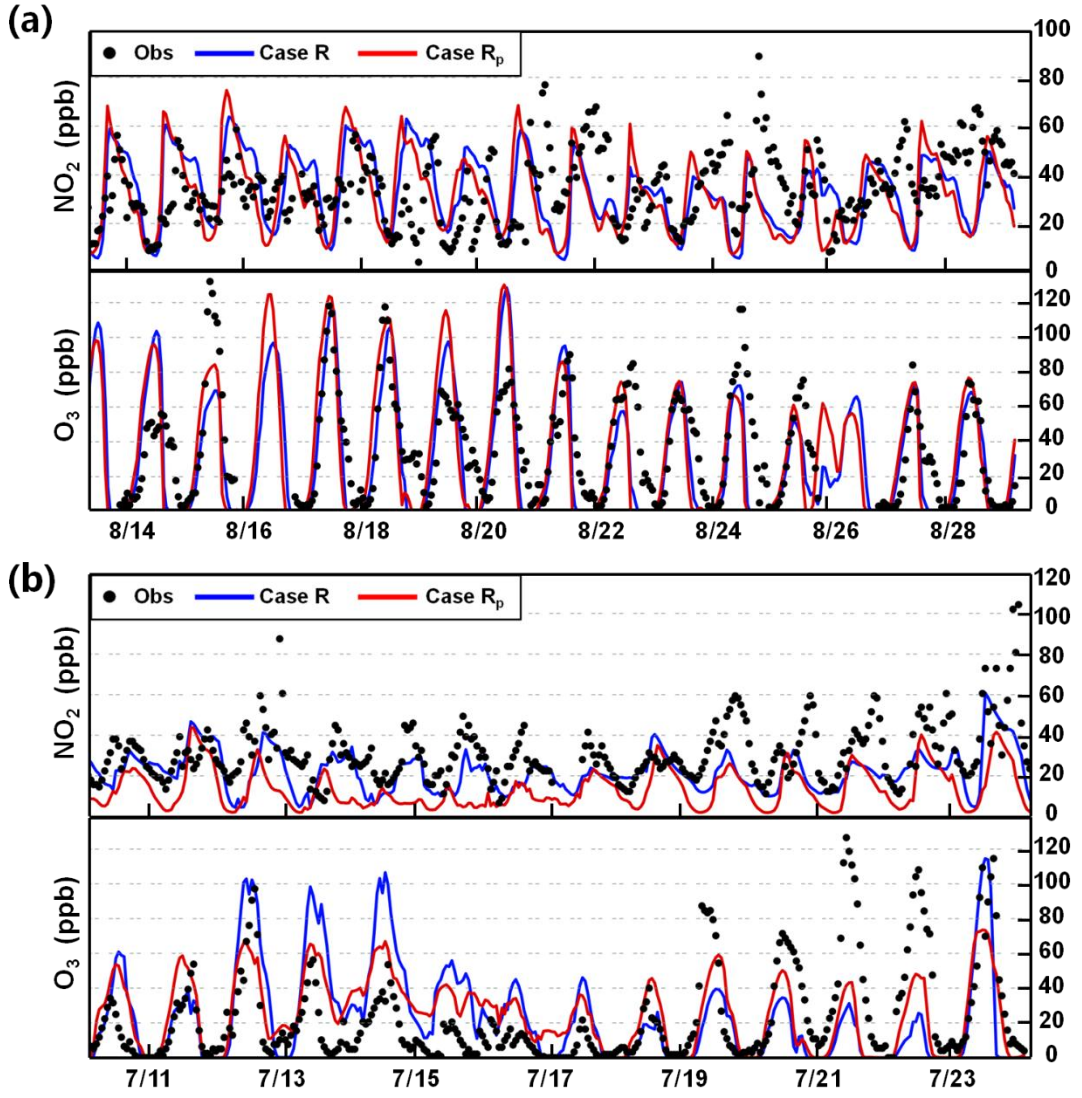

Fig. 4. Comparison of simulated and observed hourly-mean mixing ratios of NO_2 and O_3 in (a) Beijing on 14–28 August 2007 and (b) Guangzhou on 11–23 July 2006.

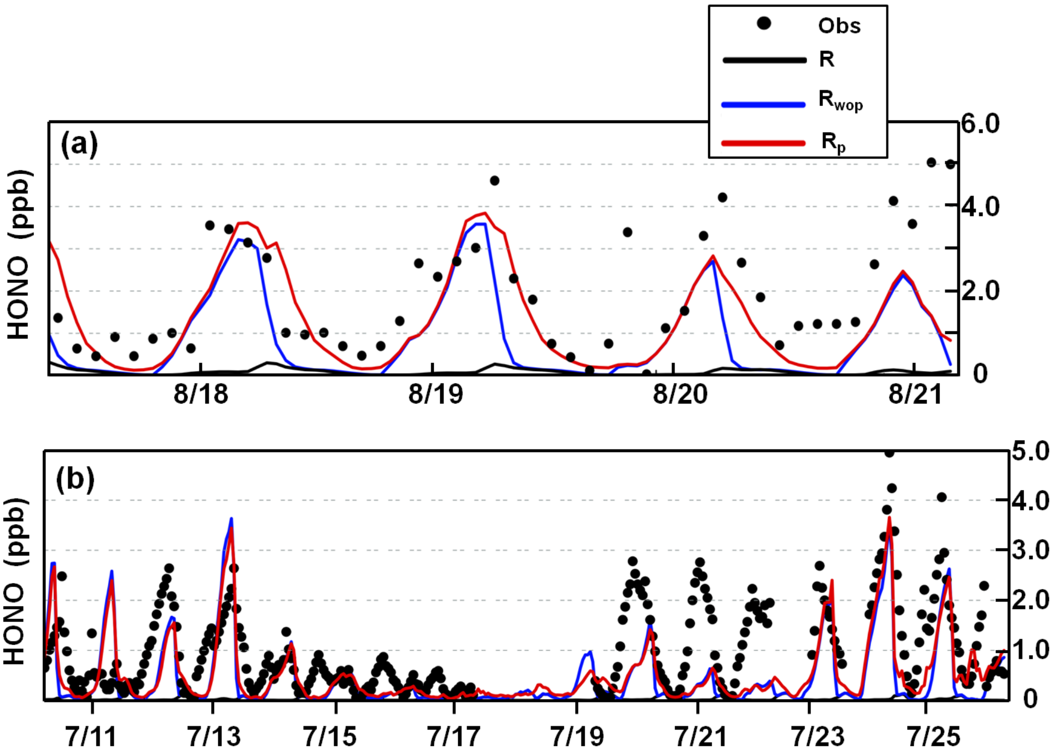

Fig. 5. Comparison of simulated and observed hourly-mean HONO mixing ratios at the Peking University site in (a) Beijing on 17–20 August 2007 (Spataro et al., 2013) and (b) the Backgarden site in Guangzhou on 11–25 July 2006 (X. Li et al., 2012).

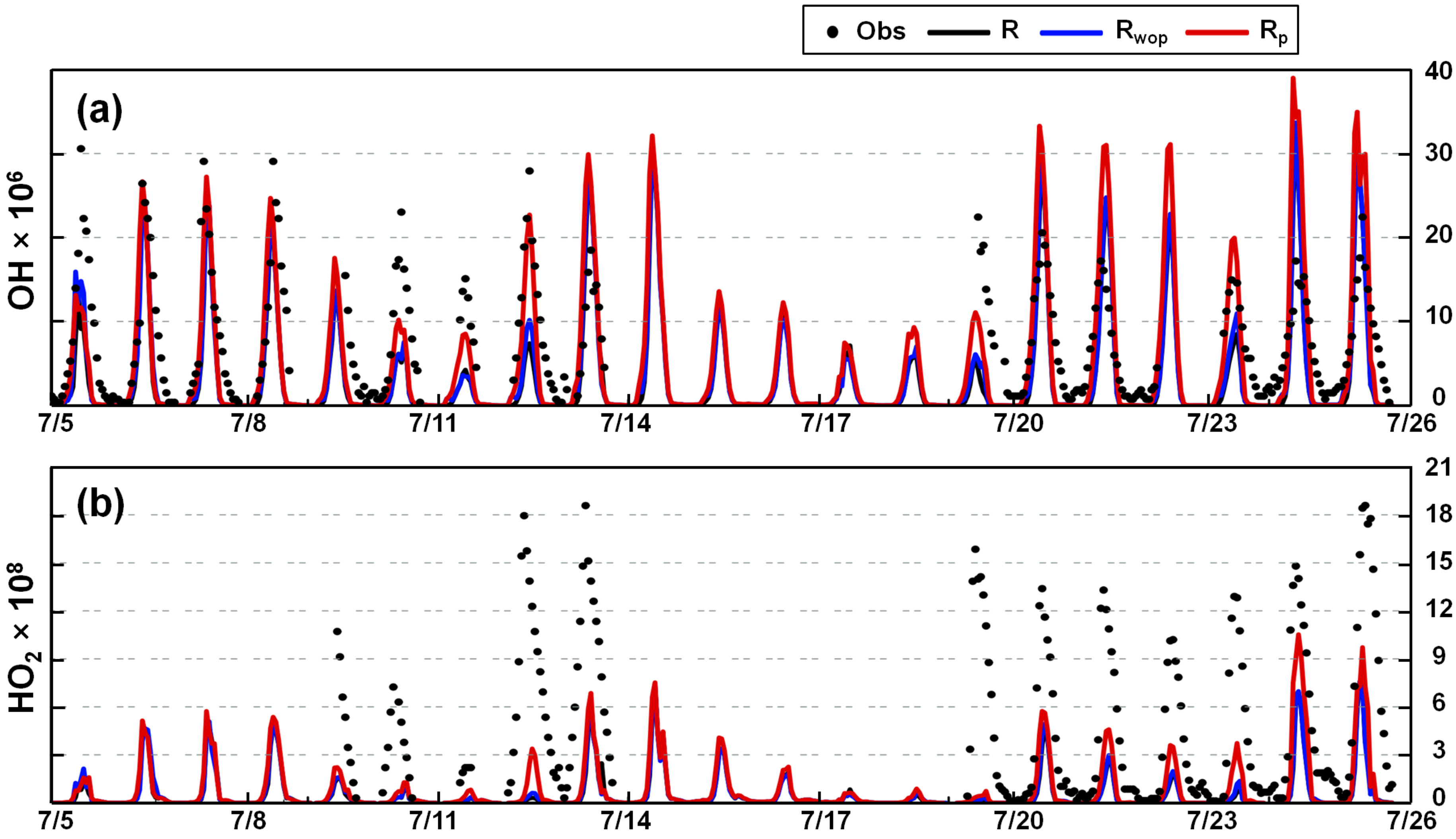

Fig. 6. Comparison of simulated and observed hourly-mean mixing ratios of OH and HO_2 at the Backgarden site in Guangzhou in July 2006 (Lu

et al., 2012).

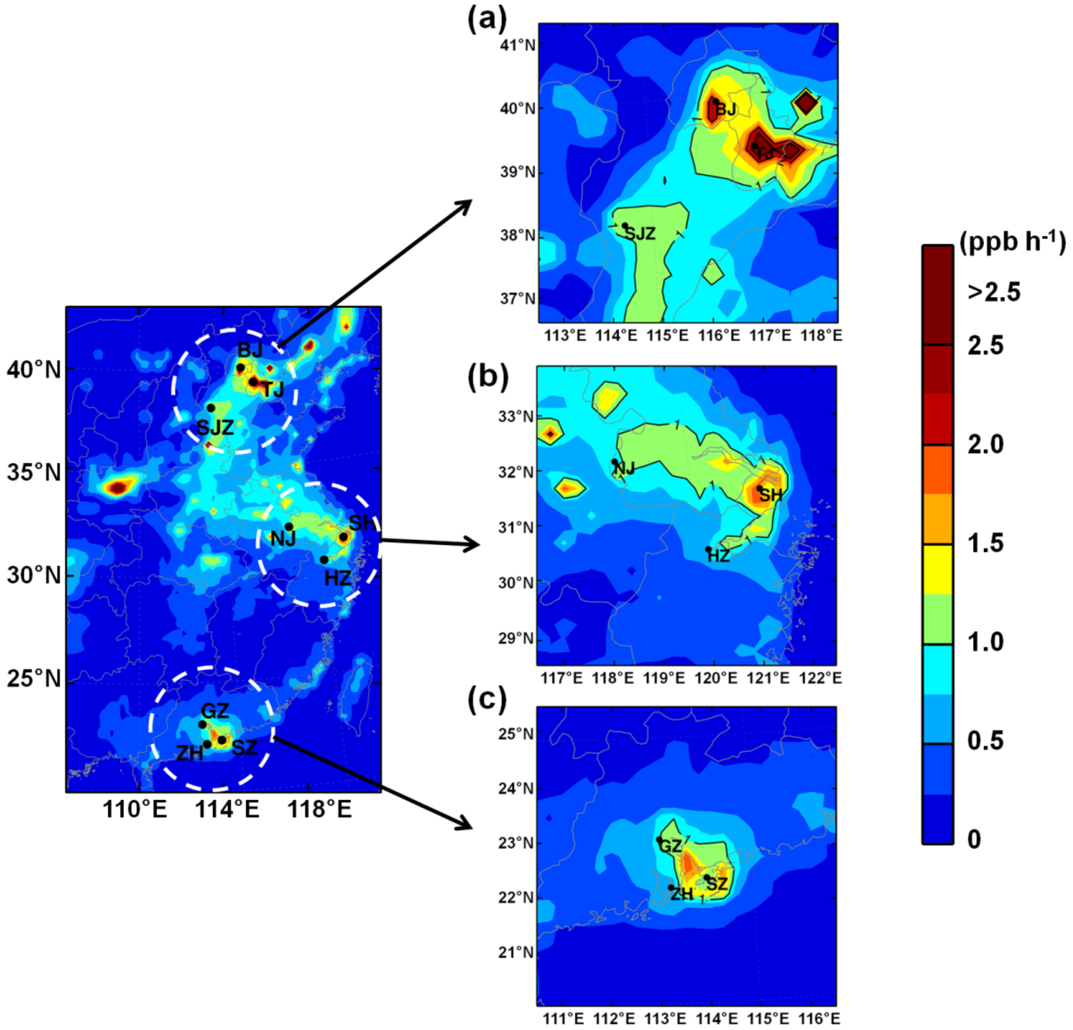

Fig. 7. Simulated unknown daytime HONO source (ppb h^{-1}) in the (a) BTH, (b) YRD, and (c) PRD regions in August 2007 (BJ, Beijing; TJ, Tianjin; SJZ, Shijiazhuang; SH, Shanghai; NJ, Nanjing; HZ, Hangzhou; GZ, Guangzhou; ZH, Zhuhai; SZ, Shenzhen).

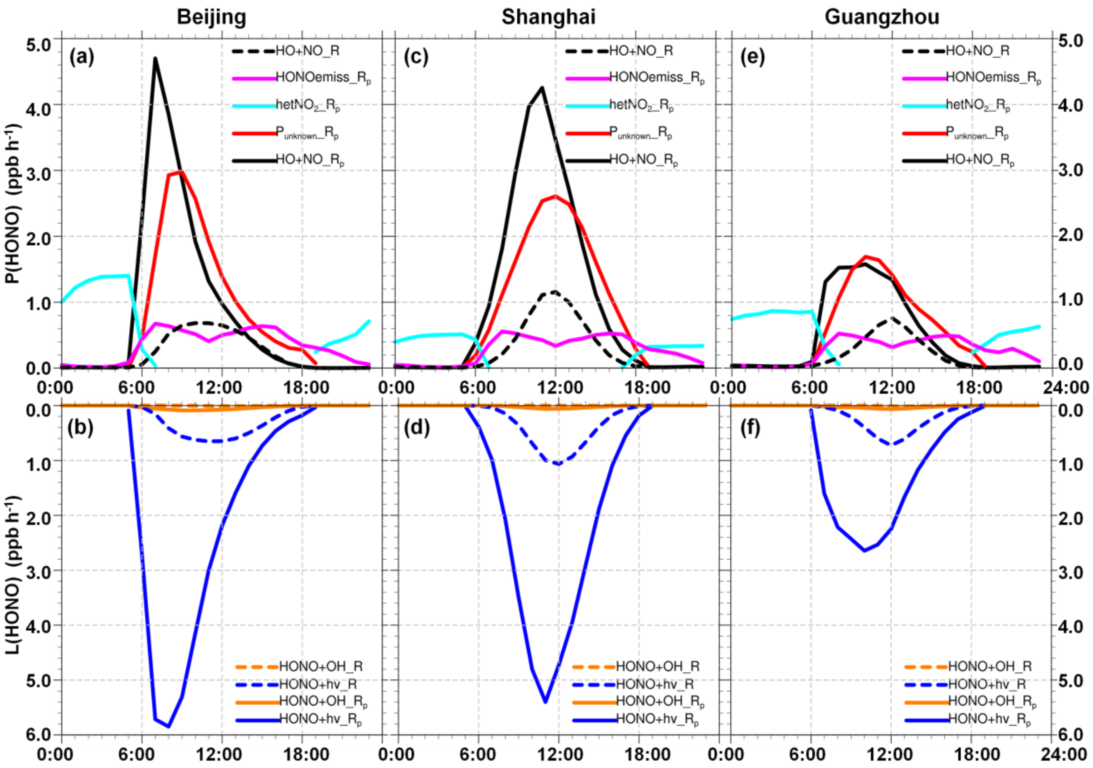

Fig. 8. Production [P(HONO)] and loss [L(HONO)] rates of HONO for cases R (dashed lines) and R_p (solid lines) in (a, b) Beijing, (c, d) Shanghai, and (e, f) Guangzhou in August 2007.

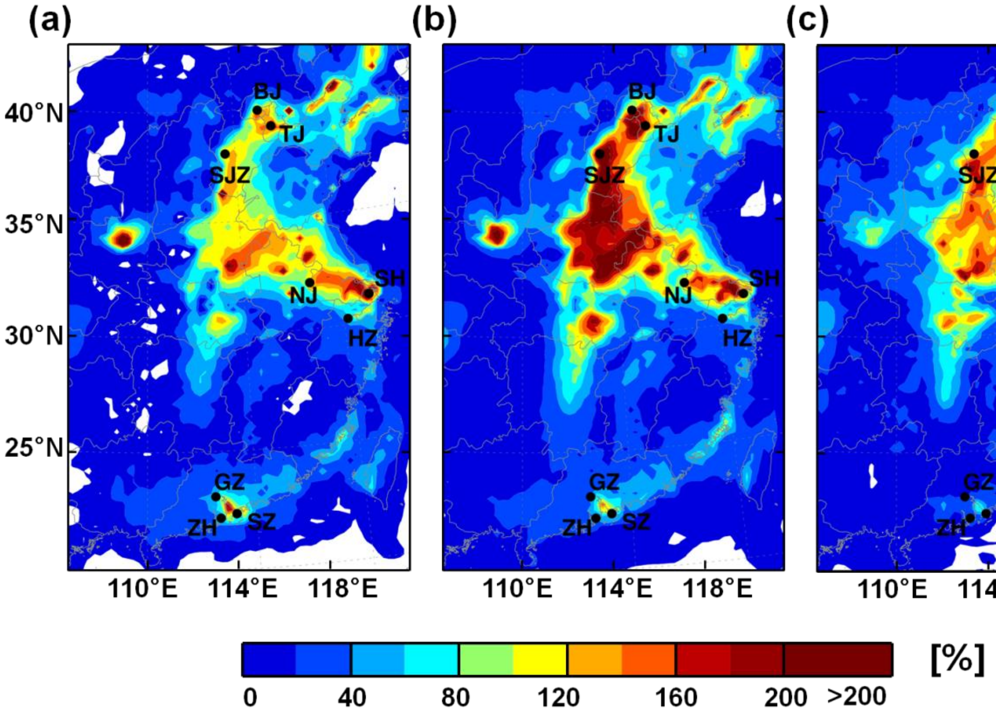

Fig. 9. Daytime (06:00–18:00 LST) percentage enhancements of (a) OH, (b) HO_2, and (c) RO_2 due to the unknown daytime HONO source (case R_p − case R_{wop}) in the coastal regions of China in August 2007.

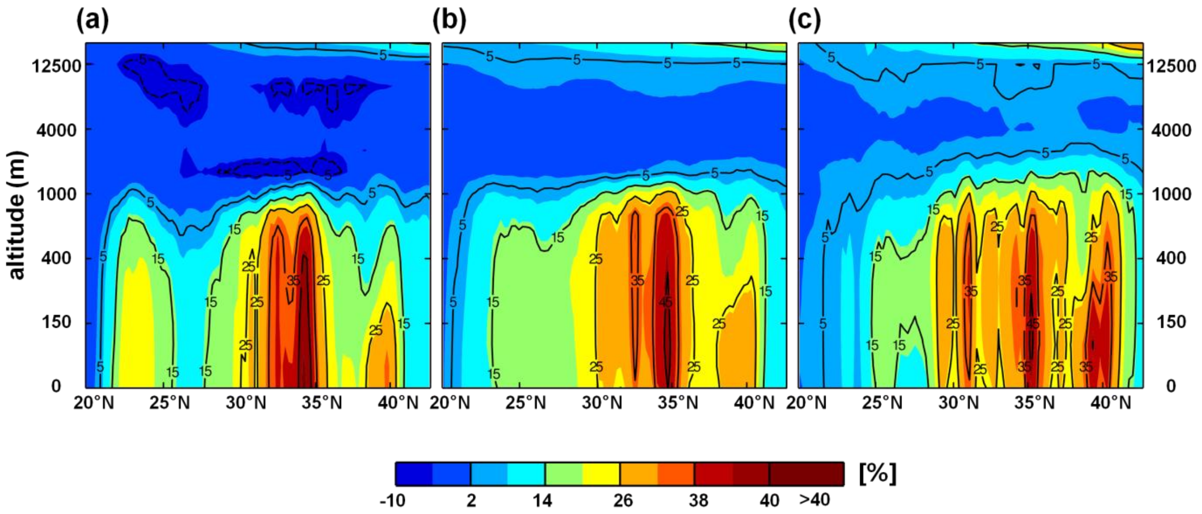

Fig. 10. Daytime (06:00–18:00 LST) meridional-mean percentage enhancements of (a) OH, (b) HO_2, and (c) RO_2 due to the unknown daytime HONO source (case R_p − case R_{wop}) in the coastal regions of China in August 2007.

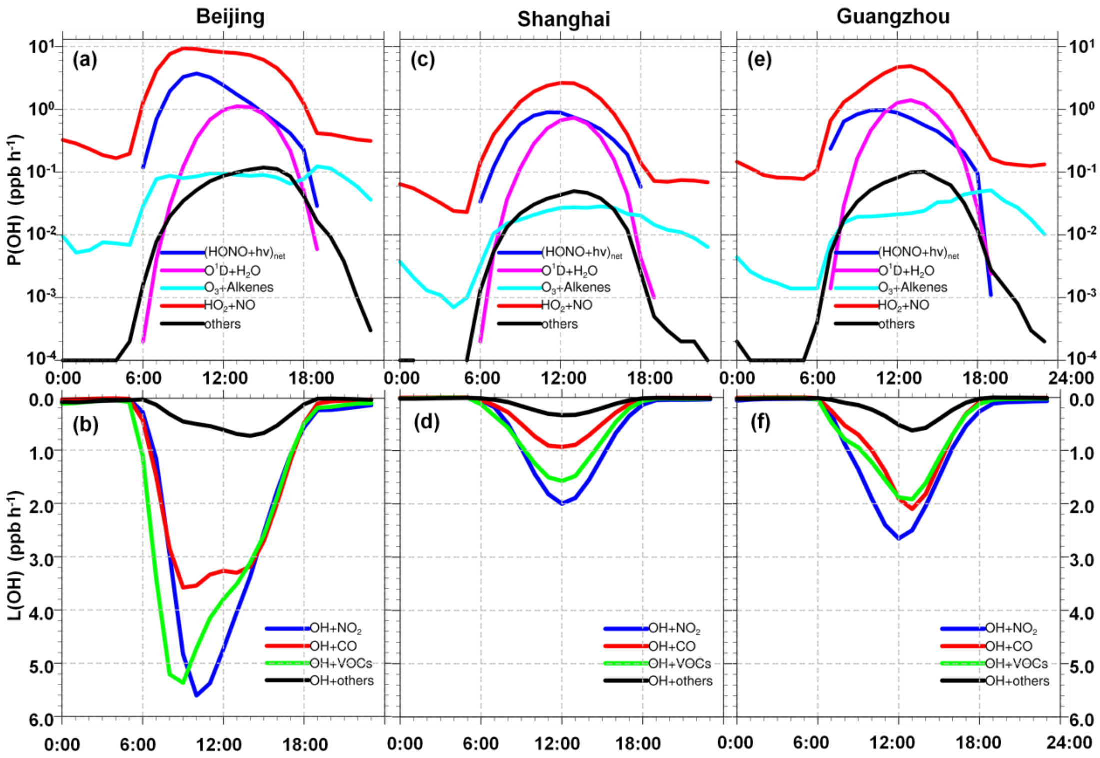

Fig. 11. Averaged production [P(OH)] and loss [L(OH)] rates of OH for case R_p in (a, b) Beijing, (c, d) Shanghai, and (e, f) Guangzhou in August 2007. $(HONO+hv)_{net}$ means the net OH production rate from HONO photolysis (subtracting OH + NO = HONO).

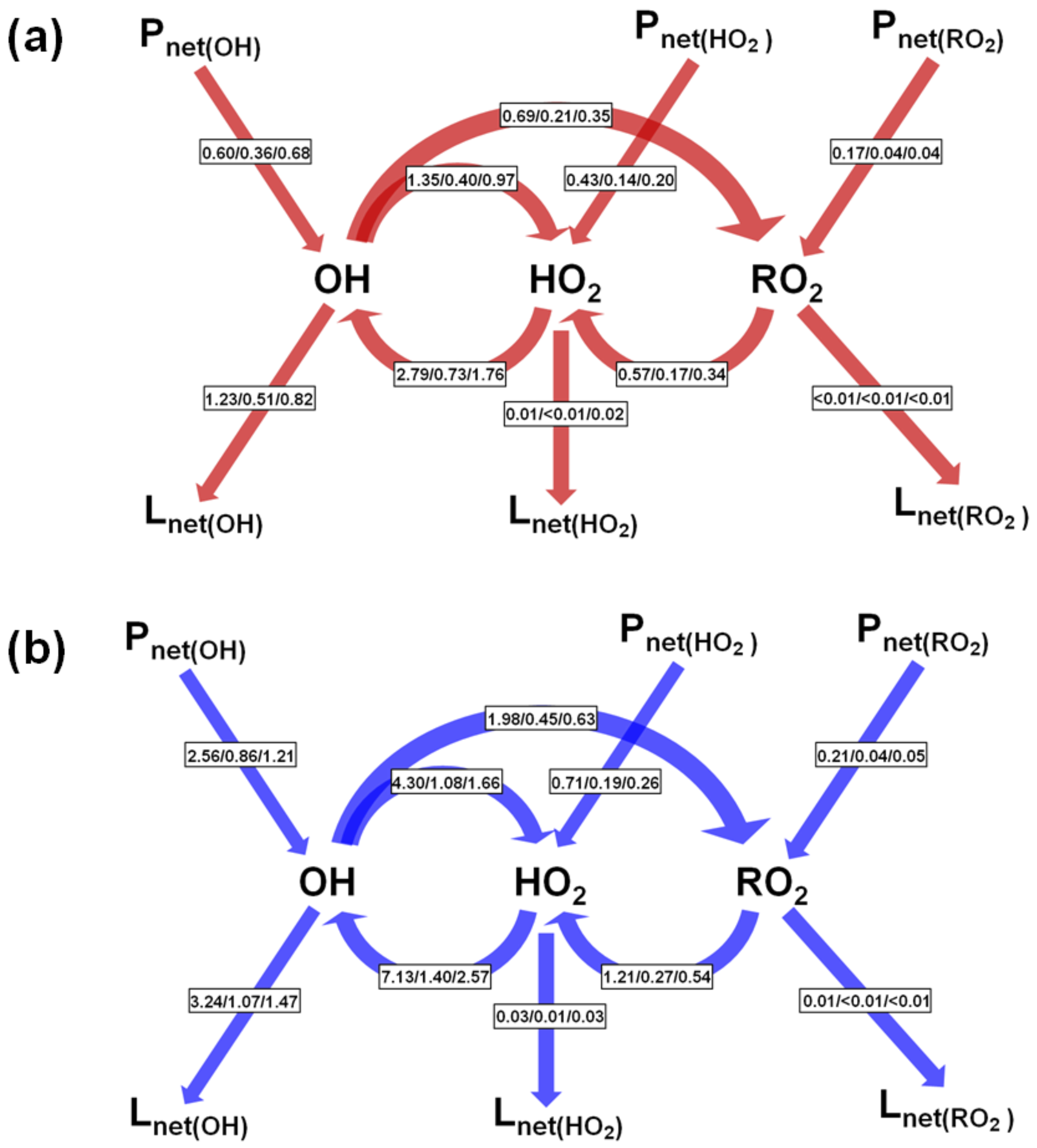

Fig. 12. Daytime (06:00–18:00 LST) average budgets of OH, HO_2 and RO_2 radicals (reaction rates, ppb h^{-1}) for cases (a) R and (b) R_p in Beijing/Shanghai/Guangzhou in August 2007.