

Nighttime observation and chemistry of HO_x in the Pearl River Delta and Beijing in summer 2006

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Abstract. Nighttime HO_x chemistry was investigated in two ground-based field campaigns (PRIDE-PRD2006 and CAREBEIJING2006) in summer 2006 in China by comparison of measured and modelled concentration data of OH and HO₂. The measurement sites were located in a rural environment in the Pearl River Delta (PRD) under urban influence and in a suburban area close to Beijing, respectively. In both locations, significant nighttime concentrations of radicals were observed under conditions with high total OH reactivities of about 40–50 s⁻¹ in PRD and 25 s⁻¹ near Beijing. For OH, the nocturnal concentrations were within the range of (0.5–3) × 10⁶ cm⁻³ implying a significant nighttime oxidation rate of pollutants in the order of several ppb per hour. The measured nighttime concentration of HO₂ was about (0.2–5) × 10⁸ cm⁻³ containing a significant, model-estimated contribution from RO₂ as an interference. A chemical box model based on an established chemical mechanism is capable to reproduce the measured nighttime values of the measured peroxy radicals and *k*_{OH}, but underestimates in both field campaigns the observed OH by about one order of magnitude. Sensitivity studies with the box model demonstrate that the OH discrepancy between measured and modelled nighttime OH can be resolved, if an additional RO_x production process (about 1 ppbh⁻¹) and additional recycling (RO₂ → HO₂ → OH) with an efficiency equivalent to 1 ppb NO is assumed. The additional recycling mechanism was also needed to reproduce the O-H observations at the same locations during daytime for conditions with NO mixing ratios below 1 ppb. This could be an indication that the same missing process operates at day and night. In principle, the required primary RO_x source can be explained by ozonolysis of terpenoids, which react

20 faster with ozone than with OH in the nighttime atmosphere. However, the amount of these highly
reactive biogenic VOC would require a strong local source, for which there is no direct evidence. A
more likely explanation for an additional RO_x source is the vertical downward transport of radical
reservoir species in the stable nocturnal boundary layer. Using a simplified 1-dimensional two-box
25 model, it can be shown that ground-based NO emissions could generate a large vertical gradient
causing a downward flux of PAN and MPAN. The downward transport and the following thermal
decomposition of these compounds can produce up to 0.3 ppbh⁻¹ radicals in the atmospheric layer
near the ground. Although this rate is not sufficient to explain the complete OH discrepancy, it
indicates the potentially important role of vertical transport in the lower nighttime atmosphere.

1 Introduction

30 The chemical removal of most atmospheric trace gases during daytime is dominated by reactions
with OH radicals, when they are efficiently generated by photodissociation of ozone, nitrous
acid and other gases. Under these conditions, OH concentrations are usually in the range of (1–
10) × 10⁶ cm⁻³ (Ehhalt, 1999; Monks et al., 2009; Lu and Zhang, 2010). During nighttime, it is
generally assumed that oxidation reactions with the nitrate radical (NO₃) and ozone are more im-
35 portant than reactions by OH (Platt et al., 1984; Platt et al., 1988; Mihelcic et al., 1993; Geyer
et al., 2003). In fact, measured OH concentrations in the night are often very small (less than a few
times 10⁵ cm⁻³) for rural conditions (Eisele et al., 1997; Holland et al., 1998, 2003; Schlosser et al.,
2009; Kanaya et al., 2012). In contrast, much larger nocturnal OH concentrations on the order of
1 × 10⁶ cm⁻³ were observed in forests (Faloona et al., 2001) and polluted urban areas in Nashville
40 (Martinez et al., 2003) and New York (Ren et al., 2003), which could not be explained by chemical
models and have raised questions about the reliability of nighttime OH measurements (Mao et al.,
2010). Unexplained high OH concentrations have also been observed at daytime under condition-
s with high VOC reactivities and low NO concentrations (Tan et al., 2001; Lelieveld et al., 2008;
Hofzumahaus et al., 2009; Lu et al., 2013, 2012; Whalley et al., 2011). As a possible explanation, it
45 has been supposed that OH radicals are efficiently recycled from intermediate products in the oxida-
tion of volatile organic compounds, such as isoprene, without involvement of NO, which is otherwise
the main agent to regenerate OH by reaction with organic peroxy (RO₂) and hydroperoxy (HO₂)
radicals. In case of the isoprene oxidation, it has been shown that there are indeed unimolecular
reactions of RO₂ that reproduce efficiently HO_x (OH and HO₂), but these processes can explain
50 only part of the high OH daytime concentrations (Peeters and Müller, 2010; Crouse et al., 2011;
Fuchs et al., 2013). There remains the question, whether the unexplained high OH concentrations at
day- and nighttime have common reasons. An opportunity to investigate this question is offered by
OH measurements collected during the PRIDE-PRD2006 and CAREBEIJING2006 field campaigns
that took place in summer 2006 in China. In these two field campaigns, the chemistry of the lower

55 troposphere was studied by measurements of OH and HO₂, k_{OH} (OH reactivity = inverse chemical
OH lifetime), trace gases, aerosols, photolysis frequencies and meteorological parameters in order
to better understand the processes controlling air pollution in the Pearl River Delta (PRD) and in the
region around the capital city of Beijing. In these regions, surprisingly high OH concentrations were
observed both at day and night. In previous publications (Hofzumahaus et al., 2009; Lu et al., 2012,
60 2013), the daytime observations of OH were analyzed and compared with model simulations. In the
present work, the focus lies on the nighttime observations. In the following, the nighttime data for
HO_x and k_{OH} will be presented and compared with box model calculations. Discrepancies of the
measured and modelled OH concentrations will be discussed and the potential impact of chemistry
as well as vertical exchange processes on the abundance of OH in the nocturnal boundary layer will
65 be presented.

2 Methodology

2.1 Experimental

The campaign PRIDE-PRD2006 was performed in the Pearl River Delta in July 2006, and CARE-
BEIJING2006 took place in Beijing from mid August to early September 2006. For each campaign,
70 one measurement supersite was set up. In PRD, the measurement site Backgarden (BG) was located
in a rural environment influenced by pollution from the megacity of Guangzhou, while the other site
was in the suburban area Yufa (YF) in the vicinity of Beijing. Almost identical instrumentation was
used at the two sites to characterize the processes of trace gas removal, photochemical ozone pro-
duction and aerosol formation (Hofzumahaus et al., 2009; Lu et al., 2013, 2012, 2010a,b; Li et al.,
75 2012; Lou et al., 2010; Xiao et al., 2009). Trace gases (HO_x, O₃, NO_x, CO, C₂–C₁₂ hydrocarbon-
s, HONO), photolysis frequencies, and meteorological parameters (temperature, pressure, relative
humidity) were measured.

OH and HO₂ concentrations were measured in both campaigns by laser induced fluorescence
(LIF) spectroscopy (Lu et al., 2012, 2013). With this technique, ambient air is sampled through
80 an orifice by gas expansion into a low-pressure (3.5 hPa) volume. OH radicals are then detected by
resonance fluorescence following electronic excitation by 308 nm UV laser radiation. Ambient HO₂
radicals are first converted into OH by reaction with added NO and then detected as OH. The two
fluorescence cells to measure the ambient OH and HO₂* radicals were physically separated and each
connected by a 3 m long vacuum line to a low-pressure pump. The accuracy of the OH and HO₂
85 measurements is estimated to be 20 % (1 σ). The accuracy is determined by the uncertainty of the
calibrations that were performed with a photochemical radical source based on the VUV (185 nm)
photolysis of water vapor in synthetic air (Holland et al., 2003). The measurement instrument has
a known interference from ambient ozone in humid air, which produces an OH signal with a strength
equivalent to an OH concentration of $(6 \pm 2) \times 10^3 \text{ cm}^{-3}$ per ppb of ozone. All OH measurements

90 presented here were corrected for the ozone interference, which had nighttime values of about $4 \times 10^4 - 2 \times 10^5 \text{ cm}^{-3}$. The limit-of-detection (1σ) of the corrected OH measurements was in the range of $(0.5-1) \times 10^6 \text{ cm}^{-3}$ at a time resolution of 5 min. The variability of the detection limit was mainly caused by variations of the 308 nm laser power (10–60 mW).

As shown by Fuchs et al. (2011), the detection of HO_2 has an interference caused by specific RO_2 radicals. When ambient HO_2 is converted in the instrument into OH by reaction with NO, a fraction of ambient RO_2 is converted first to HO_2 , followed by HO_2 to OH conversion. The magnitude of the interference depends on the specific RO_2 radical. As a result, the HO_2 measurement yields a concentration which is denoted $[\text{HO}_2^*]$,

$$[\text{HO}_2^*] = [\text{HO}_2] + \sum \alpha_i \times [\text{RO}_{2i}]. \quad (1)$$

Here, α_i denotes the detection sensitivity of specific RO_{2i} radicals relative to HO_2 . For the instru-
95 ment configuration used in PRD and Beijing, the values were relatively small for simple alkanes (e.g., 4 % for methyl peroxy radicals) and ranged between 70–90 % for RO_2 from alkenes and aromatics (Fuchs et al., 2011; Lu et al., 2012). At night, additional other organic peroxy radicals with a different chemical behaviour can be formed, if unsaturated VOCs react with NO_3 . In this case, NO_3 (rather than OH) is added to a carbon double-bond followed by addition of molecular oxy-
100 gen. For the resulting nitrate-peroxy radicals, we have estimated α_i values for the conditions in the HO_2 detection cell by means of model calculations based on the Master Chemical Mechanism (MCMv3.2; <http://mcm.leeds.ac.uk/MCM/>). Relative detection sensitivities of the NO_3 -initiated organic peroxy radicals are found to be generally small. For internal alkenes, α_i is about 0.3 % and for terminal alkenes, the value is about 1.9 %. Since the internal alkenes react almost one hundred times
105 faster with NO_3 than terminal alkenes and the nighttime concentrations of internal alkenes were several times smaller than those of terminal alkenes (Table 1), the HO_2 interference from NO_3 initiated RO_2 can be considered to be negligible in this study. The small HO_2 interference introduced by NO_3 -initiated RO_2 can be understood, since the corresponding alkoxy radicals from the $\text{RO}_2 + \text{NO}$ reaction mainly decompose to OVOCs and NO_2 as products, instead of forming HO_2 and RONO_2 .
110 The measured HO_2 concentrations in this study are reported as HO_2^* , since speciated RO_2 measurements were not available for their correction. The limit-of-detection (1σ) of the HO_2 measurements was in the range of $(1-3) \times 10^6 \text{ cm}^{-3}$ at a time resolution of 5 min. Note that the stated accuracy of 20 % (1σ) does not consider the bias by the uncorrected RO_2 contribution.

In both campaigns, total OH reactivity (k_{OH}) of ambient air was measured by a combination of
115 laser flash photolysis (LP) and LIF technique (Lou et al., 2010). Artificially high OH concentrations ($\sim 5 \times 10^9 \text{ cm}^{-3}$) were generated by laser flash photolysis of ozone in a flow of sampled ambient air. The laser wavelength was 266 nm and the laser pulse duration was 10 ns. The following OH decay was observed in realtime by the LIF technique. OH reactivities were determined as reciprocal OH lifetimes from the pseudo first-order decays of OH. The accuracy of the k_{OH} measurements was
120 7 % plus 0.3 s^{-1} , and the 1σ precision was 4–10 % during the campaigns.

NO_x, CO and O₃ were measured by commercial instruments, i.e., a Thermo Electron Model 42CTL (photolytic converter for NO₂ detection), Model 48C, and Model 49C, respectively (Takegawa et al., 2006). The measurement precisions were 50 ppt (1 min) for NO, 170 ppt (1 min) for NO₂, 1 % for CO, and 0.3 ppb (1 min) for O₃. At the BG site, a few gas canister samples were taken during
125 the campaign and analyzed by gas chromatography (GC) in order to determine concentrations of C₂ species, while C₃–C₁₂ NMHCs were measured and identified by an automated gas-chromatography flame ionization detector (GC-FID) system (Wang et al., 2008). At the YF site, C₂–C₁₂ NMHCs were measured and identified by a GC-FID/PID (photoionization detector) instrument (Xie et al., 2008). Accuracy and detection limits of the GC measurements were 10 % and 1–90 ppt, respectively.
130 ly. HONO was determined by a modified commercial instrument based on long-path liquid absorption photometry (LOPAP) (Li et al., 2012) with a detection limit of 7 ppt and an accuracy of 10 %. Surface meteorological parameters were obtained by a Vaisala Weather Transmitter WXT520 and a R.M. Young meteorological station for BG and YF, respectively. Additionally, a 3-D-ultrasonic anemometer was deployed at both measurement sites to determine the local wind and local turbulence.
135 In PRD, PAN measurements were performed with an on-line gas chromatography equipped with an electron capture detector (GC-ECD) technique (Wang et al., 2010). The accuracy of the PAN measurement is estimated to be 25% by convoluting the errors of the photochemical PAN standard, variability of the calibration results, inlet and column thermal losses, etc.

A summary of the general conditions during nighttime is given in Table 1, which presents averaged values of measurements before (20:00–24:00 CNST) and after (00:00–04:00 CNST) midnight
140 (CNST = Chinese Standard Time = UTC + 8h) for the days, when HO_x and NO_x measurements are available. The daytime conditions have been presented in Lu et al. (2012, 2013).

2.2 Chemical model

A zero-dimensional chemical box model based on the Regional Atmospheric Chemical Mechanism
145 (Stockwell et al., 1997) upgraded with the isoprene degradation scheme by Geiger et al. (2003) and Karl et al. (2006), RACM-MIM-GK, has been applied to simulate the diurnal cycles of OH, HO₂, HO₂^{*}, and RO₂, and *k*_{OH} for PRIDE-PRD2006 (Lu et al., 2012) and CAREBEIJING2006 (Lu et al., 2013). In the present work, we analyze the nighttime data. The model runs are constrained by the measured time-series of O₃, HONO, NO, NO₂, CO, VOCs, photolysis frequencies, water vapor,
150 ambient temperature, pressure for each individual night, and assumed deposition loss of model-generated species (mimicked by a lifetime of 24 h). Beside the base model runs (denoted M0), additional sensitivity runs are performed in this work to test modified chemical mechanisms for nighttime conditions (see below).

3 Results

155 3.1 Nighttime observations

During the PRIDE-PRD2006 and CAREBEIJING2006 campaigns, complete sets of nighttime measurements of HO_x and other trace gases were obtained on seven (Jul 9-10, 12-13, 19-20, 20-21, 21-22, 23-24, 24-25) and nine (Aug 18-19, 19-20, 20-21, 21-22, 22-23, 23-24, 26-27, 29-30, 30-31) nights, respectively. The nocturnal variations of HO_x, *k*_{OH}, NO, O₃, NO₂, CO and isoprene are displayed in Figs. 1 and 2. Here, nighttime is defined to be the period when the solar zenith angle was larger than 90°. In PRD, the sunrise and sunset times were 05:57 and 19:12 CNST, respectively. In Beijing, the sunrise and sunset was at 05:42 and 18:52 CNST.

Significant amounts of nocturnal OH and HO₂^{*} were observed in both campaigns well above the detection limits of the instrument for both radical species. The half-hourly averaged OH concentrations at night were on the order of $(0.5-3) \times 10^6 \text{ cm}^{-3}$, which are high values comparable to daytime observations in polluted cities (Emmerson et al., 2005) and forested areas (Whalley et al., 2011). The concentrations of HO₂^{*} were two orders of magnitude larger than those of OH, with half-hourly averaged concentrations within the range of $(0.2-5) \times 10^8 \text{ cm}^{-3}$. As a general feature, the observed OH and HO₂^{*} concentrations declined gradually from high values at sunset to low values close to the limit-of-detection shortly before sunrise. The nighttime trend of HO_x is correlated with decreasing O₃, which was titrated by nocturnal NO emissions and became depleted in the late night between 03:00 and 06:00 CNST. The NO mixing ratio was generally small in the first half of the night and started – due to ongoing anthropogenic emissions – to increase rapidly by more than three orders of magnitude after midnight when ozone became depleted. The reaction of NO with HO₂^{*} in the early morning was probably the reason for the vanishingly low HO₂^{*} concentrations at the end of the night. Diesel powered trucks and other combustion activities were the likely reason for the NO emissions in PRD (Lu et al., 2012; Garland et al., 2008). At the Yufa site, nighttime emissions came either from Beijing city, the nearby highway about 1 km to the east of the measurement site, or from highly industrialized regions outside Beijing (Lu et al., 2013; Garland et al., 2009; Matsui et al., 2009). The traces of CO and isoprene showed big differences from night to night. The variabilities of the two compounds indicate the varying influence of biogenic and anthropogenic emissions sources. We analyzed the correlations between observed OH and HO₂^{*} radicals with the CO and isoprene concentrations. We found that the corresponding correlation coefficients (*r*²) are small (see Table 2) which do not provide a useful hint to the chemical reason of the significant high nighttime HO_x concentrations. Despite the strong variability of individual trace gases, nocturnal *k*_{OH} was relatively constant and maintained high values between 40–50 s⁻¹ in PRD and 25 s⁻¹ in Yufa.

3.2 Model and measurement intercomparisons

A box model was used to calculate concentrations of OH, HO₂, HO₂^{*} and total OH reactivities at the two measurement sites. Figure 3 compares mean nighttime profiles of the model results and observations. The averaged modelled OH concentrations lie within the range of $(1-2) \times 10^5 \text{ cm}^{-3}$ during the whole night and are significantly smaller than the observed values. Shortly after sunset, the measurement-to-model ratio at PRD is about a factor of 10 and decreases to about 4 at the end of the night. In Yufa, the corresponding ratio changed from 20 after sunset to 2 before sunrise. For comparison, model results were also calculated based on the chemically more explicit Master Chemical Mechanism (MCMv3.2). The good agreement of the OH results from RACM-MIM-GK (M0) and MCMv3.2 demonstrates that the model deviations from the measurements are not caused by VOC lumping in the base mechanism.

In case of HO₂^{*}, the models (RACM-MIM-GK and MCM) reproduce well the observed magnitude of concentrations and their nocturnal variabilities, especially for the PRIDE-PRD2006 campaign. HO₂^{*} contains a substantial RO₂ contribution, which is seen as the difference of the modelled HO₂^{*} and HO₂ curves in Fig. 3. The modelled nighttime HO₂^{*}-to-HO₂ ratio has values within the range of 1.6–4 at the PRD site, and values of 1.4–2 at Yufa. The ratios are largest after sunset when NO had low mixing ratios and decrease after midnight when NO rises and thereby influences both the amount and speciation of the interfering RO₂.

The magnitude of the measured k_{OH} is reproduced well by both model mechanisms before midnight at PRD and for the whole night at Yufa (Fig. 3). For both campaigns, about half of the modelled reactivity is contributed by measured trace gases (CO, NO_x, non-oxygenated VOCs) and half by model-generated oxidation products (mainly HCHO and other OVOCs). The averaged concentration level of HCHO was 10 – 12 ppb for PRD and 9 – 11 ppb for Beijing without significant variations. Though the assumed deposition lifetime has a significant influence on the modelled HCHO and OVOC concentrations, it has a relatively small impact on the simulated results of OH, HO₂^{*} and OH reactivity, as already discussed in detail by Lou et al. (2010); Lu et al. (2012, 2013). After midnight, the OH reactivity in PRD was about 30 % larger than calculated by the model, pointing to unmeasured reactants that were likely caused by anthropogenic emissions or to oxidation products underestimated by the model. The largest model-measurement discrepancies of k_{OH} appeared in the nights of 23–24 and 24–25 July (Lou et al., 2010), probably caused by smoldering biomass fires as indicated by the analysis of measured aerosols (Garland et al., 2008). More than 70 % of the total OH reactivity at both measurement sites was caused by VOCs (Lou et al., 2010; Lu et al., 2012, 2013). It should be noted that the VOC speciation at both sites differed considerably between day and night. While isoprene had the largest reactivity among the measured hydrocarbons at daytime (70 % at PRD; 32 % at Yufa), its contribution was small at night (7–16 % at PRD; 3–7 % at Yufa). Instead, simple alkenes (e.g., propene, butenes) and aromatic compounds (e.g., toluene, xylenes) dominated the reactivities of measured VOCs at night at both measurement sites.

Nitrate radicals that are being formed by reaction of NO_2 and O_3 can be an important oxidant at night when their photolysis is negligibly small. For both campaigns, modelled nighttime concentrations of NO_3 are predicted to be largest (5–10 ppt) in the first half of the night. After midnight, when the mixing ratio of NO starts to rise, a decrease of NO_3 is predicted as a result of its fast reaction with NO (Fig. 3). Of the averaged nighttime profiles, the modeled NO_3 looks to be significant for periods in which the NO is large (e.g., >10 ppbv after midnight). This is a consequence of averaging some nights with lower NO and non-zero NO_3 together with others that have higher NO and zero NO_3 .

The total amount of modelled nighttime peroxy radicals ($\text{RO}_2 + \text{HO}_2$) and their speciation is displayed in Fig. 4a, c. The total concentration is largest before midnight when NO was small, and decreases after midnight due to the reaction of the peroxy radicals with increasing NO . Unlike at daytime (Fig. 4b, d), when HO_2 , methyl peroxy (MO_2) and isoprene peroxy (ISOP) radicals were the dominating species, peroxy radicals at night are predicted to be mostly β -nitrate alkylperoxy radicals (OLNN and OLND) resulting from addition reactions of NO_3 to alkenes. In the RACM mechanism, OLNN denotes peroxy radicals which upon reaction with NO form HO_2 , organic nitrates and NO_2 , whereas OLND decompose upon reaction with NO and yield carbonyl compounds and NO_2 without formation of HO_2 .

3.3 Nighttime oxidation rates

The measured nocturnal OH concentrations in PRD and Yufa are unexpectedly large (see Sect. 3.2). In the presence of high OH reactivities as found in the night, they imply large OH turnover rates given by the product $k_{\text{OH}} \times [\text{OH}]$ (Fig. 5). On average, the OH turnover rates are in the order of 8.5 ppbh^{-1} and 3.8 ppbh^{-1} in PRD and Yufa, respectively, with equally large oxidation rates of the sum of reactive trace gases (e.g., VOC , CO , NO_2) reacting with OH . At daytime, oxidation rates reached maximum values of about 40 ppbh^{-1} and 25 ppbh^{-1} , respectively. As a result, nocturnal OH would be responsible for about a quarter of the total trace gas oxidation by OH integrated over 24 h for the air masses characterized at the measurement sites. It should be noted that the observed high nighttime OH may be confined to a shallow layer near the surface where the measurements took place (see section 4.4.2). Thus, the general relevance of nighttime compared to daytime oxidation by OH in the lower troposphere cannot be derived from our data.

The nocturnal VOCs oxidation rates by OH (6.8 ppbh^{-1} and 2.6 ppbh^{-1} in PRD and Yufa) are significantly larger than the estimated VOCs reaction rates with NO_3 which were calculated by the base model to be around 0.6 ppbh^{-1} and 0.3 ppbh^{-1} for PRD and Beijing, respectively (Fig. 5). They represent upper limits, since the model includes only homogeneous gas-phase reactions and neglects the possible heterogeneous loss of NO_3 as well as of the major reservoir species N_2O_5 (e.g. Brown et al., 2006). Additionally, the nighttime ozonolysis rates were calculated to be around 0.3 ppbh^{-1} and 0.1 ppbh^{-1} for PRD and Beijing, respectively, which are even smaller than for

260 NO₃. Clearly, the VOC oxidation by OH appears to dominate over the VOC degradation by NO₃ and O₃ (Fig. 5), in contrast to the general view that nighttime OH should play only a minor role (e.g., Geyer et al., 2003; Sadanaga et al., 2003; Monks et al., 2009; Finlayson-Pitts and Pitts, Jr., 2000).

4 Discussion

265 4.1 Unexpectedly large nighttime OH concentrations

The comparison of the measured and modelled OH concentrations over averaged nighttime profiles in Fig. 3 shows that the observed magnitude of the nocturnal OH is unexpectedly large. We also performed a correlation analysis between observed and modelled radical concentrations for each night. The squared correlation coefficients between observed and modeled OH radicals were lower
270 than 0.07 for each night in both campaigns. The slopes of the linear regression between modelled and observed OH radicals was between 0.1 % to 4 % for individual nights in PRD and between 0.1 % to 8 % in Beijing. These correlations agree well with the behavior of the averaged data of observation and modeling so that the following discussion will use the averaged nighttime profiles.

The discrepancy of up to an order of magnitude is significant since it is much larger than the
275 measurement and model errors. In the past, higher than expected nighttime OH concentrations were reported also in other studies (Table 3). The sites where the measured OH exceeded the model predicted concentrations were located in forests (Faloona et al., 2001) and urban areas (Martinez et al., 2003; Ren et al., 2003a,b; Shirley et al., 2006; Emmerson and Carslaw, 2009; Kanaya et al., 2007). The reported concentrations in these studies have similar nighttime values of $(0.5-1) \times 10^6 \text{ cm}^{-3}$,
280 but deviate by different factors (2-46) from the model predictions. The level of nighttime OH and the model underprediction in the present work fall into the range of the other studies. All studies have in common that the OH reactivity was high, with values larger than 10 s^{-1} (Lou et al., 2010, and references therein).

The model-measurement discrepancies may be due to deficiencies in the models. Thus, previous
285 studies discussed different possibilities for missing nighttime sources of OH. For example, ozonolysis of reactive biogenic hydrocarbons as a radical source (Faloona et al., 2001), vertical transport of radical precursors and their thermal decomposition (Geyer and Stutz, 2004), or enhanced OH regeneration from the reaction of peroxy radicals with reactants other than NO (Faloona et al., 2001; Martinez et al., 2003) were investigated. However, no conclusive explanation for the observed elevated
290 nighttime OH has been found. This has raised the question whether the unexplained high OH observations at night could be caused by measurement artefacts. For the Pennstate LIF instrument (used in Faloona et al., 2001; Martinez et al., 2003; Ren et al., 2003a,b; Shirley et al., 2006), extensive instrumental tests were performed ruling out a number of suspected potential interferences. For example, it was shown that spectral interferences from SO₂ and HCHO during the laser excitation

295 of OH at 308 nm and artificial production of OH in the instrument by laser photolysis of ozone or
HONO can be neglected (Ren et al., 2004). Recently, the Pennstate group reported a measurement
artefact in their instrument that they discovered during field measurements in a pine forest (Mao
et al., 2012). OH measurements using the traditional spectral modulation of the OH resonance flu-
orescence at 308 nm were compared to a new chemical modulation technique which uses C_3F_6 for
300 OH quenching in ambient air samples. About half of the measured OH at day and night in the forest
could be identified as an artefact that produced OH inside the instrument. The artefact increases
with temperature and is possibly the result of the decomposition of biogenic VOC reaction products,
such as Criegee biradicals from the ozonolysis of alkenes (Mao et al., 2012). Thus, it could have
been a significant contributor to previous nighttime OH measurements in high VOC environments.
305 Since other LIF instruments (including the one in this work) are also using spectral modulation of
the 308 nm OH fluorescence signal, they might also be affected by the artefact. The sensitivity to
the interference is expected to depend on the instrumental design which differs from instrument to
instrument, for example, in terms of the gas inlet, the gas-flow residence time in the instrument, the
geometry of the detection cell, or cell pressure (Mao et al., 2012). Therefore, it is a-priori not clear
310 whether other OH LIF instruments are significantly affected by the problem.

In other campaigns, the LIF technique used in this work has never shown such high nighttime
OH concentrations as reported here. Previous nighttime measurements showed concentrations well
below the detection limit of typically $(3-5) \times 10^5 \text{ cm}^{-3}$ at 1-2 min time resolution. When the data
were averaged over longer time spans, concentrations were found to be in the order of $1 \times 10^5 \text{ cm}^{-3}$
315 or smaller. For example, OH concentrations of $(3 \pm 6) \times 10^4 \text{ cm}^{-3}$ (1 h average) were reported for the
POPCORN campaign in a rural environment in North-East Germany (Holland et al., 1998). During
the BERLIOZ campaign, a mean nighttime concentration of $(4 \pm 1) \times 10^4 \text{ cm}^{-3}$ (campaign average)
was determined in a rural-urban transition region near the city of Berlin (Holland et al., 2003) in good
agreement with model predictions (Geyer et al., 2003). In the latter campaign, slightly higher OH
320 concentrations of $(1.8 \pm 0.8) \times 10^5 \text{ cm}^{-3}$ were observed in one night for which the model predicted
 $(4 \pm 0.7) \times 10^5 \text{ cm}^{-3}$ (Geyer et al., 2003).

The LIF technique used in the present work was tested in several OH intercomparisons with re-
spect to its calibration and possible interferences. The majority of data of the comparisons was
collected under daytime conditions. There was good agreement typically within 20 % with an in-
325 dependent OH reference instrument based on folded long-path differential optical absorption spec-
troscopy (DOAS, Forschungszentrum Jülich) in the POPCORN field campaign (Hofzumahaus et al.,
1998), as well as in the atmosphere simulation chamber SAPHIR in Jülich (Schlosser et al., 2007,
2009). The international comparison HOxComp 2006 offered the opportunity to compare our LIF
instrument for day- and nighttime conditions with a chemical ionization mass spectrometer (CIM-
330 S; German Weather Service) which uses a completely different OH detection principle. The field
measurements took place on the campus of Forschungszentrum Jülich which is located in a mixed

deciduous forest (Schlosser et al., 2009). The data showed an OH calibration difference of a factor of 1.4, which could be explained by the calibration uncertainties of LIF (20 %) and CIMS (38 %). Only a very small, insignificant offset of $(0.04 \pm 0.03) \times 10^6 \text{ cm}^{-3}$ was found in the linear regression of the two instruments. The CIMS technique discriminates between OH and Criegee radicals by chemical modulation and its OH data are therefore expected to be free from interferences by Criegee radicals. Thus, the small offset in the regression between LIF and CIMS indicates that the LIF measurements were likely not subject to an artefact as it is discussed by (Mao et al., 2012). More recently, new measurement comparisons were performed between LIF and DOAS (both Forschungszentrum Jülich) in SAPHIR under daytime conditions simulating the air composition encountered during PRIDE-PRD2006 and CAREBEIJING2006. For high VOC reactivities up to 30 s^{-1} and low NO concentrations (0.1–0.3 ppb), good agreement between LIF and DOAS was obtained. Here, the regression analysis gave a small, significant offset of $(1.0 \pm 0.3) \times 10^5 \text{ cm}^{-3}$ (Fuchs et al., 2012). None of the above mentioned tests provides a direct indication of artefacts that would explain the magnitude of the nighttime OH data in PRD and Yufa. There is the possibility that our tests have missed interferences that were present in PRD and Yufa at night, but not during the above mentioned OH intercomparisons. For that reason, further field and laboratory measurements are planned, for example under consideration of the chemical modulation technique suggested by Mao et al. (2012).

Faloon et al. (2001) found measured nocturnal isoprene decays in a forest to be consistent with their nighttime measurements of OH. If we assume that isoprene at the measurement sites in PRD and Yufa was produced and advected from biogenic emission sources during daylight and its leftover after sunset was predominantly removed by reaction with OH, the nocturnal isoprene decays in PRD and Yufa would indicate OH concentrations of about $1 \times 10^6 \text{ cm}^{-3}$. However, such an estimate has large uncertainties which are difficult to quantify. Besides its chemical removal by OH, isoprene is also subject to transport for which we have insufficient knowledge with respect to the spatial/vertical isoprene distribution around the measurement sites. As diagnosed by Sillman et al. (2002) for the Michigan forested areas, the nighttime loss of isoprene can be attributed to three factors: chemical reaction with OH, vertical diffusion, and advection. In their model results, the observed loss of isoprene was mainly caused by the vertical diffusions. Nevertheless, Sillman et al. (2002) also pointed out that in a shallow layer near the surface, the chemical reaction with OH might be important as diagnosed by Faloon et al. (2001) for the same campaign. Furthermore, in the shallow nocturnal boundary layer, weak isoprene emitters could still play a role, such as emissions from urban traffic (Lee and Wang, 2006; Liu et al., 2008) and biogenic emissions under dark conditions which are usually neglected compared to daytime emissions (Guenther, 1999; Shao et al., 2001). Therefore, further in-depth OH estimates from nocturnal isoprene observations appear to be not meaningful.

4.2 Missing nighttime OH source

On the assumption that the nighttime OH is in steady state, a missing nocturnal OH source ($P(\text{OH})_{\text{M}}$) can be calculated for PRD and Yufa from the difference between the known OH loss and production rates.

$$P(\text{OH})_{\text{M}} = k_{\text{OH}}[\text{OH}] - k_{\text{HO}_2+\text{NO}}[\text{HO}_2][\text{NO}] - p_{\text{OH}} \quad (2)$$

The known OH production includes the reaction of HO_2 with NO and the primary OH production (p_{OH}) from the ozonolysis of alkenes. Here, as an approximation, measured HO_2^* is used for HO_2 in Eq. (2). In general, the OH production by ozonolysis of alkenes, calculated from measured O_3 and alkene concentrations, was small and roughly an order of magnitude lower than the total OH loss rate. The uncertainty of the calculated $P(\text{OH})_{\text{M}}$ is thus mainly determined by the uncertainty of observed OH, k_{OH} , NO and HO_2 including its measurement interference. The mean value of the missing nocturnal OH source is calculated to be about $7.0 \pm 1.8 \text{ ppbh}^{-1}$ and $3.3 \pm 0.8 \text{ ppbh}^{-1}$ for PRD and Beijing, respectively. These values are much smaller than the missing OH sources of 25 ppbh^{-1} and 11 ppbh^{-1} , respectively, required to explain the daytime OH observations at the same measurement sites (Lu et al., 2012, 2013).

4.3 Production and loss of RO_x

The strength of the missing OH source is considerably larger than the production rate of RO_x (the sum of OH, HO_2 and RO_2) estimated by the base model (cf., Table 4). In PRD, the primary nocturnal RO_x production is calculated to be about 0.3–1 ppbh^{-1} dominated by ozonolysis and NO_3 oxidation of VOC, with comparable contributions from O_3 and NO_3 reactions. Only 20 % of this production gives directly OH. Secondary OH formation dominated by conversion of HO_2 with NO exceeds the primary OH formation during the whole night over a large range of NO mixing ratios (cf., Fig. 1). The modelled OH reactivity is dominated by VOC (60–70 %) of which isoprene contributed only 6–12 %. For Beijing, the base model predicts similar relative strengths of the OH sources and sinks as in PRD, but the absolute values of the calculated reaction rates are roughly a factor of two smaller than in PRD. Interestingly, the factor of two also applies to the missing OH sources determined for both measurement sites (see above).

A more detailed view of the modelled reaction rates controlling RO_x in PRD and Yufa is presented in Figs. 6–9. For each site, the situation before and after midnight is shown. The figures display the total primary production rates, the radical-to-radical conversion rates, and the rates of destruction reactions which terminate the radical cycling. Compared to the daytime chemistry, the nighttime chemistry is expected to be much slower. For example, the calculated rates for the removal of OH, the HO_2 -to-OH conversion, or the primary OH production are about an order of magnitude smaller than at daytime (cf., Hofzumahaus et al., 2009; Lu et al., 2012, 2013). Thus, an additional process which would have a small impact during daytime could make a large change in nighttime

OH. Noticeably, the turnover rates describing the thermal equilibria between organic peroxyacetyl radicals (RCO_3) and peroxyacetyl nitrates (PANs), and between HO_2 and peroxy nitric acid (HNO_4) are outstandingly large. For example, the rates are 1–2 orders of magnitude larger than those of the cycling between OH, HO_2 , and RO_2 in PRD before midnight. Thus, a small imbalance in the equilibrium could have a significant impact on the nocturnal radical concentrations. This possibility will be discussed further below (Sect. 4.4.2).

4.4 Potential mechanisms for additional radical production

The general features of the model-measurement comparison of OH and HO_2^* during nighttime, namely, the serious underestimation of the observed OH and the well reproduced HO_2^* , are quite comparable to the corresponding results analyzed for daytime in both PRD (Hofzumahaus et al., 2009; Lu et al., 2012) and Beijing (Lu et al., 2013). This similarity suggests there could be an unified unknown chemical mechanism which resolves the mismatch of the current models for both the daytime and the nighttime chemistry. Therefore, the candidate mechanisms examined for the daytime chemistry are further tested herein.

The measured daytime concentrations of OH and HO_2^* in PRD could be well described when additional recycling Reactions (R1) and (R2) were introduced into the RACM-MIM-GK mechanism (Hofzumahaus et al., 2009; Lu et al., 2012).



If the rate constants for the hypothetical reactant X are assumed to be the same as for NO, a constant amount of 0.8 ppb was able to explain the missing OH daytime source. The application of a similar amount (1 ppb X) at night yields a significant increase of the simulated OH concentration compared to the measured values (Fig. 10). The modelled OH reaches 24–40 % of the measured concentrations and the modelled k_{OH} shows improved agreement. The agreement for HO_2^* , however, becomes slightly worse. A further increase of the modelled OH by raising the concentration of X even higher is limited by the growing depletion of RO_2 and HO_2 . Thus, OH, HO_2 and k_{OH} cannot be matched simultaneously within their experimental uncertainties just by enhanced recycling. Further improvement can be obtained if an additional primary RO_x source of 1 ppbh^{-1} complements the additional recycling mechanism ($\text{X}=1 \text{ ppb}$). In this case, the modelled OH is raised to the level of the observations, but the relative nocturnal variation is not fully captured (Fig. 10). However, reasonable agreement is maintained for HO_2^* and k_{OH} , with a tendency to overpredict HO_2^* at higher NO mixing ratios after midnight. Without additional recycling by X, application of an additional primary OH source in the model is not sufficient to explain the observations of OH and HO_2^* . A primary OH source can be tuned to match the OH observations, but would lead to a large overprediction of HO_2^*

resulting from the enhanced rates of the reactions of OH with CO and VOC.

430 The situation in CAREBEIJING2006 is similar to the one in PRD. Again, only a combination of an additional primary RO_x source of 1 ppbh⁻¹ and additional recycling by 1 ppb X gives a relatively good reproduction of the measured OH, HO₂^{*}, and *k*_{OH} (Fig. 10). For both measurement sites (PRD and Yufa), the required additional primary RO_x source can be implemented in the model either as a source of OH, or HO₂, or RO₂, or a combination of RO_x species, all yielding essentially the same
435 model results. The reason is that the additional input of radicals is quickly redistributed among the RO_x species by the recycling reactions.

Though the base (M0) and modified (M0+X+p_{OH}) models yield similar nighttime results for HO₂^{*}, the predicted abundances and speciation of the peroxy radicals (RO₂ and HO₂) are significantly different (see Fig. 4 and Fig. 11, respectively). In the base model, a large fraction of RO₂ (OLNN and OLND) is produced by reactions of NO₃ with VOC, whereas in the modified model, production
440 of RO₂ is dominated by OH and destruction of RO₂ is enhanced by X. Nevertheless, the introduced additional pathways in M0+X+p_{OH} that changes the RO_x budget significantly do not show an impact on the NO₃ budget since the simulated NO₃ concentration in the two model runs (M0 and M0+X+p_{OH}) were almost identical. For the VOC in PRD and Yufa, the HO₂ measurement interference is very different for RO₂ species from OH and NO₃ reactions (see section 2.1). This behavior
445 and the different RO₂ composition lead accidentally to the similarity of the HO₂^{*} concentrations in the two different model scenarios.

A new radical recycling mechanism for the oxidation of isoprene by OH has been proposed theoretically to explain the unexpected high OH concentrations observed at daytime in isoprene-rich
450 environments (Peeters et al., 2009). The corresponding Leuven isoprene mechanism (LIM) proposes two isomerization reactions of isoprene peroxy radicals each followed by reproduction of HO_x radicals without involvement of NO. One of the decomposition reactions gives hydroxy peroxy aldehydes as a co-product which can undergo photolysis and yield even more HO_x. In the present work, the potential of LIM to provide additional nighttime OH was tested. It turns out to be ineffective
455 for two reasons. First, the nocturnal isoprene mixing ratio was relatively small in PRD and Beijing, and secondly the photolysis of hydroxy peroxy aldehydes is missing in the night. Moreover, two recent experimental studies have demonstrated that the isomerization rates of the isoprene peroxy radicals implemented in LIM are largely overestimated (Crouse et al., 2011; Fuchs et al., 2013). Thus, isoprene is not a likely contributor to the enhanced nighttime OH concentrations in PRD and
460 Beijing. However, the isomerization of isoprene peroxy radicals is an example for a new type of RO₂ reactions that regenerate OH via isomerization without involvement of NO. Given the large concentrations of other nighttime RO₂ (see Fig. 4), it appears desirable in future research to further investigate the potential of other RO₂ species for HO_x regeneration.

4.4.1 Primary radical sources

465 The required additional RO_x source of 1 ppbh^{-1} is of similar magnitude as the known source
strength of VOC reactions with ozone and NO_3 in PRD and Beijing before midnight (cf., Table 4).
Yet, it is difficult to find an obvious explanation for an increase of the primary RO_x production rate
by a factor of two or more. One possible reason could be the reaction of O_3 or NO_3 with unknown
VOCs, which were not detected or not identified by the GC system. However, the relative good
470 agreement of the modelled and measured total OH reactivities leaves little room for missing reac-
tive VOC. A similar situation was investigated by Di Carlo et al. (2004) who had found evidence
for missing reactivity due to unmeasured reactive biogenic hydrocarbons in a forest and tried to ex-
plain unexpectedly high nighttime OH concentrations at the same location reported by Faloon et al.
(2001). Di Carlo et al. (2004) supposed that some specific terpenes and sesquiterpenes which are
475 known to react faster with ozone than with OH, would be able to increase the OH production rate
without a strong increase of k_{OH} , thus leading to an enhancement of the OH concentration.

The required concentration of an alkene ALK that would produce sufficient OH by ozonolysis in
PRD or Beijing is given by Eq. (3).

$$[\text{ALK}] = \frac{\Delta P_{\text{RO}_x}}{k_{\text{O}_3+\text{ALK}}[\text{O}_3]Y_{\text{OH}}} \quad (3)$$

ΔP_{RO_x} denotes the additional RO_x production rate of 1 ppbh^{-1} , while $k_{\text{O}_3+\text{ALK}}$ and Y_{OH} repre-
sent the rate coefficient and OH yield of the ozonolysis, respectively. On the other side, the required
VOC concentration is related to the concurrent increase of the OH reactivity (Δk_{OH}) as follows:

$$[\text{ALK}] = \frac{\Delta k_{\text{OH}}}{k_{\text{OH}+\text{ALK}}} \quad (4)$$

If we allow for an increase Δk_{OH} of 3 s^{-1} (which seems tolerable within the error margins of the
modelled and measured k_{OH}), then Eqs. (3) and (4) impose as a constraint for the alkene that the
ratio $k_{\text{OH}+\text{ALK}}/(k_{\text{O}_3+\text{ALK}}Y_{\text{OH}})$ must be in the range of $(3-7) \times 10^5$ in PRD and about 1×10^5 in
480 Beijing. The above requirements would be fulfilled by highly reactive terpenoids like for example
 δ -terpinene. It has rate constants for the reaction with OH and ozone of $2.3 \times 10^{-10} \text{ cm}^3\text{s}^{-1}$ and
 $1.8 \times 10^{-15} \text{ cm}^3\text{s}^{-1}$, respectively, and an assumed OH yield of unity OH ($Y = 1$) from ozonoly-
sis (Atkinson and Arey, 2003). For typical nighttime O_3 concentrations ($\approx 20 \text{ ppb}$) before mid-
night, about 500 ppt of δ -terpinene would be enough to provide a primary RO_x production rate of
485 1 ppbh^{-1} . But this kind of species are so reactive towards O_3 that their lifetime would only be
10–30 min. Thus, without a strong local emission source (for which we have no direct evidence) it
is unlikely that the concentration of such terpenoids can reach the required concentration levels.

4.4.2 Vertical transport of radicals and radical reservoir species

The box model applied in this work implicitly assumes that the air near the ground where the field
490 measurements were performed is homogeneously mixed. Such an assumption is reasonable for the

daytime when the planetary boundary-layer (PBL) is well mixed by turbulence up to 1–2 km height. In the night, however, a stable nocturnal boundary layer (NBL) is formed at the bottom of the PBL. The NBL is a stable layer and is separated by a temperature inversion from the residual layer (RL) above which contains air of the mixed layer from the previous day (Stull, 1988). In a conceptual
 495 model study, Geyer and Stutz (2004) have shown that distinct vertical profiles of RO_x radicals can evolve in the NBL depending on the chemical and meteorological conditions, in particular if NO is emitted near the ground surface. Their model study reports OH maxima in the order of (1–2) × 10⁶ cm⁻³ in the lowest two meters above ground and a decrease of the OH concentration within 10 m height to about 10⁵ cm⁻³. Besides chemistry, the model results depend on the vertical
 500 transport of RO₂ and HNO₄ (as a HO₂ reservoir) and were found to be highly sensitive to changes in the atmospheric stability and NO surface emission.

The nocturnal HO_x measurements in the present work were performed in environments with significant anthropogenic nighttime emission of NO (see Sect. 3.1) and at measurement heights (7 m) for which significant vertical radical gradients are predicted at night (Makar et al., 1999; Geyer and Stutz, 2004). Thus, it seems reasonable to apply a 1-dimensional model to simulate the nocturnal radical concentrations in PRD and Yufa. However, the conditions (vertical profiles of trace gases, micrometeorological parameters, emission rates of NO and VOC) for implementation in a detailed model are not known. As a compromise, a simple 1-dimensional model with only two boxes has been set up to investigate the sensitivity of the RO_x radical budget to vertical transport at the measurement sites in PRD and Yufa. The lower box was chosen to represent a lower layer of 50 m depth and the upper box to represent the residual layer up to 1000 m height. The chemistry in each box is represented by RACM-MIM-GK and the vertical exchange between the two boxes is parameterized by assuming diffusion with a momentum exchange coefficient K_z . The time dependent change of the trace gas concentrations in each each box can be described by Eq. (5).

$$\frac{\partial n_i}{\partial t} = n_a K_z \frac{\partial^2 (C_i)}{\partial z^2} - R_i \quad (5)$$

$\partial n_i / \partial t$ is the rate of change of the number density n_i of the i th compound in the model box, n_a is the atmospheric number density, C_i is the mixing ratio of the i th compound in the model, and R_i denotes the contribution from the chemical reactions.

The model calculations were performed for the time from sunset to sunrise. For the lower layer, the initial values were taken from the base model (M0) result at sunset (Sect. 2.2) and net emission rates for long-lived species (i.e. NO, CO, C₂–C₁₂ hydrocarbons) were introduced to resemble the measured concentrations. For the upper box, the initial values were taken from the base model M0 at half an hour before sunset and no emissions were included. For the transport between the boxes, K_z was estimated by Eq. (6)

$$K_z = \frac{kz u_*}{\Phi\left(\frac{z}{L}\right)} \quad (6)$$

505 Here, k is the von-Karman constant (= 0.4), z is the height (= 50 m), u_* is the friction velocity,

L is the Obukhov length, and Φ is the dimensionless wind shear (Stull, 1988). The values for u_* and Φ were calculated from 3-dimensional wind measurements by an in-situ ultrasonic anemometer that was operated at the height of the HO_x measurements. The nocturnal temperature lapse rate was estimated to be -5.4 K km^{-1} according to Fan et al. (2011). The observed temperature and
510 temperature at 500 m are used as model constraints for the lower and upper boxes, respectively. For both PRIDE-PRD2006 and CAREBEIJING2006, the averaged K_z coefficients were calculated to be $0.5 \text{ m}^2 \text{ s}^{-1}$ for 50 m height.

From the 1-dimensional two-box model calculations, vertical transport rates can be determined. It is found that there is a weak direct transport of radicals from the upper into the lower layer,
515 contributing in the order of $10^{-5} \text{ ppbh}^{-1}$ of OH, $10^{-3} \text{ ppbh}^{-1}$ of HO_2 , $10^{-2} \text{ ppbh}^{-1}$ of RO_2 in the lower layer. These contributions are negligible compared to the known chemical primary production rate of RO_x (Table 4).

A significantly larger influence is expected from the transport of radical reservoir species. As pointed out in Sect. 4.3, some compounds like PANs and HNO_4 are expected to be in quasi-
520 equilibrium with RO_2 and HO_2 , respectively, with high chemical interconversion rates (Figs. 6–9). Thus, a small perturbation of their thermal equilibria may have a significant impact on the abundance of RO_x . Such a perturbation can result from continuous transport of reservoir species from one into another layer. In case of the two campaigns in Yufa and PRD, the model predicts a downward flux of HNO_4 and PANs which then thermally decompose into radicals in the lower layer. The HO_2
525 production following the downward transport of HNO_4 contributes less than 0.01 ppbh^{-1} , which is again negligible compared to the required additional RO_x source of 1 ppbh^{-1} . However, downward transport and dissociation of peroxy acetyl nitrates, PAN + MPAN, makes a significant contribution which after midnight reaches up to 0.25 ppbh^{-1} in PRD (see Fig. 12). This value is in the order of the known primary RO_x production rates at nighttime in PRD and Yufa (Table 4). The relevance of
530 this mechanism increases over the course of the night while NO increases in the lower layer due to emissions. The rising NO depletes peroxy radicals and thereby lowers the concentrations of PAN and MPAN. In contrast, the NO in the upper layer remains small owing to a lack of NO sources, and PAN and MPAN remain high. Thus, an increasing gradient develops between the upper and lower layers leading to an increasing downward flux over the night. The modelled concentrations
535 of the RACM-species PAN (=PAN and other higher saturated PANs) in the lower layer in PRD are comparable to measured values and show a similar temporal variation throughout the night. The simulated MPAN concentration level is also plausible as judged by the observed PAN to MPAN ratio (e.g. 6 to 10) reported for biogenically dominated air masses (Roberts et al., 1998). The role of entrainment of PAN from the top boundary of the upper layer is difficult to estimate without more
540 detailed information about the nocturnal structure of the lower troposphere at the measurement sites. Such information is not available. Nevertheless, our analysis demonstrates that vertical transport is a possible candidate to explain at least part of the enhanced radical concentrations near the ground.

This process could eventually become the dominant nighttime RO_x source, when ozone and NO₃ become more and more depleted by NO emissions in the lower layer, resulting in decreasing RO_x formation from ozonolysis or VOC oxidation by NO₃. In principle, downward transport of NO₃ could also contribute to enhance the RO_x production in the lower layer, but the calculated downward transport rates are comparatively small ($< 0.01 \text{ ppbh}^{-1}$). Although the vertical transport of the above mentioned compounds cannot account for the full amount of required primary RO_x source strengths, the simple model demonstrates that vertical transport can play a significant role for the nighttime radicals near the ground, in agreement with the conclusions of the model study by Geyer and Stutz (2004). Thus, future field campaigns studying the nighttime chemistry would greatly benefit from additional measurement of vertical profiles of key species such as NO as well as of flux and micrometeorological measurements at different heights. The downward transport of PAN and its analogs would be especially important as an additional RO_x radical source when the near surface NO concentration becomes high.

5 Summary and conclusions

In two ground-based field campaigns, PRIDE-PRD2006 and CAREBEIJING2006, HO_x radicals, total OH reactivity, and atmospheric trace gases were measured in summer 2006. One measurement site was located in a rural environment influenced by urban emissions in the Pearl River Delta (PRD), and the other site was in the suburban area Yufa near Beijing. In both campaigns, significant nighttime concentrations of radicals were observed under conditions with high total OH reactivities of about $40\text{--}50 \text{ s}^{-1}$ in PRD and 25 s^{-1} in Yufa. For OH, the nocturnal concentrations were within the range of $(0.5\text{--}3) \times 10^6 \text{ cm}^{-3}$ implying a significant nighttime oxidation rate of pollutants in the order of several ppb per hour. A box model was used to compare the measured radical concentrations at night with the expectation from an established tropospheric chemistry mechanism (RACM-MIM-GK). The model was constrained by measured data for O₃, HONO, NO, NO₂, CO, VOC, water vapor, ambient temperature, pressure, and assumed deposition loss of model-generated species. For both field campaigns, the model is capable to reproduce the measured nighttime values of HO₂^{*} and k_{OH} , but underestimates in both cases the observed OH by about one order of magnitude. This feature is similar to results from other field studies which investigated the nighttime chemistry in urban areas and forests and found significantly more nighttime OH than expected from models (e.g., Tan et al., 2001). Noticeably, the large discrepancies between observed and modelled nighttime OH were generally found under conditions with high VOC reactivities. This finding and the recent discovery of a possibly VOC-related interference in the LIF OH instrument by the Pennstate University group (Mao et al., 2012) raises the question whether our nighttime observations in PRD and Yufa could be caused by an instrumental artefact. In previous field campaigns, nighttime OH concentrations measured by our LIF instrument were less or equal to a few 10^5 cm^{-3} in agreement with model

expectations. Moreover, several instrumental tests and intercomparisons with independent measurement techniques, such as DOAS and CIMS, have not revealed any artefacts that could explain the nocturnal OH observation in PRD and Yufa. Nevertheless, further tests of our LIF-instrument are planned in the laboratory and future field campaigns.

Sensitivity studies with the box model demonstrate that the OH discrepancy between measured and modelled nighttime OH in PRD and Yufa can be resolved, if an additional RO_x production process (about 1 ppbh⁻¹) and additional recycling (RO₂ → HO₂ → OH) with an efficiency equivalent to 1 ppb NO is assumed in the model. The additional recycling mechanism was also needed to reproduce the OH observations at the same locations during daytime for conditions with NO mixing ratios below 1 ppb. This could be an indication that the same missing process operates at day and night. Recent work has shown that isoprene peroxy radicals can undergo isomerization and regenerate HO₂ and OH with involvement of NO. Though isoprene was present in PRD and Yufa, its nighttime concentration was too small to explain the nocturnal OH. However, given the high abundance of other RO₂ at night, it appears desirable in future research to further investigate the potential of other RO₂ species for HO_x regeneration.

The required primary source of RO_x can be explained in principle by ozonolysis of terpenoids, which react faster with the given ozone than with OH in the nighttime atmosphere. Thereby, the modelled RO_x concentrations can be increased without a large enhancement of *k*_{OH}, retaining the relative good agreement of the measured and modelled OH reactivity. However, the required mixing ratio of terpenoids, for example 500 ppt of δ-terpinene, would need a strong local biogenic source, for which we have no direct evidence.

A more likely explanation for an additional RO_x source is the vertical downward transport of radical reservoir species, e.g., PAN and MPAN, in the stratified nocturnal boundary layer and thermal decomposition of these species into radicals. This possibility proposed in a conceptual model paper by Geyer and Stutz (2004) was tested in this work using a simplified 1-dimensional two-box model. In fact, a vertical gradient of RO_x radicals, HNO₄, PAN and MPAN is expected to develop in the course of the night as a result of anthropogenic NO emissions at the ground, leading to a flux of these compounds from the air aloft into the atmospheric layer near the Earth' surface. While the transport of RO_x and HNO₄ is too small to make an impact, the downward transport of PAN and MPAN is significant and reaches values after midnight up to 0.3 ppbh⁻¹ in PRD which are in the order of the known RO_x production by ozonolysis and NO₃ reactions with VOC. This mechanism appears promising, but the model is highly simplified and not enough to explain the complete OH discrepancy.

In conclusion, the reasons for the high nighttime OH observations in PRD and Yufa are not completely understood. However, recent progress in laboratory and field studies and the analysis of the present paper give directions for future work. Additional tests will be needed to quantify or exclude the possibility of measurement artefacts for OH. Further laboratory studies of the chemistry of

615 VOC and their degradation products are needed and in particular the potential of RO_2 to regenerate HO_x needs further investigation. Finally, further studies of the nighttime chemistry in the lower troposphere will require more sophisticated 1-dimensional models for analysis supported by field measurements probing the vertical distribution of trace gases and fluxes.

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Table 1. Nighttime averaged values of observed trace gases, HO_x radicals, and total OH reactivity before (20:00–24:00 CNST) and after (00:00–04:00 CNST) midnight at the measurement sites in Backgarden (BG) and Yufa (YF).

Parameter	Period 1		Period 2	
	(20:00–00:00)		(00:00–04:00)	
	BG	YF	BG	YF
O ₃ (ppb)	25.8	28.9	7.4	14.2
NO (ppb)	0.25	0.18	4.8	1.2
NO ₂ (ppb)	17.1	15.2	23.1	14.6
HONO (ppb)	1.2	0.9	2.0	1.0
CO (ppb)	998	712	1138	940
Ethane (ppb)	1.5	4.5	1.5	4.6
Ethene (ppb)	3.0	4.6	3.0	4.6
1,3–Butadiene (ppb)	N/A	0.2	N/A	0.2
Isoprene (ppb)	1.6	0.6	0.8	0.1
HC3 (ppb)	4.7	4.7	7.1	6.1
HC5 (ppb)	4.2	3.5	7.5	3.4
HC8 (ppb)	2.9	1.5	5.7	1.3
OLI (ppb)	0.4	0.1	0.7	0.1
OLT (ppb)	2.7	2.6	3.8	2.6
TOL (ppb)	7.0	8.4	13.0	6.2
XYL (ppb)	3.6	2.4	5.5	0.7
H ₂ O (%abs)	3.4	2.2	3.4	2.2
OH (10 ⁶ cm ⁻³)	1.6	1.5	0.9	1.0
k _{OH} (s ⁻¹)	40.3	26.1	54.1	25.0
HO ₂ [*] (10 ⁸ cm ⁻³)	2.6	1.9	0.7	0.6
Temperature (°C)	31.1	24.0	29.8	22.3
Pressure (hPa)	1000.3	1006.0	1000.7	1006.3

Table 2. Correlation coefficients (r²) between observed OH and HO₂^{*} radicals with the CO and isoprene concentrations in both PRD and Beijing.

	r ² (CO,OH)	r ² (CO,HO ₂ [*])	r ² (ISO,OH)	r ² (ISO,HO ₂ [*])
PRD	0.070	0.066	0.062	0.340
Beijing	4×10 ⁻⁶	0.036	0.190	0.371

Table 3. Overview of mean nighttime OH concentrations, observed-to-modelled OH ratios (OHobs/OHmod) and limit of OH detection (LOD) from our studies and from other field campaigns where higher-than-expected nighttime OH concentrations were reported.

Field campaign	Environment	OH [cm^{-3}]	OHobs/OHmod	LOD [cm^{-3}]	References
PROPHET ^a	Forest	1.1×10^6	46	0.05×10^6 (0.5 h)	Faloona et al. (2001)
SOS-Nashville ^a	Urban	0.8×10^6	> 10	0.8×10^6 (1 min)	Martinez et al. (2003)
PMTACS ^a	Urban	1.0×10^{6b}	9 ^b	0.3×10^6 (1 min)	Ren et al. (2003a,b)
MCMA ^a	Urban	0.6×10^{6b}	1.5 ^b	0.2×10^6 (1 min)	Shirley et al. (2006)
TORCH	Urban	0.3×10^6	2	0.03×10^6 (15 min)	Emmerson and Carslaw (2009)
IMPACT-L	Urban	0.4×10^6	4	0.13×10^6 (10 min)	Kanaya et al. (2007)
PRIDE-PRD	Rural ^c	1.3×10^6	11	0.14×10^6 (1 h)	this study
CareBeijing	Suburban	1.2×10^6	18	0.14×10^6 (1 h)	this study

^a The Pennstate LIF instrument was used for OH measurement. It is possible that the reported nighttime data are enhanced by an artefact as reported by Mao et al. (2012).

^b The concentrations are scaled up by a factor of 1.44 herein according to Mao et al. (2010).

^c Strongly urban influenced.

Table 4. Radical sources and sinks calculated by the base model for the time before (20:00–24:00 CNST) and after (00:00–04:00 CNST) midnight at the measurement sites in Backgarden (BG) and Yufa (YF).

Parameter	Period 1		Period 2	
	(20:00–00:00)		(00:00–04:00)	
	BG	YF	BG	YF
Primary RO _x sources (ppbh^{-1})	1.03	0.47	0.34	0.17
O ₃ + alkenes	43 %	44 %	49 %	46 %
NO ₃ + VOC	57 %	56 %	51 %	54 %
HO ₂ → OH conversion (ppbh^{-1})	0.40	0.21	0.99	0.23
HO ₂ + NO	92 %	83 %	99 %	94 %
Total OH reactivity (s^{-1})	33	24	39	22
OH + NO _x	10 %	14 %	14 %	15 %
OH + CO	17 %	17 %	17 %	25 %
OH + VOC*	73 %	69 %	69 %	60 %
OH + Isoprene	12 %	6 %	5 %	2 %

* The VOC contribution includes isoprene which is listed separately in the line below.

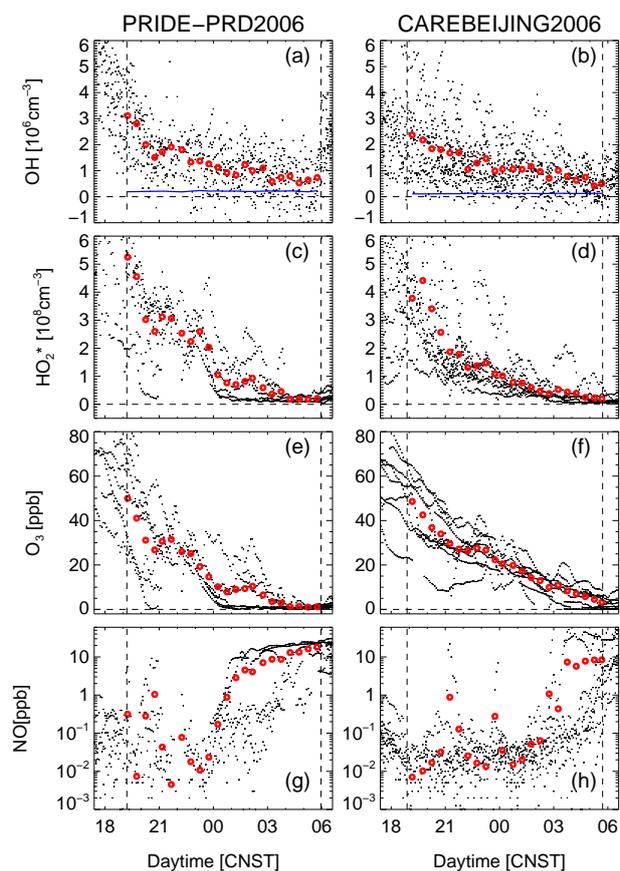


Fig. 1. Observed concentrations of OH, HO₂^{*}, O₃ and NO during PRIDE-PRD2006 and CAREBEIJING2006. The black symbols denote the original measurements, the red circles denote half-hourly averaged values. NO is displayed on a logarithmic scale. In (a) and (b), the corresponding 1σ OH detection limits (1 h) are shown as solid blue lines. The local sunset and sunrise time are marked by the dashed vertical lines.

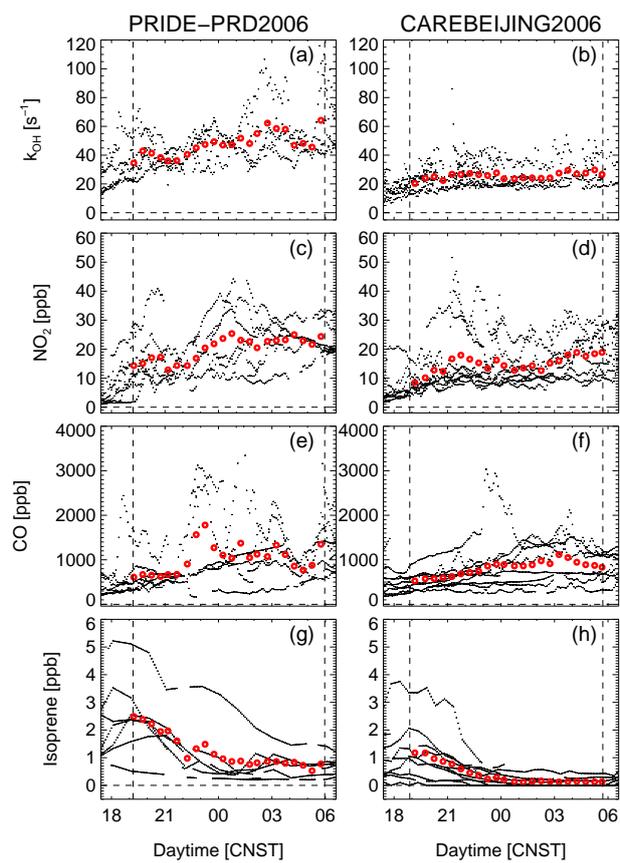


Fig. 2. Observed values of k_{OH} , NO_2 , CO and isoprene during PRIDE-PRD2006 and CAREBEIJING2006. The black symbols denote the original measurements, the red circles denote half-hourly averaged values for k_{OH} , NO_2 , CO and isoprene. The local sunset and sunrise time are marked by the dashed vertical lines.

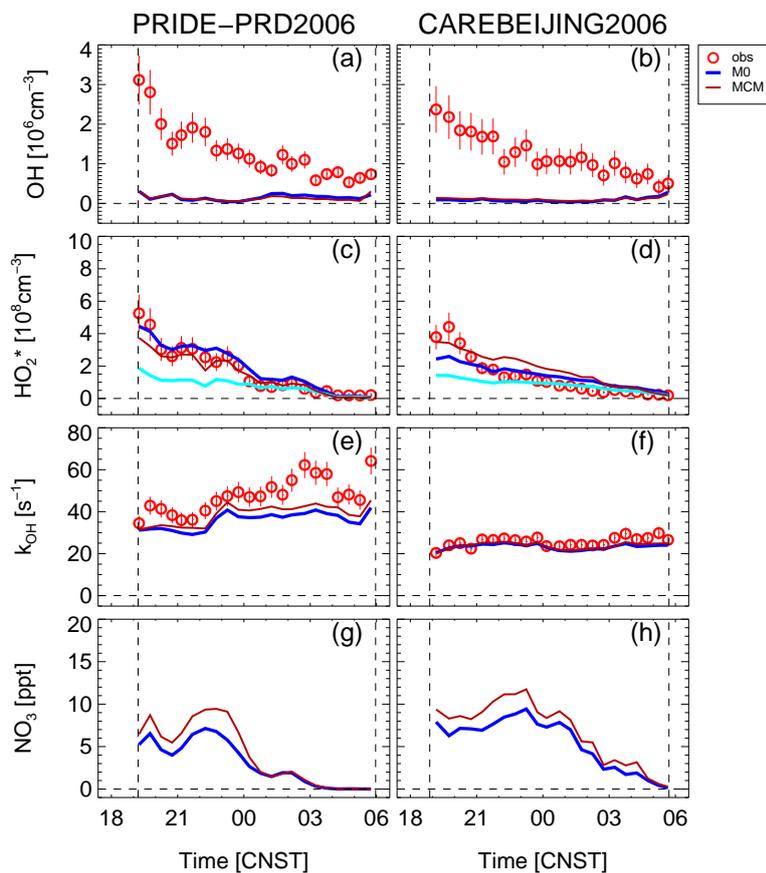


Fig. 3. Model-measurement comparison of mean nighttime variations of OH, HO_2^* , and k_{OH} for PRIDE-PRD2006 and CAREBEIJING2006. The error bars attached to the observed data points denote the combined uncertainty from precision and accuracy (1σ). In addition, model simulated concentrations of HO_2 (M0, cyan lines in (c) and (d)) and NO_3 ((g) and (h)) are shown.

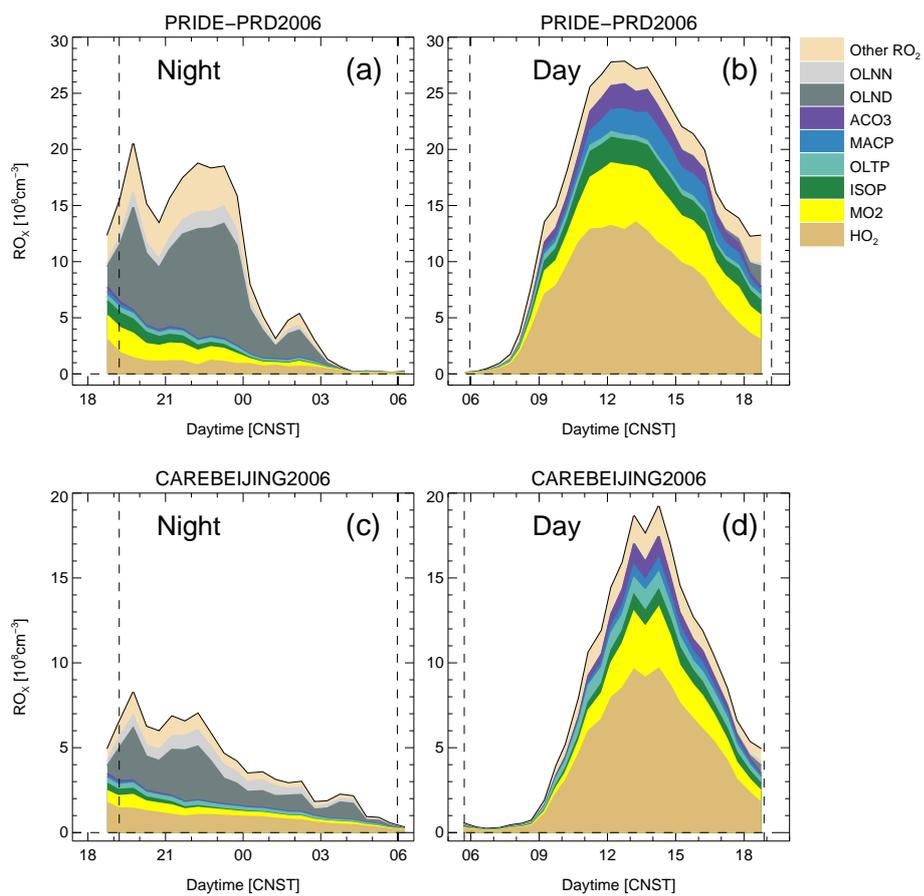


Fig. 4. Modelled (M0) peroxy radical ($= \text{RO}_2 + \text{HO}_2$) concentrations and their speciation at night (left panels) and during daytime (right panels).

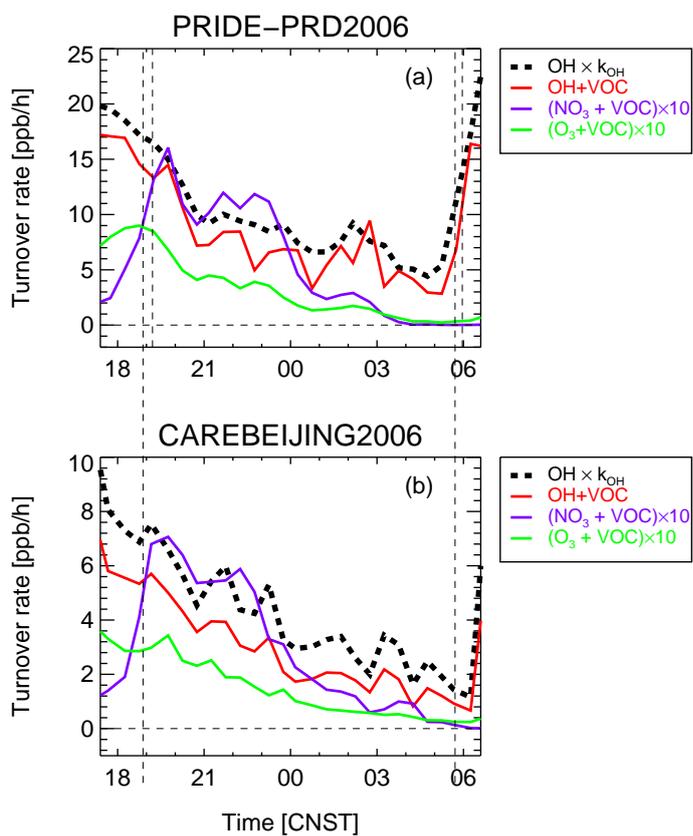


Fig. 5. Nighttime oxidation rates of VOCs (=observed HCs + modelled OVOCs) for their reaction with OH, NO₃ and O₃ during PRIDE-PRD2006 and CAREBEIJING. The VOC oxidation rate for OH was estimated as the difference of the measured total OH reaction rate ($k_{\text{OH}} \times [\text{OH}]$, black dashed line) and the calculated reaction rates of OH with CO and NO_x. The reaction rates of NO₃ and O₃ are taken from the base model and use modelled NO₃ and measured O₃ concentrations, respectively. The vertical dashed lines denote the sunset and sunrise.

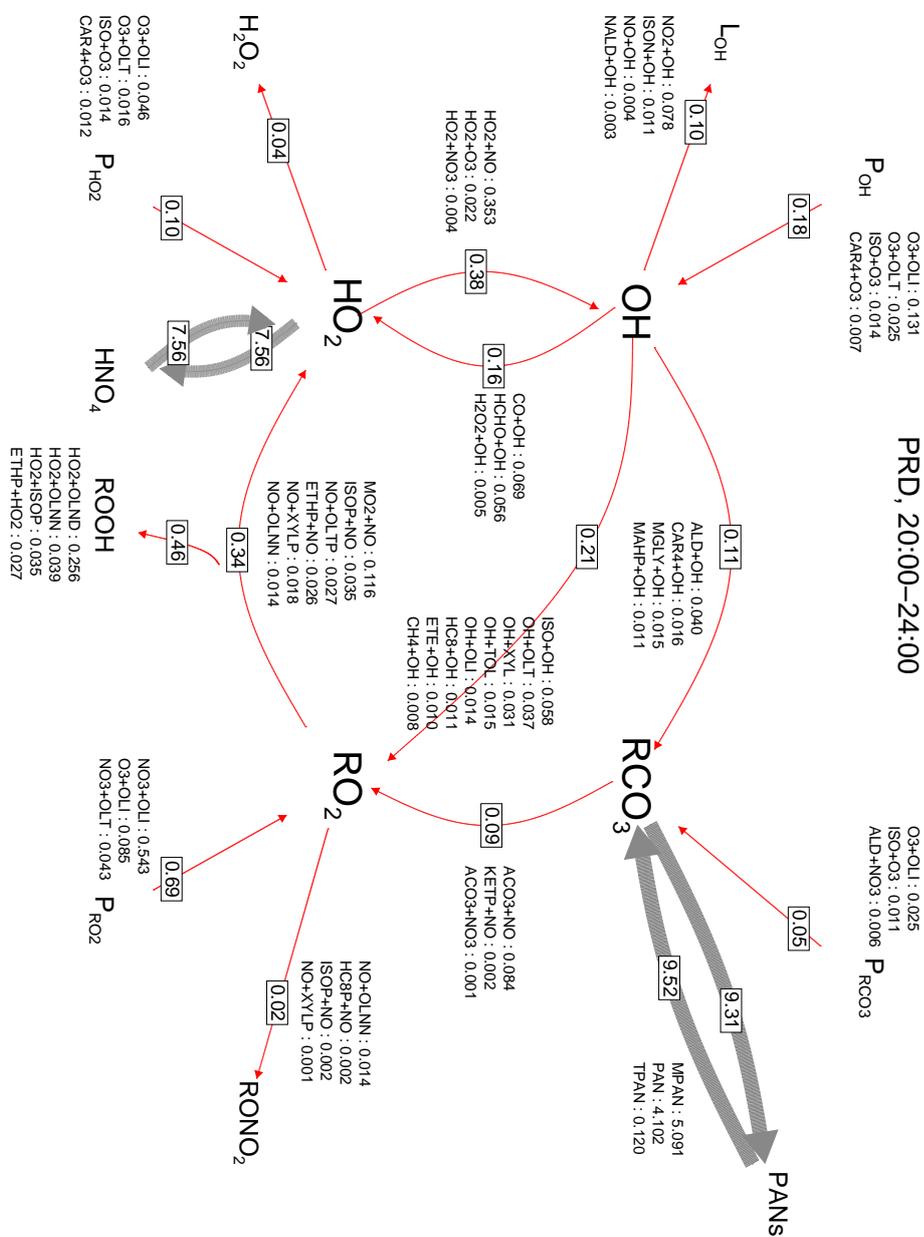


Fig. 6. Mean RO_x production, conversion and destruction rates calculated by the base model (M0) for PRIDE-PRD2006 conditions during 20:00–24:00 CNST. The thickness of the arrows represents the relative magnitude of the reaction rates given in ppbh⁻¹.

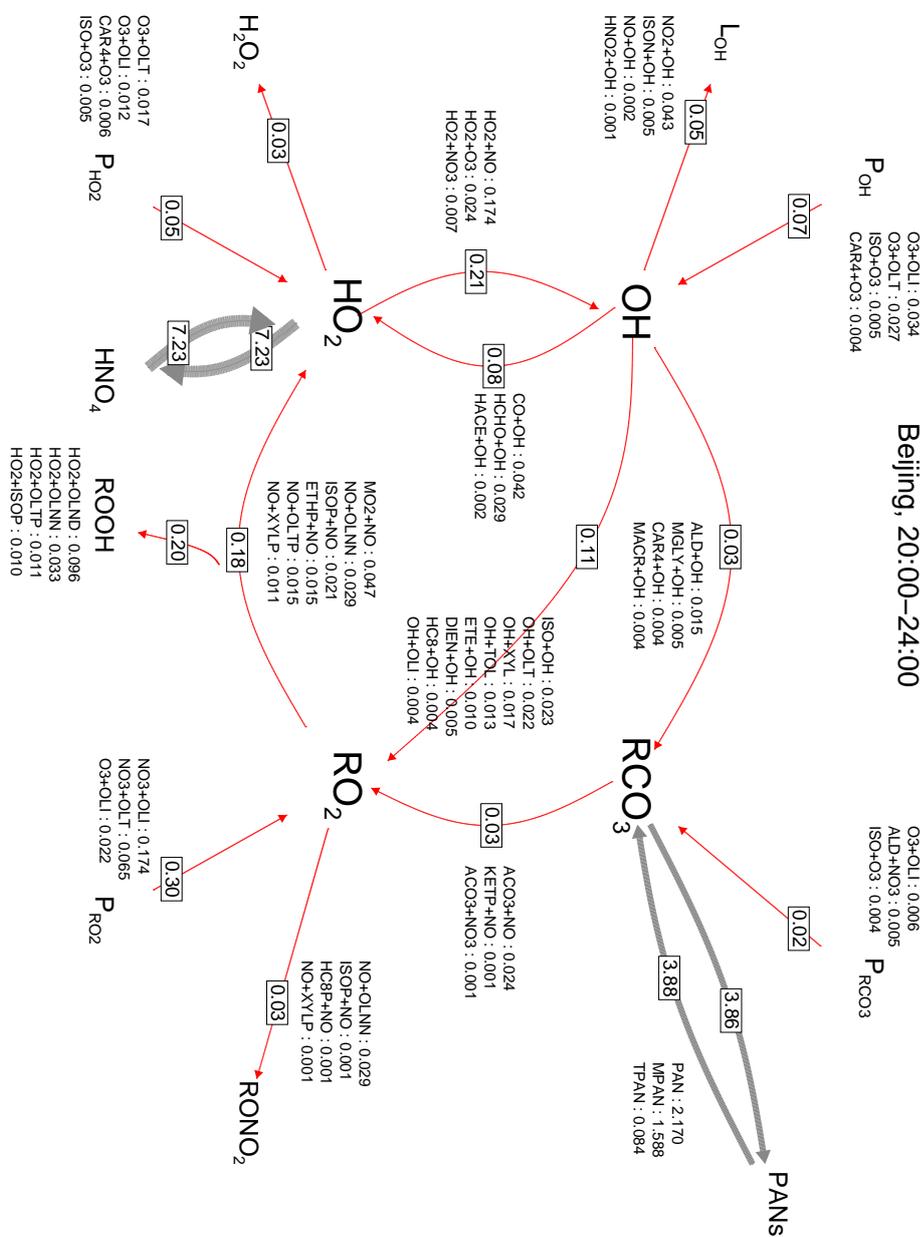


Fig. 8. Mean RO_x production, conversion and destruction rates calculated by the base model (M0) for CARE-BEIJING2006 conditions during 20:00–24:00 CNST. The thickness of the arrows represents the relative magnitude of the reaction rates given in ppbh⁻¹.

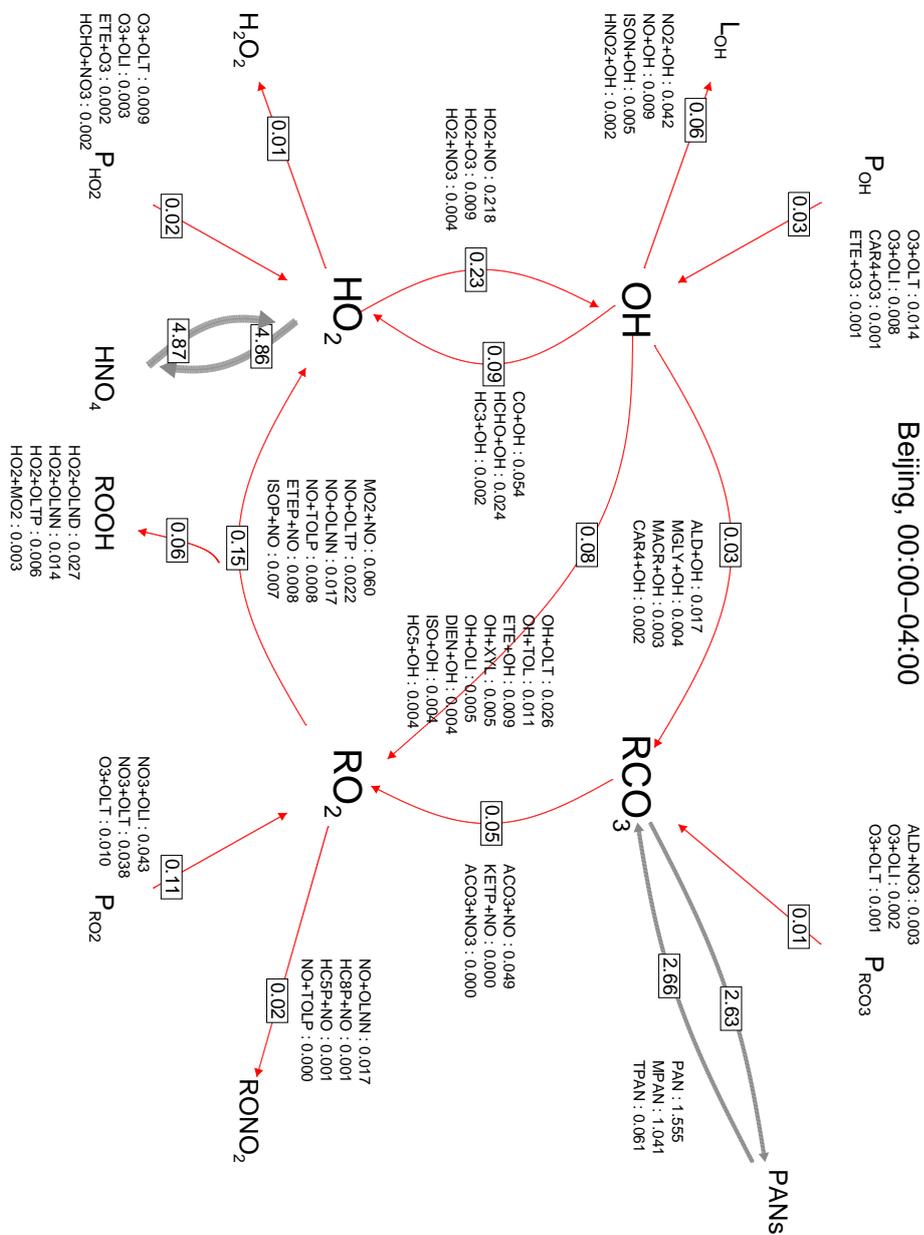


Fig. 9. Mean RO_x production, conversion and destruction rates calculated by the base model (M0) for CARE-BEIJING2006 conditions during 00:00–04:00 CNST. The thickness of the arrows represents the relative magnitude of the reaction rates given in ppbh^{-1} .

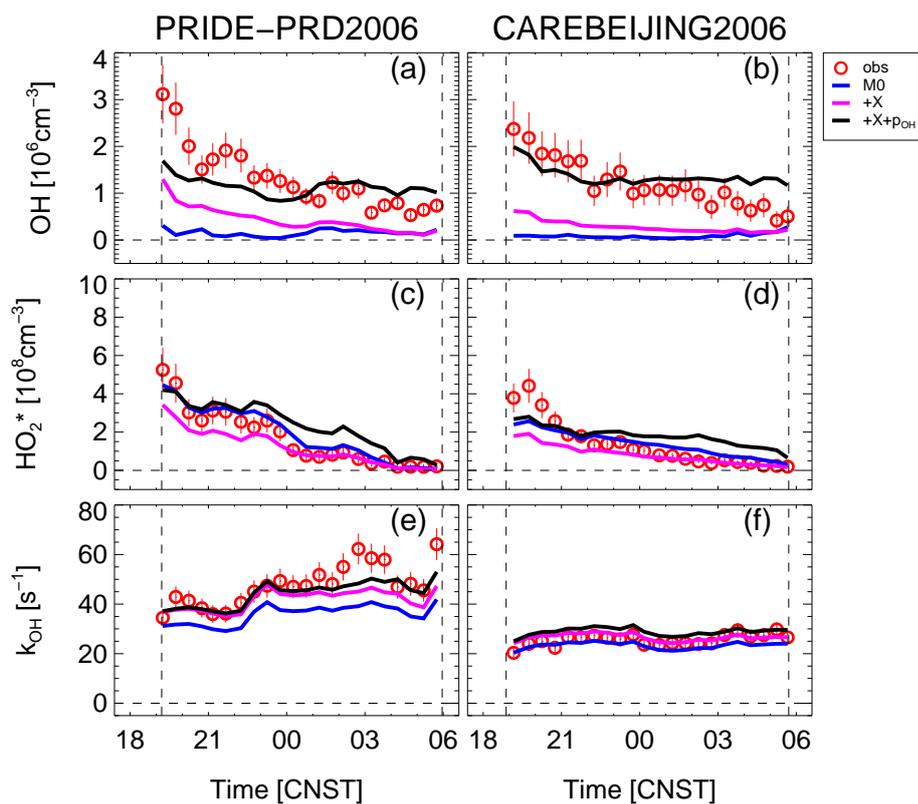


Fig. 10. Model-measurement comparison of mean nighttime variations of OH, HO_2^* , and k_{OH} for PRIDE-PRD2006 and CAREBEIJING2006. The model runs M0+X+ p_{OH} and M0+X assume additional radical recycling by X and are calculated with and without extra primary OH production ($p_{\text{OH}} = 1 \text{ ppbh}^{-1}$), respectively. For comparison, observational and base model (M0) data from Fig. 3 are shown. Error bars attached to the observed data points denote the combined uncertainty from precision and accuracy (1σ).

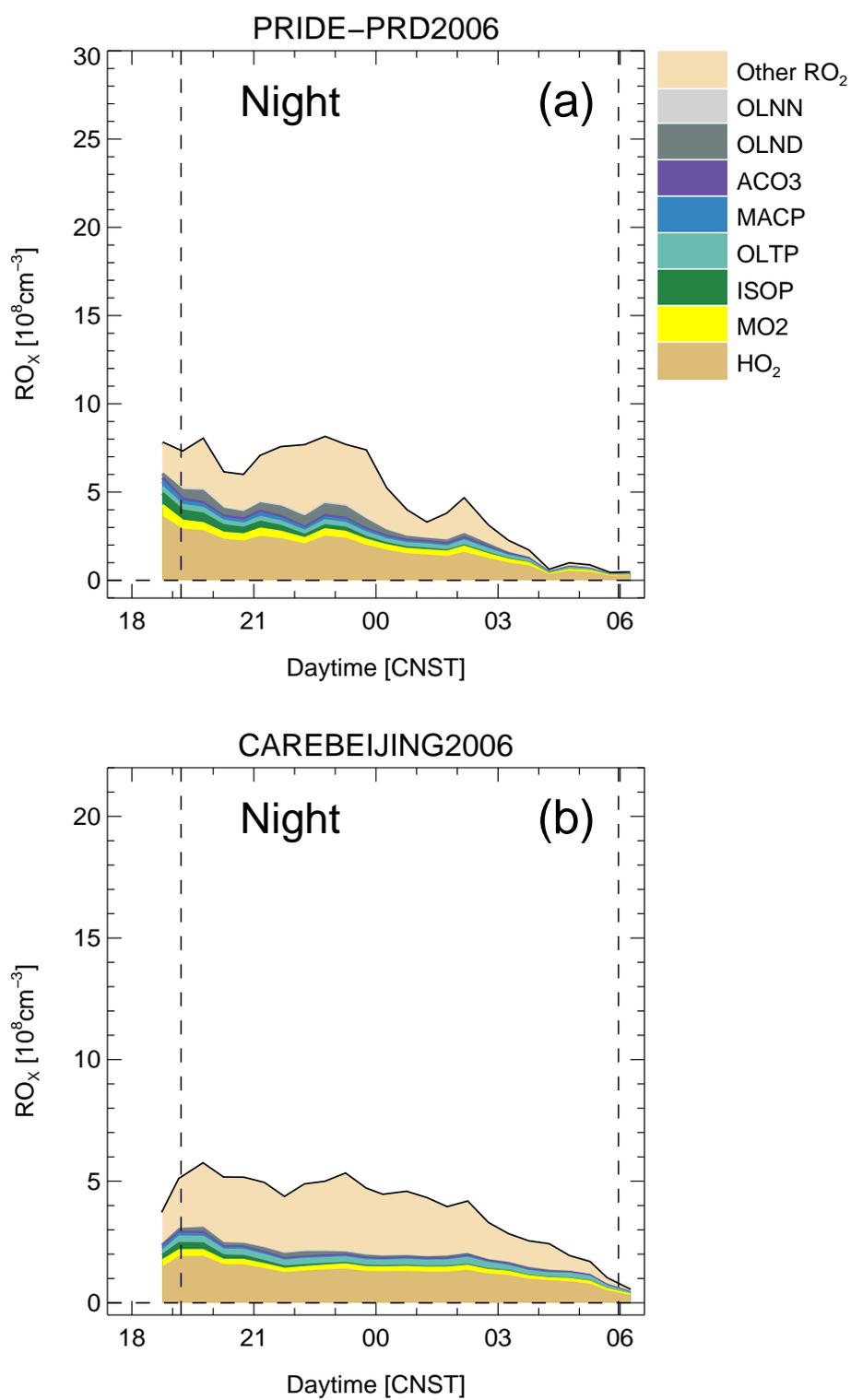


Fig. 11. Modelled ($M0+X+p_{OH}$) peroxy radical ($= RO_2 + HO_2$) concentrations and their speciation at night.

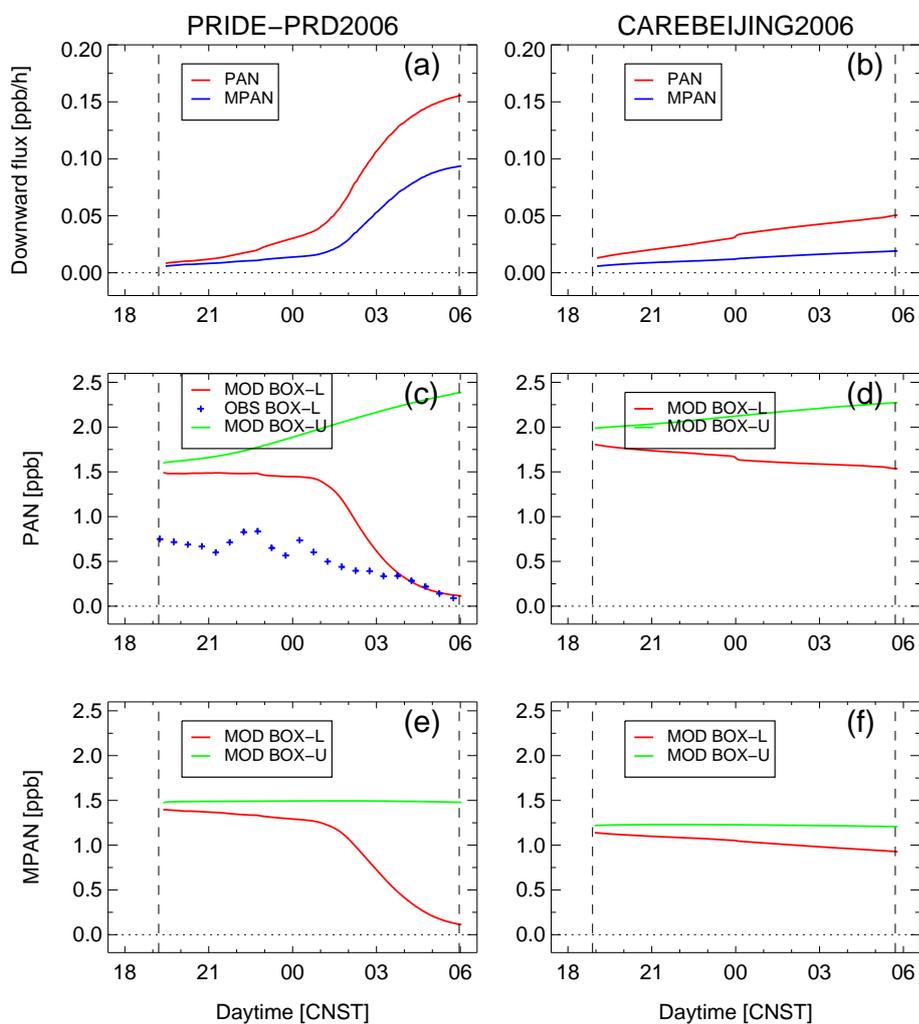


Fig. 12. Estimated fluxes of PAN and MPAN transported downward from the residual layer to the stable surface layer during PRIDE-PRD2006 (a) and CAREBEIJING2006 (b). In the lower layer, the transported compounds decompose thermally and produce peroxy radicals at a rate approximately equal to the downward fluxes. The observed (if available) and modelled PAN and MPAN concentrations are shown in (c)-(f).