Radical chemistry in the Pearl River Delta: observations and modeling of OH and HO_2 radicals in Shenzhen 2018

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Abstract. The ambient radical concentrations were measured continuously by laser-induced fluorescence during the STORM (STudy of the Ozone foRmation Mechanism) campaign at the Shenzhen site, located in the Pearl River Delta in China, in autumn 2018. The diurnal maxima were 4.5×10^6 cm^{-3} for OH and 4.5×10^8 cm^{-3} for HO_2 (including an estimated interference of 23%-28% from RO_2 radicals during the daytime), respectively. The state-of-the-art chemical mechanism underestimated the observed OH concentration, similar to the other warm-season campaigns in China. The OH underestimation was attributable to the missing OH sources, which can be explained by the X mechanism. Good agreement between the observed and modeled OH concentrations was achieved when an additional numerical X equivalent to 0.1 ppb NO concentrations was added to the base model. The isomerization mechanism of RO_2 derived from isoprene contributed approximately 7% to the missing OH sources and the oxidation of isoprene oxidation products (MACR and MVK) had no significant impact on the missing OH sources, demonstrating further exploration of unknown OH sources is necessary. Photolysis reactions dominated the ROx primary production rate. The HONO, O_3, HCHO, and carbonyls photolysis accounted for 29%, 16%, 16%, and 11% during the daytime, respectively. The ROx termination rate was dominated by the reaction of OH + NO_2 in the morning, and thereafter the radical self-combination gradually became the major sink of ROx in the afternoon. As the sum of the respective oxidation rates of the pollutants via reactions with oxidants, the atmospheric oxidation capacity was evaluated, with a peak of 11.8 ppb h^{-1} around noontime. The ratio of $P(O_3)$ to AOC_{VOCs}, which indicates the O_3 production from VOCs oxidation, trended to increase and then decrease as the NO concentration increased. Additionally, the maximum of the ratios existed when the NO concentration was approximately 1 ppb, with a median of about 2, indicating that the yield of ozone production from VOCs oxidation was about 2 in this campaign.

1 Introduction

Severe ambient ozone (O_3) pollution is one of China's most significant environmental challenges, especially in urban areas (Shu et al., 2020; Li et al., 2019; Wang et al., 2020; Ma et al., 2019b; Wang et al., 2017). Despite the reduction in emissions of O_3 precursors, O_3 concentration is increasing, especially in urban cities. The O_3 average trends for the focus megacity clusters are 3.1 ppb a^{-1}, 2.3 ppb a^{-1}, 0.56 ppb a^{-1}, and 1.6 ppb a^{-1} for North China Plain (NCP), Yangtze River Delta (YRD), Pearl River Delta (PRD), and Szechwan Basin (SCB), respectively (Li et al., 2019). The nonlinearity between O_3 and precursors illustrates that it is necessary to explore the cause of O_3 production. The tropospheric O_3 is only generated in the photolysis of nitrogen dioxide (NO_2), produced as the by-product within the radical cycling. Thus, the investigation of radical chemistry is critical to controlling secondary pollution.

Hydroxyl radicals (OH), the dominant oxidant, control the atmospheric oxidation capacity (AOC) in the troposphere. The OH radicals convert primary pollutants to secondary pollutants and are simultaneously transformed into peroxy radicals (HO_2 and RO_2). Within the interconvert of ROx (= OH, HO_2, and RO_2), secondary pollutants are generated, and thus the further exploration of radical chemistry is significant. The radical closure experiment, an effective indicator for testing our understanding of radical chemistry, has been conducted since the central role of OH radicals was recognized in the 1970s (Levy, 1971; Hofzumahaus et al., 2009). The underestimation of OH radicals inenvironments characterized by low nitrogen oxides (NO) and high volatile organic compounds (VOCs) has been identified (Lu et al., 2013; Lu et al., 2012; Tan et al., 2017; Tan et al., 2019; Yang et al., 2021; Hofzumahaus et al., 2009; Lelieveld et al., 2008; Whalley et al., 2011). New radical mechanisms involving unclassical OH regeneration have been proposed, including Leuven Isoprene Mechanism (LIM) and X mechanism (Peeters and Muller, 2010; Peeters et al., 2014; Peeters et al., 2009; Hofzumahaus et al., 2009). The LIM has been incooperated into the current mechanism and is still insufficient to explain the OH missing sources. The X mechanism was identified several times, but the amount of the numerical species, X, varied in different environments, and the nature of X is unknown (Hofzumahaus et al., 2009; Lu et al., 2013; Lu et al., 2012; Tan et al., 2017; Tan et al., 2019; Yang et al., 2021). Therefore, further exploration of radical regeneration sources is necessary.

Due to the strong photochemistry influenced by high temperatures, high O_3 pollution appeared to occur in YRD and PRD, especially in PRD (Ma et al., 2019b; Wang et al., 2017). Radicals, the dominant oxidant in the troposphere, have been measured during warm seasons in NCP (Yufa 2006, Wangdu 2014, and Beijing 2016), YRD (Taizhou 2018), SCB (Chengdu 2019), and PRD (Backgarden 2006, and Heshan 2014) in China (Lu et al., 2013; Lu et al., 2012; Tan et al., 2017; Tan et al., 2019; Yang et al., 2021; Tan et al., 2021). The radical observations in PRD, where the cities are suffering from severe O_3 pollution, have not been conducted since 2014, and thus the oxidation capacity here has not been clear in recent years. Therefore, we carried out a continuous comprehensive field campaign (STudy of the Ozone foRmation Mechanism - STORM) involving radical observations in Shenzhen, one of the megacities in PRD, in autumn 2018. Overall, the following will be reported in this study.

(1) The observed radical concentrations, and the comparison between the radical observations and simulations.

(2) The exploration of the unclassical OH regeneration sources based on the experimental budget.

(3) The sources and sinks of radicals.

(4) The evaluation of the atmospheric oxidation capacity.

2 Methodology

2.1 Measurement site and instrumentation

The STORM campaign was conducted from September to October 2018 in Peking University Shenzhen Graduate School (22.60 deg N, 113.97 deg E), in the west of Shenzhen, Guangdong province. As shown in Fig. 1, this site, which belongs to the urban site, is located in the university town, and is surrounded by residential and commercial areas. The northwest of the site is close to the Shenzhen Wildlife Park, and the northeast is close to the Xili Golf Club (Yu et al., 2020). The Tanglang Mountain Park with active biogenic emissions is located about 1 km southeast of the site. Overall, this site has no significant local pollution sources nearby, but can represent the urban pollution characteristics (Huang et al., 2012b; Huang et al., 2012a; Gao et al., 2018).

Figure 1: Geographical location and surrounding environmental conditions of the measurement site in STORM campaign (The maps are from https://map.baidu.com).

Most instruments were set up on the top of a four-story academic building (about 20 m). Besides HOx radicals measured by the Peking University Laser-Induced Fluorescence system (PKU-LIF) (see the details in Sect. 2.2), a comprehensive set of trace gases was conducted to support the exploration of the radical chemistry, including meteorological parameters (temperature, pressure, relative humidity), photolysis frequency, OH reactivity (k_{OH}) and the trace gases (NO, NO_2, O_3, VOCs, *etc.*). k_{OH} was measured by the laser flash photolysis-laser induced fluorescence (LP-LIF) system. Most of the inorganic trace gases (O_3, CO, NO, NO_2, and SO_2) were simultaneously measured by two sets of instruments, and good agreement was achieved within the uncertainty. VOCs (aldehydes, alkenes, aromatics, isoprene, and oxygenated VOCs (OVOCs)) were

measured using a gas chromatograph following a mass spectrometer (GC-MS). In addition, HONO and HCHO were measured as well. Table S1 in the Supplementary Information describes the experimental details of the meteorological and chemical parameters during this campaign.

2.2 The OH and HO_2 measurements

The OH and HO_2 radicals were measured by Peking University laser-induced fluorescence system (PKU-LIF) based on the fluorescence assay by gas expansion (FAGE) technique. The principle has been reported in previous studies, only a brief description of the instrument is presented here. Further detailed information on the instrument can be found in previous studies (Heard and Pilling, 2003; Fuchs et al., 2008; Holland et al., 1995; Hofzumahaus et al., 1996; Fuchs et al., 2011).

In principle, OH resonance fluorescence is released in the OH excitation by a 308 nm pulsed laser, and then OH radicals are detected directly. HO_2 radicals are converted into OH via NO, and then they are detected. The system contains a laser module and a detection module. Ambient air was drawn into two independent, parallel, low-pressure (3.5 mBar) cells through two parallel nozzles with 0.4 mm diameter pinhole. The OH radicals are excited into resonance fluorescence in the OH detection cell and detected by micro-channel plate detectors (MCP). In the HO_2 detection cell, NO is injected and converts HO_2 to OH radicals, which then are excited by the laser and release resonance fluorescence. Besides, an OH reference cell in which a large OH concentration is generated by pyrolysis of water vapor on a hot filament is applied to automatically correct the laser wavelength.

Owing to the failure of the reference cell in this study, the NO mixing ratios injected into the HO_2 cell were set to be higher than that in other campaigns in China because the HO_2 cell needed to be used as a reference cell to correct laser wavelength. In this campaign, NO mixing ratios were switched between 25 ppm (low NO mode) and 50 ppm (high NO mode). We calculated the HO_2 conversion rates under the two different NO concentrations by calibrating the PKU-LIF system. HO_2 conversion rates in low NO mode ranged within 80%-95%, while those in high NO mode were over 100%, demonstrating that the HO_2 measurement was affected by RO_2 radicals. Prior studies have reported the relative detection sensitivities (α_{RO_2}) for the major RO_2 species, mainly from alkenes, isoprene and aromatics, when the HO_2 conversion rate was over 100% (Fuchs et al., 2011; Lu et al., 2012; Lu et al., 2013). Therefore, only the HO_2 observations in high NO mode were chosen and they were denoted as $[HO_2^*]$, which was the sum of the true HO_2 concentration and a systematic bias from the mixture of RO_2 species *i* which were detected with different relative sensitivities $\alpha^i_{RO_2}$, as shown in Eq. (1) (Lu et al., 2012). The true HO_2 concentration was difficult to calculated because the RO_2 concentration measurements and their speciation were not available. Herein, we simulated the HO_2 and HO_2^* concentrations by the model. The interference from RO_2 radicals was estimated to be the difference between the modeled HO_2 and HO_2^* concentrations.

$$[HO_2^*] = [HO_2] + \sum(\alpha^i_{RO_2} \times [RO_2]_i) \quad (1)$$

Additionally, prior studies reported that OH measurement might be affected by the potential interference, when the sampled

air contained ozone, alkenes and BVOCs (Mao et al., 2012; Fuchs et al., 2016; Novelli et al., 2014), indicating the environmental conditions are important to the production of interference. The pre-injector is usually used to test the potential OH interference, and has been applied to our PKU-LIF system to quantify the possible interferences for several campaigns, including the campaigns conducted in Wangdu, Heshan, Huairou, Taizhou and Chengdu sites (Tan et al., 2017; Tan et al., 2019; Tan et al., 2018; Yang et al., 2021). No significant internal interference was found in the prior studies, demonstrating the accuracy of the PKU-LIF system has been determined for several times. Moreover, to further explore the potential interference in this campaign, we compared the major environmental conditions, especially O_3, alkenes and isoprene, between Shenzhen and Wangdu sites, as shown in the Supplementary Information. The environmental condition in Shenzhen was less conducive to generating interference than that in Wangdu, and the details were presented in the Supplementary Information. Therefore, it is not expected that the OH measurements in this campaign were affected by the internal interference. Overall, the measurement uncertainties of OH and HO_2^* radicals were 11% and 15%, respectively, as shown in Table S1 in the Supplementary Information.

2.3 Closure experiment

As an effective tool to explore the atmospheric radical chemistry, the radical closure experiment can investigate the state-of-the-art chemical mechanism because of the extremely short lifetime of radicals (Stone et al., 2012; Lu et al., 2019). A zero-dimensional box model was used to conduct the radical closure experiment, and the overall framework was reported by Lu et al. (2019). In this work, we conducted the radical closure experiment based on the Regional Atmospheric Chemical Mechanism updated with the latest isoprene chemistry (RACM2-LIM1), as Tan et al. (2017) described in detail. The model was constrained to the measured meteorological, photolysis frequency, and the critical chemical parameters (CO, NO, NO_2, VOCs, *etc.*). The H_2 and CH_4 mixing ratios were set to 550 ppb and 1900 ppb, respectively. The model was operated in time-dependent mode with a 5-min time resolution, and a 2-d spin-up time was to make the unconstrained species approach the steady state relative to the constrained species.

As Lu et al. (2012) described, there are two types of radical closure experiment. One is the comparison of observed and modeled radical concentrations, and the other is the comparison of radical production and destruction rates. The most significant difference between the above is that the latter is conducted with the observed radical concentrations and k_{OH} constrained. The comparison of radical production and destruction rates, also called radical experimental budget, can test the accuracy of the state-of-the-art chemistry mechanisms based on the equivalent relationship between the radical production and destruction rates. The production rates of OH, HO_2, and RO_2 radicals are quantified from all the known sources. The destruction rates of HO_2 and RO_2 radicals are the sum of the known sources. The OH destruction rate can be directly calculated as the product of the observed OH concentrations and the observed k_{OH} (Tan et al., 2019; Yang et al., 2021). The OH destruction rate

is the total sinks of OH radicals because of the direct k_{OH} observation, and thus the discrepancy between the OH destruction and production rates denotes the missing OH sources. The detailed reactions and the reaction rate constants related to OH, HO_2, and RO_2 radicals can be found in Tan et al. (2019) and Yang et al. (2021).

2.4 AOC evaluation

The life time of the trace gases is controlled not only by the oxidant concentration but also by its second-order rate constant, so the atmospheric oxidation capacity (AOC) proposed by Geyer et al. (2001) is most suitable to evaluate the relative importance of each oxidant (Elshorbany et al., 2009). AOC is the core driving force of complex air pollution, and determines the removal rate of trace gases and the production rates of secondary pollutants (Liu et al., 2021). As an effective indicator for atmospheric oxidation intensity, the evaluation of AOC can provide crucial information on the atmospheric composition of harmful and climate forcing species (Elshorbany et al., 2009). AOC is defined as the sum of the respective oxidation rates of the pollutants via reactions with oxidants (Elshorbany et al., 2009; Geyer et al., 2001; Zhu et al., 2020). According to the definition of AOC, it can be calculated by the Eq. (2).

$$\mathrm{AOC} = \sum_i k_{Y_i}[Y_i][X] \quad (2)$$

where Y_i are the pollutants (CO, CH_4, and VOCs), X are the main atmospheric oxidants (OH, O_3, NO_3), and k_{Y_i} is the bi-molecular rate constant for the reaction of Y_i with X. AOC includes all combination of pollutants *Y* and oxidants *X*. The higher AOC, the higher removal rate of the most pollutants, and thus the higher production rate of secondary pollutants (Yang et al., 2020a). Simultaneous measurements of OH and the key trace gases are available in the study. NO_3 concentration could be simulated by the box model with the observed parameters constrained.

3. Results

3.1 Meteorological and chemical conditions

Figure 2 gives an overview of the meteorological and chemical parameters from 05 October to 28 October 2018, when OH and HO_2 radicals were measured. The diurnal variations of the temperature (T), relative humidity (RH), $j(O^1D)$, and $j(NO_2)$ followed a regular pattern from day to day. The overall meteorological conditions were characterized by high temperature (about 20~30 °C), high relative humidity (60~80%), and intensive radiation with $j(O^1D)$ up to 2.0×10^{-5} s^{-1} and $j(NO_2)$ up to 6.0×10^{-3} s^{-1}. The relative humidity and photolysis-frequency in this autumn campaign were similar to those in the summer campaign conducted at Chengdu site (Yang et al., 2021). The temperature in this campaign was lower than that at Chengdu site, but similar to that in the autumn campaign at Heshan site located in PRD as well (Tan et al., 2019; Yang et al., 2021).

The concentration of CO showed weak diurnal variation, indicating there was the non-obvious accumulation of anthropogenic emissions on a regional scale. NO concentration peaked at 12 ppb during morning rush hour when the traffic

emission was severe, and thereafter, O_3 concentration started to increase with the decreasing of NO concentration. The maxima of O_3 hourly concentration were high up to 120 ppb. According to the updated National Ambient Air Quality Standard of China (GB3095-2012), O_3 concentration exceeded the Class-II limit values (hourly averaged limit 93 ppb) on several days (6, 7, 8, and 26 October) when the environmental condition was characterized by high temperature and low relative humidity. NO_2 concentration was high at night because of the titration effect of O_3 with NO.

Along with the high O_3 concentration on 6, 7, 8, and 26 October, high HCHO concentration was also recorded during the corresponding periods, indicating HCHO was mainly produced as secondary pollutions because of the active photochemistry in this campaign. Isoprene, mostly derived from biogenic emissions and mainly affected by temperature, peaked around noontime. Tan et al. (2019) reported the median concentration of HCHO and isoprene concentrations were 6.8 ppb and 0.6 ppb during 12:00-18:00 at Heshan site. Similarly, the median concentration of HCHO and isoprene concentrations in this study were 4.9 ppb and 0.4 ppb during the corresponding periods, respectively. As a proxy for traffic intensity, the toluene to benzene ratio (T/B), which is below 2, means the traffic emissions are the major sources of VOCs (Brocco et al., 1997). The T/B gradually dropped from 07:00 until it reached the minimum value at 09:00, indicating traffic emission contributed more to VOCs during morning rush hour than during other periods. However, the T/B, which varied within a range of 7-12, was above 2, and thus VOCs emission during this campaign was mainly from other sectors such as those involving solvent evaporation.

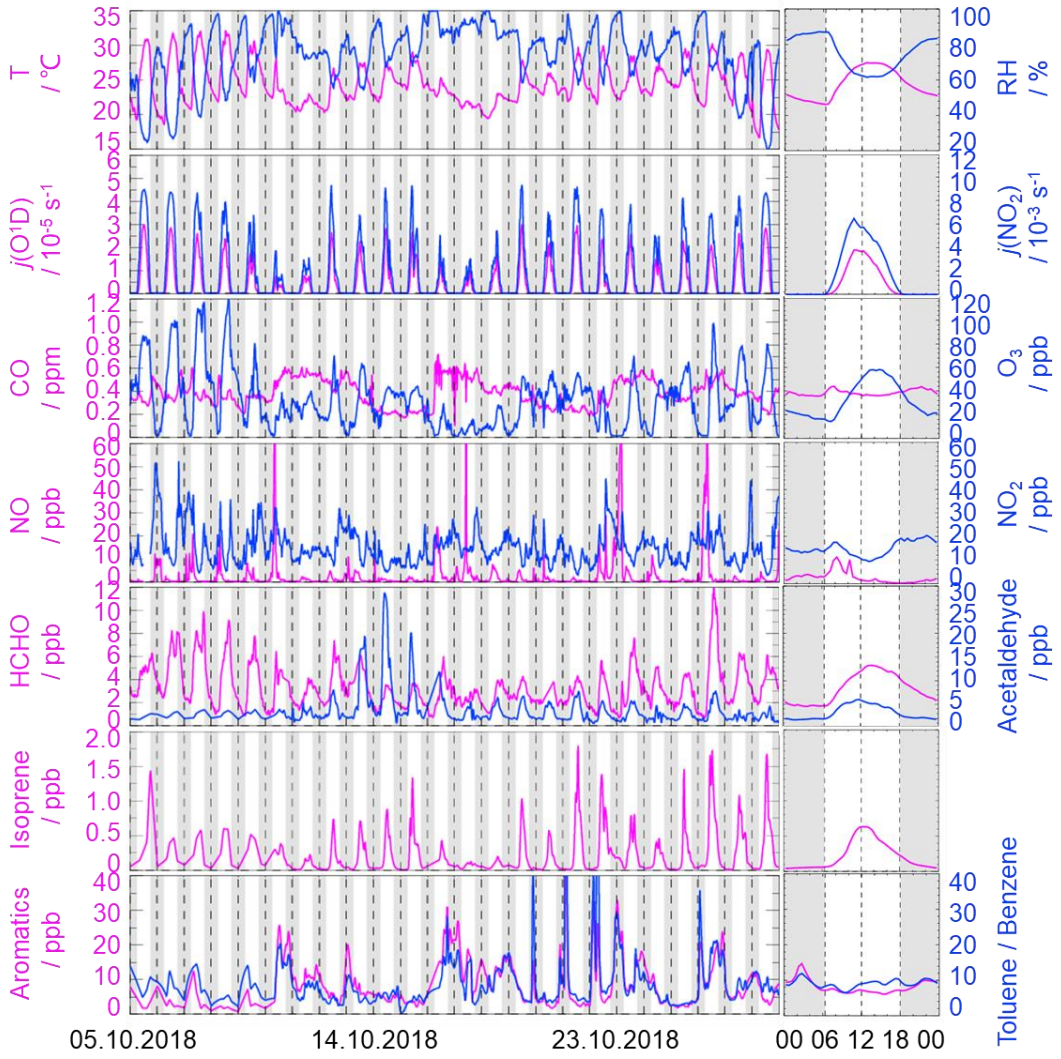

Figure 2: Timeseries and diurnal profiles of the observed meteorological and chemical parameters in STORM campaign. The grey areas denote nighttime.

Moreover, we compared the environmental conditions between the Backgarden (rural site), Heshan (suburban site), and Shenzhen (urban site) campaigns conducted in PRD in Table S3 in the Supplementary Information. No significant discrepancy in temperature was found in the Shenzhen and Heshan campaigns, which were both conducted in autumn. The temperature in the Backgarden campaign conducted in summer was higher than those in Shenzhen and Heshan. The relative humidity in Shenzhen and Backgarden was higher than that in Heshan. Compared to the chemical conditions in the Heshan campaign conducted in autumn as well, the concentrations of CO, NO, NO_2, HONO, alkenes, aromatics, and HCHO in Shenzhen were lower, which might be because there were no significant local pollution sources nearby in the Shenzhen site although it was an urban site. However, the concentration of O_3 which is the typical secondary pollutant in Shenzhen was higher than that in Heshan. Compared to the environmental conditions in Heshan, the higher O_3 concentration in Shenzhen might benefit from the weather condition which was characterized by the stronger solar radiation and slightly higher temperatures.

3.2 Observed and modeled OH and HO_2 radicals

The OH and HO_2 radicals were measured during 05-28 October 2018. The timeseries of the observed and modeled HOx concentrations are displayed in Fig. S1 (a-b) in the Supplementary Information. Data gaps were caused by the rain, calibration,

and maintenance. The daily maxima of the observed OH and HO_2^* concentrations varied in the range of (2-9) × 10^6 cm^{-3} and (2-14) × 10^8 cm^{-3}, respectively. As in previous campaigns, the largest OH concentrations appeared around noontime and showed a high correlation with $j(O^1D)$, a proxy for the solar UV radiation driving much of the primary radical production (Tan et al., 2019).

Figure 3 (a-b) shows the diurnal profiles of the observed and modeled HOx concentrations. The HOx radicals showed similar diurnal behavior to those reported in other campaigns (Ma et al., 2019a; Tan et al., 2017; Tan et al., 2019; Tan et al., 2018; Yang et al., 2021). The observed OH and HO_2^* concentrations reached a maximum around 12:00 and 13:30, respectively. The diurnal maxima of the observed and modeled OH concentrations were 4.5 × 10^6 cm^{-3} and 3.5 × 10^6 cm^{-3}. Compared to the other campaigns conducted in PRD (Backgarden and Heshan), the diurnal maximum of the observed OH concentration in Shenzhen was equal to that observed in Heshan, and much lower than that observed in Backgarden where the observed OH concentration was nearly 15 × 10^6 cm^{-3} (Hofzumahaus et al., 2009; Tan et al., 2019). The higher OH concentration in Backgarden site was closely correlated to the stronger solar radiation, as shown in Table S3 in the Supplementary Information. The diurnal observed and modeled OH concentrations agreed within their 1-σ uncertainties of measurement and simulation (11% and 40%). However, when the NO mixing ratio (Fig. 2) dropped from 10:00 gradually, a systematic difference existed, with the observed OH concentration being about 1 × 10^6 cm^{-3} higher than the modeled OH concentration. The OH concentrations observed in the environments with low NO levels were underestimated by the state-of-the-art models at Backgarden (summer) and Heshan (autumn) sites in PRD as well, and the OH underestimation was identified to be universal at low NO conditions in China (Lu et al., 2013; Lu et al., 2012; Ma et al., 2019a; Tan et al., 2017; Yang et al., 2021). The reasons on OH underestimation was further discussed in Section 4.1.

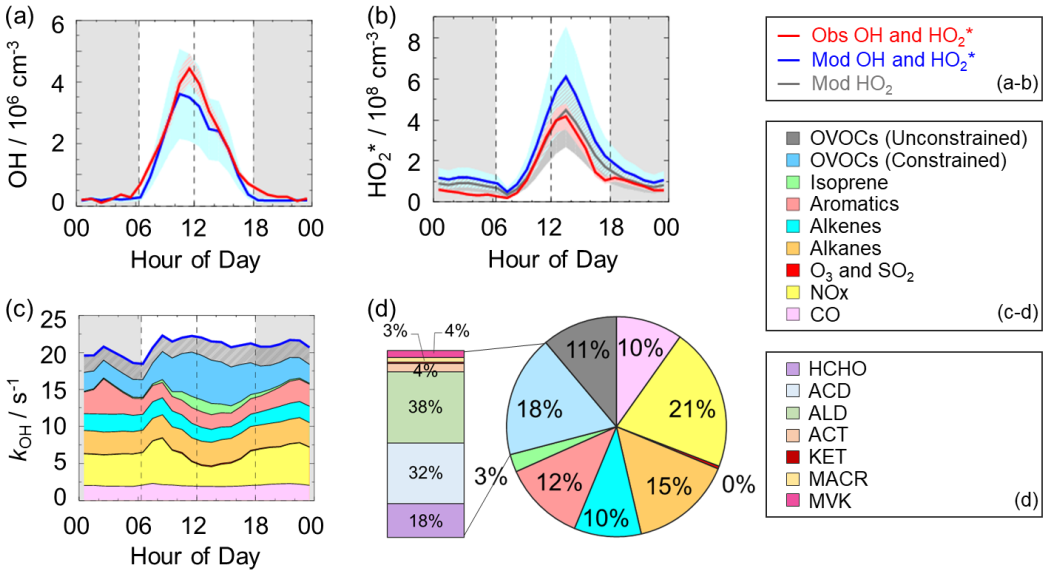

Figure 3: (a-b) The diurnal profiles of the observed and modeled OH, HO_2^* and HO_2 concentrations. (c) The diurnal profiles of the modeled k_{OH}. (d) The composition of the modeled k_{OH}. The red areas in (a-b) denote 1-σ uncertainties of the observed OH and HO_2^*

concentrations. The blue areas in (a-b) denote 1-σ uncertainties of the modeled OH and HO_2^* concentrations, and the grey area in (b) denotes 1-σ uncertainties of the modeled HO_2 concentrations. The grey areas in (a-c) denote nighttime. ACD denotes acetaldehydes. ALD denotes the C3 and higher aldehydes. ACT and KET denote acetone and ketones. MACR and MVK denote methacrolein and methyl vinyl ketone.

The diurnal maximum of the observed HO_2^*, the modeled HO_2^* and the modeled HO_2 concentrations were 4.2×10^8 cm^{-3}, 6.1×10^8 cm^{-3}, and 4.4×10^8 cm^{-3}, respectively. The difference between the modeled HO_2^* and HO_2 concentrations can be considered a modeled HO_2 interference from RO_2 (Lu et al., 2012). The RO_2 interference was small in the morning, while it became larger in the afternoon. It ranged within 23%-28% during the daytime (08:00-17:00), which was comparable with those in the Backgarden and Yufa sites in China, Borneo rainforest in Malaysia (OP3 campaign, aircraft), and UK (RONOCO campaign, aircraft) (Lu et al., 2012; Lu et al., 2013; Jones et al., 2011; Stone et al., 2014). The observed HO_2^* was overestimated by the model, indicating the HO_2 heterogeneous uptake might have a significant impact during this campaign. The diurnal maximum of HO_2^* concentration observed in Shenzhen was much lower than those observed in the Yufa and Backgarden sites (Hofzumahaus et al., 2009; Lu et al., 2012; Lu et al., 2013). The high modeled HO_2/OH ratio around noontime (11:00-15:00), which was about 138, was found in this campaign, which was higher than those in the Backgarden and Chengdu sites (Yang et al., 2021; Hofzumahaus et al., 2009). High HO_2/OH ratio is normally found only in clean air at low concentrations of NOx (Hofzumahaus et al., 2009; Stevens et al., 1997). As an indicator that can reflect the interconversion reaction between HO_2 and OH, the conversion efficiency in this campaign was slightly slower than that in the Backgarden and Chengdu sites.

3.3 OH reactivity

k_{OH} is the pseudo-first-order loss rate coefficient of OH radicals, and it is equivalent to the reciprocal OH lifetime (Fuchs et al., 2017; Lou et al., 2010; Yang et al., 2019). In this campaign, k_{OH} was measured only for several days (05-19 October 2018) by the LIP-LIF system, which has been reported in the previous study (Liu et al., 2019). The timeseries of the observed and modeled k_{OH} during 05-19 October 2018 are presented in Fig. S2 in the Supplementary Information. A good agreement between the observed k_{OH} and modeled k_{OH} within the uncertainties was achieved, and thus the model can be believed to reproduce the observed k_{OH} values within the whole campaign. Moreover, to reflect the k_{OH} in the whole campaign, the modeled values were shown in the k_{OH} diurnal profiles (Fig. 3c) during 05-28 October 2018. The modeled k_{OH} showed weak diurnal variation and varied from 18 s^{-1} to 22 s^{-1}. Compared to the k_{OH} variation in Shenzhen, the k_{OH} observed in Backgarden and Heshan sites in PRD showed a stronger diurnal variation, with a minimum value at around noontime and a maximum value at daybreak. The k_{OH} ranges in Backgarden and Heshan sites were 20-50 s^{-1} and 22-32 s^{-1} (Lou et al., 2010; Tan et al., 2019). Similar with the good agreement between the observed and modeled k_{OH} during the several days in Shenzhen, the observed k_{OH} in Backgarden was matched well with the modeled k_{OH} which has included the OVOCs reactivity. In terms of the k_{OH} in Heshan, Tan et al. (2019) reported that only half of the observed k_{OH} was explained by the calculated k_{OH} which was calculated from the measured

trace gas concentrations. The missing k_{OH} in Heshan was likely caused by unmeasured VOCs, demonstrating the necessary to measure more abundant VOCs species, especially OVOCs species.

As shown in Fig. 3(d), we presented the composition of modeled k_{OH}. The inorganic compounds contributed approximately 31% to k_{OH}, in which the CO and NOx reactivity accounted for 10% and 21%, respectively. The NOx reactivity was displayed versus time, with a maximum during the morning peak. The peak concentration during the morning peak was associated with traffic emissions.

Compared with the inorganics reactivity, the larger fraction of k_{OH} came from the VOCs group, with a contribution of 69% to k_{OH}. The contribution of alkanes, alkenes, and aromatics were 15%, 10%, and 12%, respectively. The isoprene reactivity related to temperature was mainly concentrated during the daytime, whereas the aromatics reactivity at night was higher. As for the OVOCs species, we measured several OVOCs species, including HCHO, acetaldehydes (ACD) and higher aldehydes (ALD), acetone (ACT), ketones (KET) and isoprene oxidation products (MACR and MVK), so we constrained these species in the model. The constrained OVOCs species accounted for 18% in the total k_{OH}, where HCHO, ACD, and ALD were the major contributors, with contributions of 18%, 32%, and 38% to the constrained OVOCs, respectively. The contribution of aldehydes in this study (16%) was larger than that in Beijing (Whalley et al., 2021) and smaller with that in Wangdu (Fuchs et al., 2017). The remaining reactivity was attributed to the unconstrained OVOCs reactivity, which came from the model-generated intermediate species (glyoxal, methylglyoxal, methyl ethyl ketone, methanol, etc.), with a contribution of 11% to the total k_{OH}. Large fraction of OVOCs reactivities in k_{OH} was also found in some previous studies (Lou et al., 2010; Lu et al., 2013; Fuchs et al., 2017; Whalley et al., 2021). About 50% of k_{OH} was explained by OVOCs in Backgarden site, and HCHO, ACD and ALD, and oxygenated isoprene products were the most important OH reactants in OVOCs, with a contribution of 30-40%, and other 10-20% came from other oxygenated compounds (ketones, dicarbonyl compounds, alcohols, hydroperoxides, nitrates etc.) (Lou et al., 2010). HCHO, ACD, MVK, MVCR and glyoxal accounted for one-third of the total k_{OH} in Wangdu site (Fuchs et al., 2017). The large unconstrained OVOCs reactivity indicated it is necessary to measure more VOCs species in the future.

4. Discussion

4.1 Radical closure experiment

In this study, we conducted OH radical closure experiment which is called OH experimental budget as well. As discussed in Section 3.3, it is believed that the model can reproduce the observed k_{OH}. Herein, to conduct the OH experiment budget in the whole campaign, we used the modeled k_{OH} to calculate the OH destruction rate because the k_{OH} was only measured on several days. The diurnal profiles of OH production and destruction rates, and compositions of OH production rate were displayed in Fig. 4, with maxima of 14 ppb h^{-1} and 17 ppb h^{-1} around noontime, respectively. The OH production rate from known sources

is quantified from the primary sources (photolysis of HONO, photolysis of O_3, ozonolysis of alkenes) and secondary sources (dominated by HO_2 + NO, and HO_2 + O_3). The primary and secondary sources were account for 78% and 22% of the total calculated production rate, respectively. Similar with the prior studies, the largest fraction of OH production rate comes from HO_2 + NO, with a contribution up to 76% of the known OH production rate. The contributions of HONO and O_3 photolysis were 13% and 7% to the primary production rate.

The OH production rate matched well with the destruction rate only in the early morning to about 10:00. Thereafter, the OH destruction rate was larger than the production rate, which could explain the underestimation of OH concentration by the model. The discrepancy between the OH production and destruction rates was attributed the missing OH sources. The biggest additional OH source was approximately 4.6 ppb h^{-1}, which occurred at about 12:00, when the OH production and destruction rates were 11.9 ppb h^{-1} and 16.5 ppb h^{-1}, respectively. The unknown OH source accounted for about one third of the total OH production rate, indicating the exploration of missing OH source was significant to study the radical chemistry. It is noted that the OH production rate was overestimated because we used HO_2^* concentrations instead of HO_2 concentrations here. Thus, the missing OH source was the lower limit here, demonstrating more unknown OH sources need to be further explored. Details on unknown OH sources are given below (Sect. 4.2).

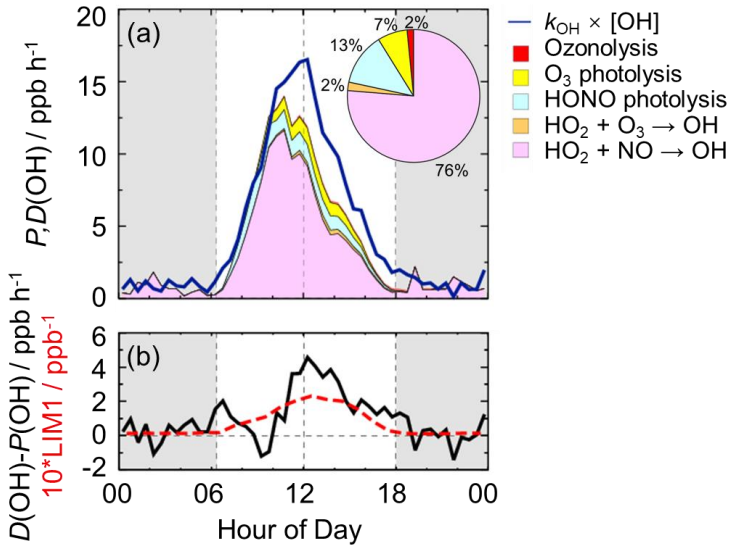

Figure 4: (a) The diurnal profiles of OH production and destruction rates and the proportions of different known sources in the calculated production rate during the daytime. The blue line denotes the OH destruction rate, and the colored areas denote the calculated OH production rates from the known sources. (b) The missing OH source which was the discrepancy between the OH destruction and production rates, and the OH production rate which was ten times the production rate derived from LIM1 mechanism. The grey areas denote nighttime.

4.2 Radical chemistry in low NO regime

4.2.1 Influencing factors of OH underestimation

As analyzed in Sect. 4.1, the underestimation of OH concentration was attributable to the missing OH source. It is necessary

to explore the influencing factor for gaining further insight into the missing source. Scientists reported that more significant OH underestimation would appear with the decreasing NO concentration and increasing isoprene concentration (Lu et al., 2012; Ren et al., 2008; Hofzumahaus et al., 2009; Lelieveld et al., 2008; Whalley et al., 2011; Tan et al., 2017; Yang et al., 2021). Herein,we further explored the effect of NO concentration on missing OH source. NO dependence of OH and HO_2 radicals was illustrated in Fig. 5. The OH concentrations were normalized by the averaged $j(O^1D)$ to eliminate the influence of radiation on radicals. The OH concentration showed a increasing trend with the increase of NO concentrations in low NO regime (below 1 ppb) due to the increased OH radicals from propagation via peroxy reactions with NO, and then decreased with the increase of NO concentrations in high NO regime (above 1 ppb) due to the loss by the reaction of OH with NO_2 (Ehhalt, 1999). The base model can reproduce the observed OH concentration in high NO regime and underestimate OH concentration in low NO regime. As for HO_2^* radicals, the observed and modeled HO_2^* concentrations decreased with the increase of NO concentrations. The model overestimated the observations, indicating the heterogeneous uptake might make a significant role in HO_2 sinks in this campaign. Overall, NOx (= NO + NO_2) plays a crucial role in radical chemistry due to the impact of NO on radical propagation and termination reactions.

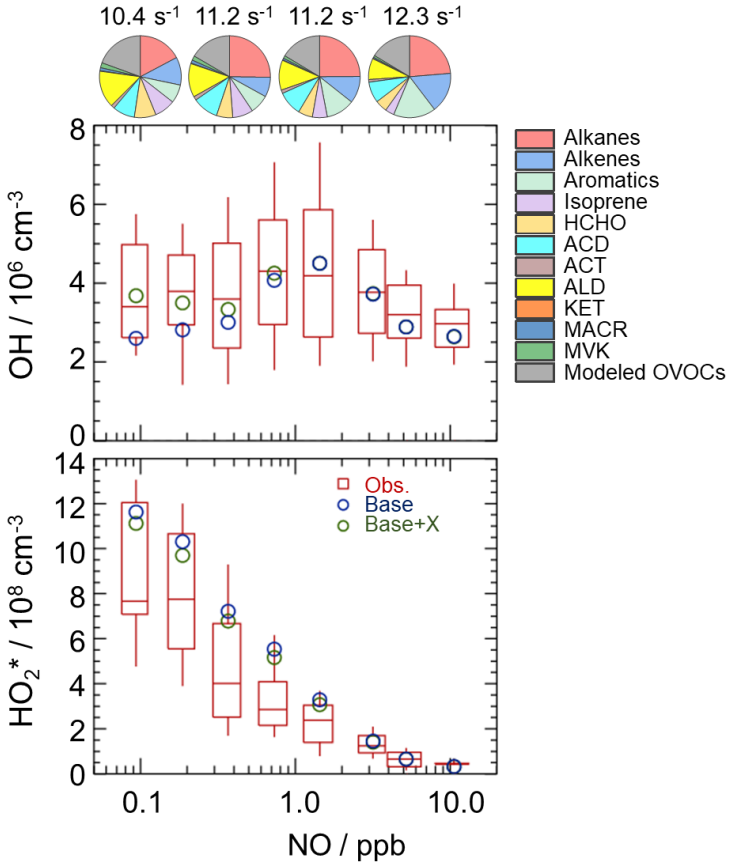

Figure 5: NO dependence of OH and HO_2^* radicals. The red box-whisker plots give the 10%, 25%, median, 75%, and 90% of the HOx observations. The blue circles show the median values of the HOx simulations by the base model, and the green circles show the HOx simulations by the model with X mechanism. Total VOCs reactivity and their organic speciation are presented by pie charts at the different NO intervals at the top. Only daytime values and NO concentration above the detection limit of the instrument were

chosen. ACD and ACT denote acetaldehyde and acetone, respectively. ALD denotes the C3 and higher aldehydes. KET denotes ketones. MACR and MVK, which are both the isoprene oxidation products, denote methacrolein and methyl vinyl ketone, respectively.

To further explore the influencing factors of OH underestimation, we presented the speciation VOCs reactivity under the different NO intervals, as shown in Fig. 5 and Table S4 in the Supplementary Information. The isoprene reactivity and total OVOCs reactivity (the sum of HCHO, ACD, ACT, ALD, KET, MACR, MVK and the modeled OVOCs) increased with the decrease of NO concentrations, while the anthropogenic VOCs reactivity (alkanes, alkenes and aromatics) was higher in high NO regime. Additionally, the O_3 concentration in low NO regime was significantly higher than those in high NO regime, and the temperature was slightly higher in low NO regime, demonstrating the photochemistry was more active in low NO regime in this campaign. Overall, the photochemistry and composition of VOCs reactivity, especially the isoprene and OVOCs species (mainly ACD, ACT and the modeled OVOCs), might closely impact the missing OH sources.

4.2.2 Quantification of missing OH sources

Hofzumahaus et al. (2009) proposed an existence of a pathway for the regeneration of OH independent of NO, including the conversions of $RO_2 \rightarrow HO_2$ and $HO_2 \rightarrow OH$ by a numerical species called X. With a retrospective analysis, the unclassical OH recycling pathway was identified to be universal at low NO conditions in China. The amount of X varies with environmental conditions, and the X concentrations were 0.85 ppb, 0.4 ppb, 0.1 ppb, 0.4 ppb, and 0.25 ppb at Backgarden, Yufa, Wangdu, Heshan, and Chengdu sites (Hofzumahaus et al., 2009; Lu et al., 2012; Lu et al., 2013; Tan et al., 2017; Yang et al., 2021).

In this study, we tested this unclassical X mechanism. Good agreement between observations and simulations of OH radicals was achieved when a constant mixing ratio of 0.1 ppb of X was added into the base model. As shown in Fig. 5, the model with X mechanism agreed with the observed OH concentrations even at low NO conditions. Unclassical OH recycling was identified again in this study. However, X is an artificial species that behaves like NO, and thus the nature of X is still unknown to us. Compared to Shenzhen site, the required X concentration in the Backgarden and Heshan sites in PRD were higher, which might be affected by the different air masses in the three sites. The k_{OH} in Shenzhen site was much lower than those in Backgarden and Heshan sites, and the weaker diurnal variation of k_{OH} in Shenzhen was observed. Under the influence of the East Asian monsoon, the prevailing wind for PRD area is mostly southerly during the summer months and mostly northerly during the winter months (Fan et al., 2005; Zhang et al., 2008). The Backgarden site is located in Guangzhou, and the Heshan site is located in Jiangmen. The two cities are along the north-south axis, and thus the air masses of the Backgarden and Heshan sites are intimately linked with each other, while the air mass in Shenzhen is more similar to Hongkong (Zhang et al., 2008). Therefore, further exploration on this unclassical OH recycling is needed to improve our understanding of radical chemistry.

As discussed in Section 4.2.1, isoprene and OVOCs might have potential influence on the missing OH source. RO_2

isomerization reactions have also been shown to be of importance for the atmospheric fate of RO_2 from isoprene (Peeters et al., 2009; Peeters et al., 2014). The latest isoprene isomerization mechanism, which is called LIM1, has been coupled into our current base model. However, LIM1 mechanism was not included in the OH experimental budget which was conducted with the observations constrained, as shown in Section 4.1. Herein, we evaluated the contribution of LIM1 mechanism to the missing OH sources, as shown in Fig. 4 (b). LIM1 mechanism can explain approximately 7% of the missing OH sources during 10:00-16:00, when the missing OH production rate and the OH production rate derived from LIM1 mechanism were 2.47 ppb h^{-1} and 0.17 ppb h^{-1}, respectively.

Additionally, prior studies also reported that OH regeneration might be achieved from the oxidation of MACR and MVK, which are the major first-generated products of isoprene (Fuchs et al., 2018; Fuchs et al., 2014). As a potential explanation for the high OH concentration, the impacts of MACR and MVK oxidation were evaluated here. The modification of MACR oxidation scheme added the H-migration reactions of MACR oxidation products (Fuchs et al., 2014). The modification of MVK oxidation scheme added the reactions of MVK oxidation products with HO_2 radicals and the H-migration reactions of MVK oxidation products (Fuchs et al., 2018). As presented in Fig. S3 in the Supplementary Information, no significant of the MACR and MVK oxidation schemes was found in this campaign.

Overall, a large part of missing OH sources was not explained by the isoprene chemistry. In the future, the impact of OVOCs species which was another potential OH source on missing OH sources need to be further evaluated.

4.3 Sources and sinks of ROx

The detailed analysis of radical sources and sinks was crucial to exploring radical chemistry. The experimental budget for HO_2 and RO_2 radicals could not be conducted because RO_2 was not measured during this campaign. Herein, we showed the simulated results by the base model. Figure 6 illustrates the diurnal profiles of ROx primary production rate (P(ROx)) and termination rate (L(ROx)), and the contributions of different channels during the daytime.

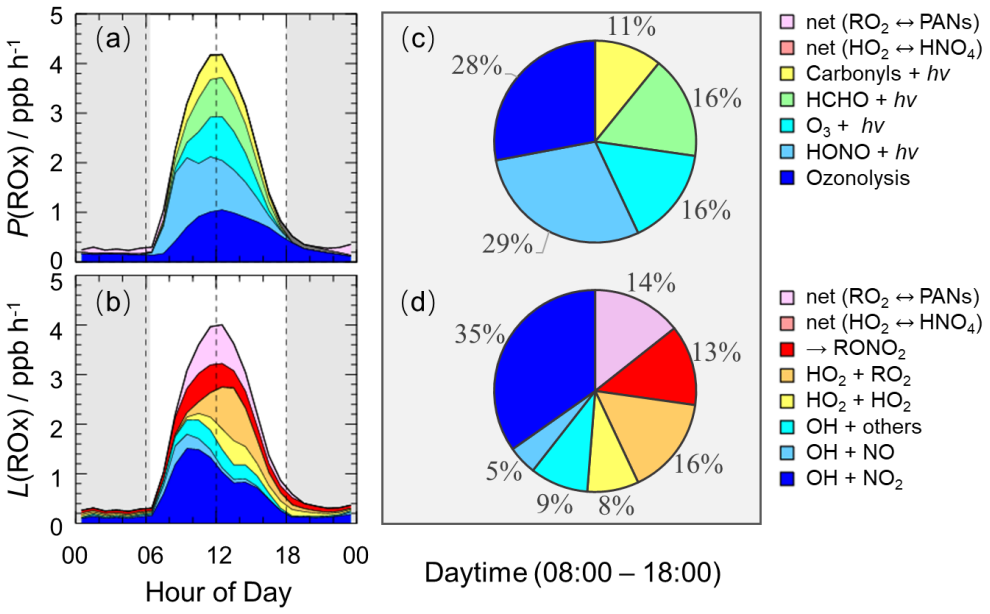

Figure 6: The diurnal profiles of ROx primary production rate (a) and termination rate (b) simulated by the base model, and the contributions of different channels to ROx primary production rate (c) and termination rate (d) during the daytime (08:00-18:00). The grey areas denote nighttime.

The ROx primary production and termination rates were basically in balance for the entire day, with maxima of 4 ppb h^{-1} around noontime. The ROx primary production rate was similar to those at Heshan (4 ppb h^{-1}) and Wangdu (5 ppb h^{-1}) sites, but lower than those at Backgarden (11 ppb h^{-1}), Yufa (7 ppb h^{-1}), and Chengdu (7 ppb h^{-1}) sites (Lu et al., 2013; Lu et al., 2012; Tan et al., 2017; Tan et al., 2019; Yang et al., 2021). During the daytime, the *P*(ROx) mainly came from the OH and HO_2 primary production. HONO and O_3 photolysis dominated the OH primary production, and HCHO photolysis dominated the HO_2 primary production. Thus, *P*(ROx) was dominated by the photolysis reactions, in which the photolysis of HONO, O_3, HCHO, and carbonyls accounted for 29%, 16%, 16%, and 11% during the daytime, respectively. In the early morning, HONO photolysis was the most important primary source of ROx, and the contribution of O_3 photolysis became progressively larger and was largest at noontime. A large discrepancy between the ratio of HONO photolysis rate to O_3 photolysis rate in summer/autumn and that in winter occurs generally. The vast majority of OH photolysis source is attributed to HONO photolysis in winter because of the higher HONO concentration and lower O_3 concentration. About half of *L*(ROx) came from OH termination, which occurred mainly in the morning, and thereafter, radical self-combination gradually became the major sink of ROx in the afternoon. OH + NO_2, OH + NO, and OH + others contributed 35%, 5%, and 9% to *L*(ROx), respectively. HO_2 + HO_2 and HO_2 + RO_2 accounted for 8% and 16% in *L*(ROx).

4.4 AOC evaluation

AOC controls the abundance of precursors and the production of secondary pollutants (Yang et al., 2020b; Elshorbany et al., 2009), and thus it is necessary to quantify AOC for understanding photochemical pollution. The AOC has been evaluated in previous studies, as shown in Table 1. Overall, the AOC values in summer are higher than those in autumn and winter, and the

values at lower latitudes are higher than those at higher latitudes for the same season. The vast majority of AOC in previous studies are evaluated based on the non-observed radical concentrations.

Table 1: Summary of OH concentrations and AOC values reported in previous field campaigns.

Location	Season, year	Site	Observed or non-observed of OH radicals	AOC / 10^8 molecules cm^{-3} s^{-1}	References
Beijing, China	summer, 2018	urban	non-observed values	0.89[a]	(Liu et al., 2021)
Beijing, China	summer, 2018	suburban	non-observed values	0.85[a]	(Liu et al., 2021)
Beijing, China	winter, 2018	urban	non-observed values	0.21[a]	(Liu et al., 2021)
Beijing, China	winter, 2018	suburban	non-observed values	0.16[a]	(Liu et al., 2021)
Hongkong, China	summer, 2011	suburban	non-observed values	2.04[a,b]	(Xue et al., 2016)
Santiago, Chile	summer, 2005	urban	non-observed values	3.4[a]	(Elshorbany et al., 2009)
Hong Kong, China	late summer, 2012	coastal	non-observed values	1.4[c]	(Li et al., 2018)
Hong Kong, China	autumn, 2012	coastal	non-observed values	0.62[c]	(Li et al., 2018)
Hong Kong, China	winter, 2012	coastal	non-observed values	0.41[c]	(Li et al., 2018)
Shanghai, China	summer, 2018	urban	non-observed values	1.0[c]	(Zhu et al., 2020)
Berlin, Germany	summer, 1998	suburban	non-observed values	0.14[d]	(Geyer et al., 2001)
Xianghe, China	autumn, 2019	suburban	non-observed values	0.49[c]	(Yang et al., 2020b)
Beijing, China	summer, 2014	urban	non-observed values	1.7[a]	(Feng et al., 2021)

Note that:
[a] Peak values in the diurnal profiles; [b] Values on 25 August 2021; [c] Maximum over a period of time; [d] Maximum on some day.

Herein, we explored the AOC in Shenzhen based on the observed radical concentrations for the first time. As illustrated in Fig. 7 (a), the diurnal profile of AOC exhibits a unimodal pattern, which is the same as the diurnal profile of OH concentration and $j(NO_2)$, with a peak around noontime. The diurnal peak of AOC was 0.75 × 10^8 molecules cm^{-3} s^{-1} (11.8 ppb h^{-1}). Comparatively, AOC in this study can be comparable to those evaluated in Beijing (summer, 2018) and Hong Kong (autumn, 2012) (Li et al., 2018; Liu et al., 2021), but much lower than those evaluated in Hong Kong (summer, 2011) and Santiago (summer, 2005) (Xue et al., 2016; Elshorbany et al., 2009).

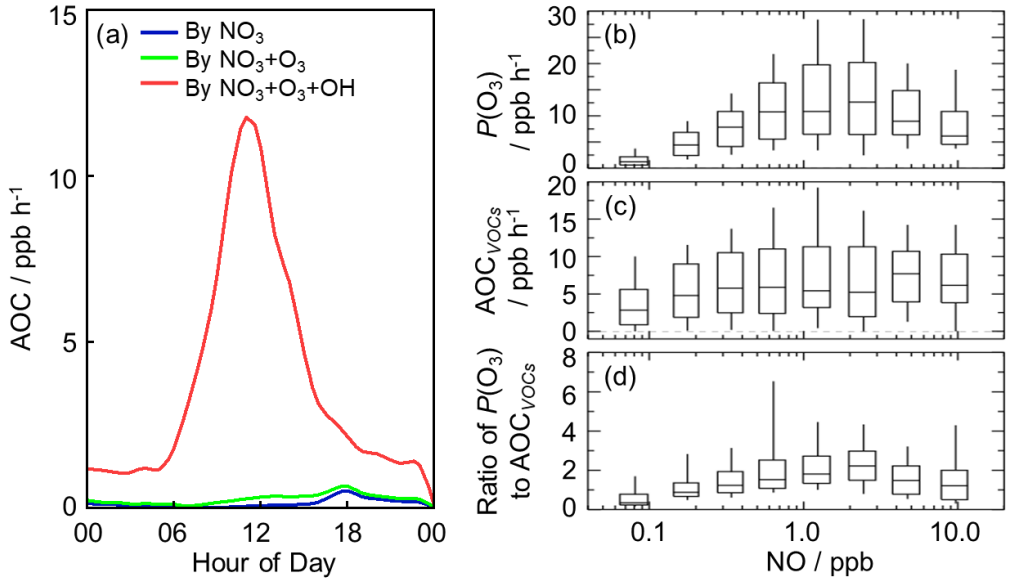

Figure 7: (a) The diurnal profiles of AOC in this campaign. (b) NO dependence of $P(O_3)$ during the daytime. (c) NO dependence of AOC_{VOCs} during the daytime, and AOC_{VOCs} denotes the atmospheric oxidation capacity only from the VOCs oxidation. (d) NO dependence of the ratio of $P(O_3)$ to AOC_{VOCs} during the daytime. The box-whisker plots in (b-d) give the 10%, 25%, median, 75%, and 90% $P(O_3)$, AOC_{VOCs} and the ratio of $P(O_3)$ to AOC_{VOCs}, respectively.

As expected, the dominant contributor to the AOC during this campaign was OH, followed by O_3 and NO_3. Figure S4 shows the fractional composition of the total AOC. The OH radical contributed about 95.7% of AOC during the daytime (08:00-18:00). O_3, as the second important oxidant, accounted for only 2.9% of AOC during the daytime. The contribution of NO_3 to AOC during the daytime can be ignored, with a contribution of 1.4%. At night, the contributions of O_3 and NO_3 to AOC were higher. OH, O_3 and NO_3 accounted for 75.7%, 6.4%, and 18% in the first half of night (18:00-24:00), and they accounted for 87.8%, 5%, and 7.3% in the second half of night (00:00-08:00).

As the indictor for secondary pollution, net O_3 production rate, $P(O_3)$, can be calculated from the O_3 formation rate ($F(O_3)$) and the loss rate ($L(O_3)$), as shown in Eq. (3-5) (Tan et al., 2017). The diurnal profiles of the speciation $F(O_3)$ and $L(O_3)$ were shown in Fig. S5 in the Supplementary Information. The diurnal maxima of the modeled $F(O_3)$ and $L(O_3)$ were 18.9 ppb h^{-1} and 2.8 ppb h^{-1}, with the maximum $P(O_3)$ of 16.1 ppb h^{-1} at 11:00. The modeled $P(O_3)$ was comparable to that in Wangdu site in summer and much higher than that in Beijing in winter (Tan et al., 2017; Tan et al., 2018).

$$F(O_3) = k_{HO_2+NO}[HO_2][NO] + \sum_i k_{RO_2i+NO}[RO_2]_i[NO] \quad (3)$$

$$L(O_3) = \theta j(O^1D)[O_3] + k_{O_3+OH}[O_3][OH] + k_{O_3+HO_2}[O_3][HO_2] + (\sum(k^i_{alkenes+O_3}[alkenes^i]))[O_3] \quad (4)$$

$$P(O_3) = F(O_3) - L(O_3) \quad (5)$$

where θ is the fraction of O^1D from ozone photolysis that reacts with water vapor.

Herein, we presented the NO dependence of $P(O_3)$, AOC_{VOCs}, and the ratio of $P(O_3)$ to AOC_{VOCs} in Fig. 7 (b-d), in which AOC_{VOCs} denotes the atmospheric oxidation capacity only from the VOCs oxidation. An upward trend $P(O_3)$ was presented with the increase of NO concentration when NO concentration was below 1 ppb, while a downward trend was shown with the

increase of NO concentration when NO concentration was above 1 ppb. In terms of the NO dependence of AOC_{VOCs}, no significant variation was found, indicating VOCs oxidation was weakly impacted by NO concentrations in this campaign. Since AOC_{VOCs} can represent the VOCs oxidant rate, and thus the ratio of $P(O_3)$ to AOC_{VOCs} can reflect the yield of ozone production from VOCs oxidation. Similar to $P(O_3)$, the ratio increased with the increase of NO concentration when NO concentration was below 1 ppb. When NO concentration was above 1 ppb, the ratio decreased with the increase of NO concentration because NO_2 became the sink of OH radicals gradually. The maximum of the ratios existed when NO concentration was approximately 1 ppb, with a median of about 2, indicating the yield of ozone production from VOCs oxidation was about 2 in this study.

5 Conclusions

The STORM field campaign was carried out at Shenzhen site in autumn 2018, providing the continuous OH and HO_2^* observations in PRD since the Heshan campaign in 2014. The maximum diurnal OH and HO_2^* concentrations, measured by laser-induced fluorescence (LIF), were 4.5×10^6 cm^{-3} and 4.5×10^8 cm^{-3}, respectively. The observed OH concentration was equal to that measured at Heshan site but was lower than those measured in summer campaigns in China (Backgarden, Yufa, Wangdu, and Chengdu sites).

The base model (RACM2-LIM1) could reproduce the observed OH concentration before 10:00, and thereafter, OH was underestimated by the model when NO concentration dropped to low levels. The results of the radical experimental budget indicated that OH underestimation was likely attributable to an unknown missing OH source at low NO conditions. We diagnosed the missing OH source by sensitivity runs, and unclassical OH recycling was identified again. A constant mixing ratio of the numerical species, X, equivalent to 0.1 ppb NO, was added to the base model to achieve the agreement between the modeled and observed OH concentrations. Additionally, we found isoprene and OVOCs might closely influence the missing OH sources by comparing the composition of VOCs reactivity under the different NO intervals. Isoprene isomerization mechanism (LIM1) can explain approximately 7% of the missing OH sources, and no significant contribution of MACR and MVK oxidation was found. As another potential OH source, OVOCs species should be further explored to explain the remaining missing OH sources. As for HO_2 radicals, the overestimation of HO_2^* concentration was found, indicating that HO_2 heterogeneous uptake might make a significant role in HO_2 sinks.

The quantification of production and destruction channels of ROx radicals is essential to explore the chemical processes of radicals. The ROx primary production and termination rates were balanced for the entire day, with maxima of 4 ppb h^{-1}, similar to those in the Heshan and Wangdu sites. Photolysis channels dominated the ROx primary production rate. HONO, O_3, HCHO, and carbonyls photolysis accounted for 29%, 16%, 16%, and 11% during the daytime, respectively. The most fraction of ROx

termination rate came from the reaction of OH + NO_2 in the morning. The radical self-combination gradually became the major sink of ROx in the afternoon with the decreasing of NO concentrations. The reaction of OH + NO_2 and radical self-combination accounted for 35% and 24% during the daytime, respectively.

In this campaign, AOC exhibited well-defined diurnal patterns, with a peak of 11.8 ppb h^{-1}. As expected, OH radicals, which were the dominant oxidant, accounted for 95.7% of the total AOC during the daytime. O_3 and NO_3 contributed 2.9% and 1.4% to total AOC during the daytime, respectively. The ratio of $P(O_3)$ to AOC_{VOCs} trended to increase and then decrease as NO concentration increased, demonstrating the non-linear relationship between O_3 production and VOCs oxidation. The maximum of the ratios existed when NO concentration was approximately 1 ppb, with a median of about 2, indicating that the yield of ozone production from VOCs oxidation was about 2 in this campaign.

Data availability. The data used in this study are available from the corresponding author upon request (k.lu@pku.edu.cn).

Author contributions. YH Zhang and KD Lu conceived the study. XP Yang analyzed the data and wrote the manuscript with inputs from KD Lu. XP Yang, XF Ma, Y Gao contributed to the measurements of the HOx concentrations. All authors contributed to the discussed results and commented on the manuscript.

Competing interests. The authors declare that they have no conflict of interest.

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Appendix A. Supplementary data

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