OH and HO$_2$ radical chemistry at a suburban site during the EXPLORE-YRD campaign in 2018

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Abstract

The first OH and HO$_2$ radical observation in Yangtze River Delta, one of the four major urban agglomerations in China, was carried out at a suburban site Taizhou in summer 2018 from May to June, aiming to elucidate the atmospheric oxidation capacity in this region. The maximum diurnal averaged OH and HO$_2$ concentrations were 1.0×10^7 cm^{-3} and 1.1×10^9 cm^{-3}, respectively, which were the second highest HO$_x$ (sum of OH and HO$_2$) radical concentrations observed in China. HONO photolysis was the dominant radical primary source, accounting for 42% of the total radical initiation rate. Other contributions were from

27 carbonyl photolysis (including HCHO, 24%), O_3 photolysis (17%), alkenes ozonolysis (14%), and NO_3

28 oxidation (3%). A chemical box model based on RACM2-LIM1 mechanism could generally reproduce the

29 observed HO_x radicals, but systematic discrepancy remained in the afternoon for OH radical, when NO

30 mixing ratio was less than 0.3 ppb. Additional recycling mechanism equivalent to 100 ppt NO was capable

31 to fill the gap. The sum of monoterpenes was on average up to 0.4 ppb during daytime, which was allocated

32 all to α-pinene in the base model. Sensitivity test without monoterpene input showed the modelled OH and

33 HO_2 concentrations would increase by 7% and 4%, respectively, but modelled RO_2 concentration would

34 significantly decrease by 23%, indicating that monoterpene was an important precursor of RO_2 radicals in

35 this study. Consequently, the daily integrated net ozone production would reduce by 6.3 ppb if without

36 monoterpene input, proving the significant role of monoterpene on the photochemical O_3 production in this

37 study. Besides, the generally good agreement between observed and modelled HO_x concentrations suggested

38 no significant HO_2 heterogeneous uptake process during this campaign. Incorporation of HO_2 heterogeneous

39 uptake process would worsen the agreement between HO_x radical observation and simulation, and the

40 discrepancy would be beyond the measurement-model combined uncertainties using an effective uptake

41 coefficient of 0.2. Finally, the ozone production efficiency (OPE) was only 1.7 in this study, a few folds

42 lower than other studies in (sub)urban environments. The low OPE indicated a slow radical propagation rate

43 and short chain length. As a consequence, ozone formation was suppressed by the low NO concentration in

44 this study.

45 **1. Introduction**

46 Stringent air quality regulations have been implemented in China for more than a decade to combat the

47 severe air pollution problems, and dramatic reduction of primary air pollutants such as sulfur dioxide (SO_2),

48 nitrogen oxides (NO_x), and coarse particulate matters (PM_{10}) has achieved. Besides, a significant decrease

49 in fine particulate matters ($PM_{2.5}$) is found since 2013, when the Chinese government took the strictest

50 measures to reduce the anthropogenic emission in the polluted regions (Wang et al., 2020b;Wang et al.,

51 2019b). However, the surface ozone (O_3) showed a contrasting trend with an increasing rate of 1-3 ppb a^{-1}

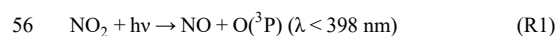
52 over the Chinese eastern megacity clusters, among which North China Plain and Yangtze River Delta regions

53 are of the most significant increase of 3-12 ppb a^{-1} (Wang et al., 2020b). The only known formation pathway

54 to O_3 in the troposphere is the photolysis of NO_2 (R1 and R2). The increasing O_3 despite the successful

55 reduction in NO_2 demonstrates the nonlinearity of the photochemistry caused by the dual role of NO_x.

56 $NO_2 + hv \rightarrow NO + O(^3P)$ ($\lambda < 398$ nm) (R1)

57 $O(^3P) + O_2 + M \rightarrow O_3 + M$ (R2)

58 The ozone formation nonlinearity can be described by investigating HO_x radical chemistry (Tan et al.,

59 2018a;Tan et al., 2018b). In low NO_x conditions, the local ozone production rate $P(O_3)$ increases with NO_x

60 due to the efficient NO to NO_2 conversion by peroxy radicals (R3-R4). In high NO_x conditions, $P(O_3)$

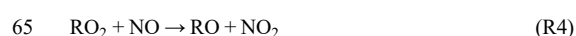
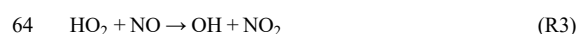
61 decreases with NO_x because the radical termination (R5) overwhelms the radical propagation processes. The

62 key is to find the optimized reduction strategy for both NO_x and VOCs to efficiently control the O_3 production,

63 which the radical measurement could give insight to.

64 $HO_2 + NO \rightarrow OH + NO_2$ (R3)

65 $RO_2 + NO \rightarrow RO + NO_2$ (R4)

66 $OH + NO_2 \rightarrow HNO_3$ (R5)

67 Numerous field campaigns focusing on the hydroxyl (OH) and hydroperoxy radical (HO_2) measurements

68 have been performed worldwide for the past decades, covering various environments including forest,

69 marine, remote, polar, rural, suburban, and urban (Stone et al., 2012). The measured OH concentrations

70 varied in an order of magnitude (in the range of 10^6-10^7 cm^{-3}) among different types of environments, and

71 the OH daily maximum concentrations showed a tendency of higher values in urban areas. Six field

72 campaigns have been implemented in China during summer periods, namely the Backgarden (2006), Heshan

73 (2014), Shenzhen (2018) campaigns in Pearl River Delta (PRD) (Lu et al., 2012;Tan et al., 2019a;Wang et

74 al., 2019a), and Yufa (2006), Wangdu (2014), and Beijing (2017) campaigns in North China Plain (NCP)

75 (Lu et al., 2013;Tan et al., 2017;Whalley et al., 2021) to investigate the atmospheric oxidation capacities and

76 photochemistry characteristics of two of the most polluted regions in China, in which Backgarden campaign

77 reported the highest OH concentration (15×10^6 cm^{-3}) ever observed (Lu et al., 2019). Chemical box model

78 simulation based on conventional mechanisms could generally reproduce the OH radical concentrations in

79 these Chinese campaigns at NO concentration above 1 ppb, but a tendency to underestimate OH radical are

80 continuously observed at NO concentration less than 1 ppb, which is a common feature in isoprene-rich

81 forest environments and OH concentration could be underestimated by a factor of up to 10 (Rohrer et al.,

82 2014;Tan et al., 2001;Lelieveld et al., 2008). Novel recycling mechanism related to isoprene and its

83 degradation products without the involvement of NO has been considered as a possible reason for the OH

84 measurement-model discrepancy in isoprene-rich environments (Peeters et al., 2009;Peeters et al.,

85 2014;Lelieveld et al., 2008), but it is not sufficient to explain the large discrepancy for campaigns in urban

86 and suburban environments. Moreover, even in isoprene-rich environments, the inclusion of the novel

87 recycling mechanism of isoprene is still not sufficient to reproduce the observed OH concentrations (Stone

88 et al., 2011b). It is worth noting that the high OH concentration might be caused by an unknown interference

89 in OH measurements by laser induced fluorescence (LIF) (Mao et al., 2012;Novelli et al., 2014;Hens et al.,

90 2014;Feiner et al., 2016). Mao et al. (2012) reported that up to 80% of OH measurement is interference in a

91 pine forest. However, the interference was minimal and within the instrumental detection limit in other

92 campaigns under urban and suburban environments by different LIF instruments (Griffith et al., 2016;Tan et

93 al., 2017;Woodward-Massey et al., 2020). Therefore, the OH measurement accuracy needs to be addressed

94 prior to critical discussion about defects in our knowledge of the radical chemistry.

95 Yangtze River Delta (YRD) region is one of the four major polluted regions in China and O_3 has become the

96 most critical pollutant in this region (Li et al., 2019). A four-year continuous observation showed the ozone

97 pollution days have more than doubled from 2014 to 2017 (28 to 76 days) in YRD region (Liu et al., 2020b).

98 Lu et al. (2018) reported that the monthly averaged daily maximum 8-h concentrations of O_3 were even

99 higher in YRD than in the NCP. Plenty of studies have been performed to investigate the ozone pollution

100 characteristics and diagnose the sensitivity of ozone formation to its precursors over this region (Zhang et

101 al., 2020;Ding et al., 2013;Tie et al., 2013;Geng et al., 2015;Xing et al., 2017), but none of the studies were

102 deployed with HO_x radical observations. In the present study, we report a new radical observation in YRD

103 region during the campaign EXPLORE-YRD (EXPeriment on the eLucidation of the atmospheric Oxidation

104 capacity and aerosol foRmation, and their Effects in Yangtze River Delta) together with a comprehensive set

105 of trace gases measurements. It provides a unique chance to investigate the photochemistry with the support

106 of HO_x radical observation in this region. Besides, the in-situ HO_x radical observation also allows to

107 investigate the impact of potential mechanisms such as HO_2 heterogeneous uptake on the photochemistry.

2. Methodology

2.1 Measurement site

The EXPLORE-YRD campaign was conducted in the summer of 2018 (14 May to 20 June) in the park of meteorological radar station in suburban Taizhou (32.56˚N, 119.99˚E), Jiangsu Province, which is approximately 200 km north-west and 100 km north-east of the two major megacities, Shanghai and Nanjing, in Yangtze River Delta region (Fig. S1). The site was surrounded by fishponds and grass lands, featured with strong biogenic emission and occasionally biomass burning. No major industrial emissions were found within 500 meters. The closest road with slight traffic was about 100 meters to the South, and to the North and East of the measurement site were the highways S28 and S35 with moderate traffic. For most of the campaign, southerly and easterly winds prevailed, and brought air from the megacities and sea in upwind to this site during the daytime. Thus, the sampled air mass during this campaign could generally embody the atmospheric chemical characteristics in this region.

2.2 OH and HO_2 radical measurements

OH and HO_2 radicals were measured by the Peking University Laser Induced Fluorescence system (called PKU-LIF), which was successfully deployed several times in previous campaigns in Pearl River Delta and North China Plain regions in China (Tan et al., 2017;Tan et al., 2018c;Tan et al., 2019a;Ma et al., 2019). OH radical is detected by laser-induced fluorescence at a low pressure cell (4 hPa) after a sampling nozzle (Hofzumahaus et al., 1998;Holland et al., 2003). The OH signal is determined by tuning the laser wavelength (308 nm) on- and off-line, so-called wavelength modulation. Specific description of the instrument configuration could be found in (Tan et al., 2017) and references therein.

HO_2 radical is chemically converted to OH by reaction with NO that is injected into the flow through a ring-shaped injector installed below the sampling nozzle and then is detected in the form of OH in the second detection cell. Previous studies indicated that part of the RO_2 species derived from longer chain alkanes (> C3), alkenes, and aromatic compounds (namely complex-RO_2) have the potential to rapidly convert to OH on the same time scale as HO_2 inside the fluorescence cell, and thus, might cause interference for HO_2 measurement (Fuchs et al., 2011;Whalley et al., 2013). To minimize the potential interference from RO_2, the

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134   added NO mixing ratio was switched between 2.5 ppm and 5 ppm every 2 minutes, corresponding to the

135   HO_2 conversion efficiencies of 10% and 20%, respectively. The expected RO_2 conversion efficiency for both

136   modes was below 10% for this experimental setup for isoprene derived RO_2 from laboratory tests (Fuchs et

137   al. 2011). The extent of the RO_2-interference was also proportional to the complex-RO_2-to-HO_2 ratio.

138   Unfortunately, RO_2 was not measured during this campaign but one would expect a strong correlation

139   between RO_2 (or complex-RO_2) and HO_2 (Tan et al., 2017; Whalley et al., 2021). Previous field summer

140   campaigns in China showed that, the ratio of complex-RO_2 to HO_2 varies from 0.6 at a rural site in Wangdu

141   (Tan et al., 2017) to 2 at an urban site in Beijing (Whalley et al., 2021). As the chemical condition

142   encountered in YRD was more similar to that of Wangdu (the Beijing campaign was conducted at an urban

143   site), it was reasonable to assume the complex-RO_2 to HO_2 ratio in this study was closer to 0.6. Therefore,

144   by applying the RO_2 conversion efficiency of 0.1 as an upper limit, the maximum HO_2 interference from

145   RO_2 radicals should be closer to 6% of the HO_2 measurement in this study assuming complex-RO_2 to HO_2

146   ratio to be 0.6.

147   The PKU-LIF instrument was calibrated every 2 days during the campaign using a radical calibration source

148   (Hofzumahaus et al., 1996;Holland et al., 1998). Stable sensitivities were found over the whole campaign

149   with reproducibility of 1.2% and 8.0% for OH and HO_2, respectively (1σ standard deviation). Thus, averaged

150   sensitivity was applied for the radical concentration determination. Considering the combined uncertainty of

151   calibration source (10%, 1σ) with reproducibility of calibrated sensitivities, the accuracies of OH and HO_2

152   measurement were 10% and 13%, respectively. The detection limits of OH and HO_2 measurements using

153   LIF technique depend on the sensitivity, the laser power, the background signal, and the integration time

154   (Holland et al., 1995), and were 6.0×10^5 cm^{-3} for OH and 1.0×10^7 cm^{-3} for HO_2 at a typical laser power of

155   12 mW for a data acquisition time of 30 s (for signal-to-noise ratio of 2).

156   Several studies conducted in forested environments indicated that OH measurements by Laser-Induced

157   Fluorescence technique using wavelength modulation method might suffer from unknown internal-produced

158   interference (Mao et al., 2012;Novelli et al., 2017), and the magnitude of interference is highly dependent

159   on the specific design of the instrument, the operating parameters, and the type of environment in which the

160   instrument is deployed (Fuchs et al., 2016;Novelli et al., 2014;Woodward-Massey et al., 2020;Cho et al.,

161   2021). To investigate the possible OH interference in this campaign, we performed an extended chemical

删除了：maximum NO mixing ratio was chosen to be 5 ppm, resulting in the maximum HO_2 conversion efficiency being 20%. Furthermore, the

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删除了：If RO_2 interference was significant, the HO_2 measurement would be different between two NO injection modes. The HO_2 measurements with different NO injection rates only showed a difference of 6%, indicati…

171   modulation experiment on 7 June. During the experiment, a chemical modulation device consisting of a

172   Teflon tube with an inner diameter of 1.0 cm and a length of 10 cm was placed on the top of the OH sampling

173   nozzle. About 17 slpm (standard liter per minute) of ambient air was drawn through the tube by a blower, 1

174   slpm of which entered the fluorescence cell. Tests on the transmission efficiency of OH through the chemical

175   modulation device showed that the signals differed by less than 7% with or without chemical modulation

176   device, indicating the losses of ambient OH to the chemical modulation device were insignificant. For

177   ambient measurement application, either propane (a 12% mixture in nitrogen, 6 sccm) diluted in a carrier

178   flow of pure nitrogen (200 sccm) or pure nitrogen (200 sccm) was injected into the center of the tube

179   alternatively every 5 minutes via two oppositely posited needles at the entrance of Teflon tube. The ambient

180   OH signal can be then deduced by differentiating the signals from adjacent measurement modes with and

181   without propane injection. The amount of the scavenger added is typically selected to be sufficiently high

182   for reacting with ambient OH but not in excess in case reacting with internal-produced OH, and thus, the

183   scavenging efficiency is usually kept around 90%. Calibrations of OH sensitivity with and without propane

184   injection showed the scavenging efficiency of OH was around 93% in this experiment, and the kinetic

185   calculation indicated the added propane removed less than 0.7% of the internal-produced OH. Therefore, the

186   real ambient OH concentration can be obtained by multiplying the differential OH signal by the scavenging

187   efficiency and by the instrument sensitivity. More details about the prototype chemical-modulation reactor

188   used with PKU-LIF and the calculation method can be seen in Tan et al. (2017).

189   2.3 Trace gases measurements

190   A large number of trace gases and aerosol properties related to the atmospheric oxidation chemistry

191   investigation were measured simultaneously. Instruments were placed in sea-containers with their sampling

192   inlets mounted 5 meters above ground. The detail of instrumentation is described by (Wang et al., 2020a).

193   In Table 1, the measured species related to photochemistry study are listed together with the performance of

194   instruments.

195   O_3, NO, NO_2, SO_2 and CO were detected by a series of commercial analyzers from Thermo Inc. O_3 was

196   measured by a UV Photometric analyzer (Model 49i). Both NO and NO_2 were measured by a trace-level

197   analyzer (Model 42i) using chemiluminescence method. Therein, NO_2 measurement was accomplished by a

198   home-built photolytic converter to avoid interference from other NO_y species. HONO measurement was

199   deployed by a Long-path Absorption Photometry with a time resolution of 1 min. A gas chromatograph

200   coupled with a flame ionization detector and mass spectrometer (GC-FID-MS) was deployed to measure

201   volatile organic compounds (VOC) including non-methane hydrocarbons (C2-C11 alkanes, C2-C6 alkenes,

202   C6-C10 aromatics, isoprene, sum of monoterpenes), and oxygenated VOCs including methyl vinyl ketone

203   (MVK)/Methacrolein (MACR), methyl-ethyl-ketone (MEK), acetaldehyde (ACD), acetone (ACT) in a time

204   resolution of 1 hour. The sum of monoterpenes was also detected by proton transfer reaction mass

205   spectrometry (PTR-MS). Formaldehyde and glyoxal were measured by a commercial and a home-built

206   instruments, namely Hantzsch and CEAS, respectively. Additionally, meteorological parameters including

207   temperature, relative humidity, pressure, wind speed, and wind direction were all measured simultaneously.

208   Photolysis Frequencies was calculated by integrated actinic flux measured by a spectroradiometer.

209   **2.4 Model description**

210   An observation-constrained box model based on RACM2-LIM1 mechanism (Goliff et al., 2013;Peeters et

211   al., 2014) was used to simulate the OH and HO_2 radical concentrations. Briefly, observations of the

212   photolysis frequencies $j(O^1D)$, $j(NO_2)$, $j(HONO)$, $j(H_2O_2)$, $j(HCHO)$, and $j(NO_3)$, O_3, NO, NO_2, CO, CH_4,

213   SO_2, HONO, C2-C12 VOCs, and certain oxygenated VOCs such as HCHO, acetaldehyde, glyoxal and

214   acetone as well as the meteorological parameters were used to constrain the model with a time resolution of

215   5 min. Photolysis frequencies of other species were calculated in the model using the following function of

216   solar zenith angle (χ) and scaled to the ratio of measured to calculated $j(NO_2)$ to represent the effect from

217   clouds. :

218    $J = l \times (\cos \chi)^m \times e^{-n \times \sec \chi}$ (Eq. 1)

219   where the optimal values of parameters l, m, and n for each photolysis frequency were adopted (Saunders et

220   al., 2003). The organic compounds were not treated individually but assigned to different lumped species

221   according to the reactivities with OH. The classification of the constrained organic compounds in RACM2

222   were listed in Table 2 in detail. The sum of monoterpene was allocated to α-pinene in the model and the

223   uncertainty due to such simplification was discussed in Sect. 4.2.2. Isomerization of isoprene-derived peroxy

224   radicals was also considered. Other lumped secondary species were unconstrained due to the technical limits

225 but generated numerically by the model calculation.

226 Additional first-order loss term equivalent to a lifetime of 8 hours was given to all species to represent

227 physical losses by means of deposition, convection, and advection. The observed-to-model ratio of PAN

228 concentration was 1.09 using this physical loss rate, while the modelled PAN concentration agreed to

229 measurements from late morning to the midnight but slightly lower than measurements in the early morning

230 (Fig. S2), which might be related to the effect of boundary layer height variation. To test the influence of

231 boundary layer height diurnal variation, we performed a sensitivity test by imposing a boundary layer height

232 (BLH, reanalysis data from European Centre for Medium-Range Weather Forecasts) dependent loss rate to

233 all species. In this scenario, the model continuously underpredicted the concentration in the early morning,

234 and additionally, the model overestimated the observed PAN in the midday and afternoon (Fig. S2). This

235 was because the boundary layer height dependent loss rate was largest at night, which made the loss of PAN

236 greater and further worsened the measurement-model comparison. Therefore, the treatment of a first-order

237 loss term equal to 8 hours to all species in the model might not reflect the loss due to deposition but gave a

238 reasonable approximation on the overall physical loss of the model-generated intermediates. Nevertheless,

239 the modelled OH and HO_2 concentrations were insensitive to the imposed loss rate (Fig. S3). The

240 concentrations differed less than 0.5% between two cases for both OH and HO_2. In addition, sensitivity test

241 without HCHO and glyoxal constrained indicated that model would under-predicted the HCHO and over-

242 predicted the glyoxal concentrations (Fig. S2), which might be related to the significant primary emission of

243 HCHO and missing sinks of glyoxal in the current mechanisms. However, the missing sources and sinks of

244 HCHO and glyoxal are not the scope of this study. To avoid interruption from incapability of model

245 performance, both HCHO and glyoxal were constrained to observations in this study.

246 According to the Monte-Carlo simulation tests, the estimated 1σ uncertainty of the model calculation was

247 32% and 40% for OH and HO_2, respectively, arising mainly from the uncertainties of both observational

248 constraints and kinetic rate constants, among which the rate constant between HO_2 and NO, dilution time

249 and NO concentration were of most significant importance in this study.

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3. Results

3.1 Meteorological and chemical conditions

The meteorological condition encountered during the campaign was characterized by high temperature (up to 35 ˚C), high relative humidity (54% on average) and strong solar radiation. The wind speed was usually below 2 m s^{-1} during the daytime. Back trajectory analysis demonstrated that the air masses were predominately transported from the South and East during the campaign (Fig. S4). High O_3 concentrations were frequently observed on days when the air masses transported to the measurement site had passed through the South especially the Southwest large city clusters. As shown in Fig. 1, the daytime O_3 concentrations exceeded the Chinese national air quality standard level II (hourly averaged limit 93 ppb) on several days and reached as high as 150 ppb on 5 and 6 June.

Figure 2 shows mean diurnal profiles of the key parameter observations. The averaged period is selected when HO_x measurements were available (23 May-17 June excluding the break). Solar radiation was intense during the whole campaign indicated by photolysis frequencies $j(O^1D)$ and $j(NO_2)$. NO concentration peaked at 4 ppb during morning rush hour and then dropped to 0.2 ppb at noon. O_3 concentration started to increase after sunrise and reached the peak of 86 ppb around noon and lasted until sunset. Subsequently, O_3 concentration decreased and partially converted to NO_2 due to the absence of sunlight. The total oxidant (O_x), the sum of O_3 and NO_2 also decreased after sunset. Along with the increased NO_2 at night, HONO concentration increased and reached the maximum of up to 1.3 ppb at sunrise and then declined rapidly due to the fast photolysis. The averaged HONO concentration was 0.6 ppb on the daytime basis. Peroxyacyl nitrates (PAN) is an indicator for active photochemistry which increased since sunrise reaching maximum of 1.6 ppb at 12:00 and then decreased in late afternoon during this campaign. However, other oxidation products, including HCHO and glyoxal, similar to CO and SO_2, peaked at 8:00 CNST rather than in the noon and late afternoon and decreased afterwards, indicating an anthropogenic emission-related origin of these species. Since this campaign was conducted during a harvest season, agriculture biomass burning might be responsible for the elevated HCHO and glyoxal in the early morning (Guo et al., 2021;Liu et al., 2020a;Wang et al., 2017;Silva et al., 2018).

Isoprene showed a broad peak of 0.2 ppb from 09:00 to 15:00, which was several times lower than during

280 the previous summer campaigns (Lu et al., 2012;Lu et al., 2013;Tan et al., 2017). The sum of monoterpene

281 concentrations varied from 0.2 ppb to 0.4 ppb showing a diurnal peak around noon. Though the speciation

282 is not known, the daytime monoterpene concentration was comparable to monoterpene dominated pine forest

283 (Kim et al., 2013;Hens et al., 2014). The role of monoterpene to HO_x chemistry is discussed in section 4.2.2.

284 **3.2 OH and HO_2 radical observation**

285 Figure 3 shows the time series of the observed and calculated OH and HO_2 radical concentrations.

286 Continuous measurement of HO_x radicals was interrupted by the rainfalls and calibration or instrument

287 maintenance. Distinct diurnal variation was observed for both OH and HO_2 radical. The daily maxima of OH

288 and HO_2 concentration were in the range of $(8\text{-}24)\times10^6$ cm^{-3} and $(4\text{-}28)\times10^8$ cm^{-3}, respectively. The mean

289 diurnal profiles showed that averaged OH and HO_2 peak concentrations (1-h averaged) were 1.0×10^7 cm^{-3}

290 and 1.1×10^9 cm^{-3}, respectively (Fig. 4). Additionally, the chemical modulation tests performed on 7 June, an

291 O_3 polluted day, indicated the unknown OH interference, if existed, was insignificant and below the detection

292 limits during this campaign (Fig. S5).

293 For comparison, the daytime measured OH concentration in this campaign together with the OH

294 concentrations in Yufa and Wangdu campaigns in NCP region and in Backgarden, Heshan and Shenzhen

295 campaigns in PRD region, where OH radical observations were available in China were summarized in Table

296 3 and Figure 5. Overall, the OH radical concentration at present study was relatively higher than during other

297 campaigns except for the Backgarden campaign in 2006 (Hofzumahaus et al., 2009). A recent winter

298 observation in Shanghai in YRD region reported an averaged noontime OH concentration of 2.7×10^6 cm^{-3}

299 (Zhang et al., 2022), which was comparable to or even higher than that was observed in winter Beijing

300 $(1.7\sim3.1\times10^6$ $cm^{-3})$ (Tan et al., 2018c;Ma et al., 2019;Slater et al., 2020). It demonstrated the strong

301 atmospheric oxidation capacity in this region among the three megapolitan areas (NCP, PRD, and YRD) in

302 China from the perspective of OH concentration.

303 We also found strong correlation between observed OH radical concentration and photolysis frequency

304 $(j(O^1D))$ during the EXPLORE-YRD campaign, with the correlation coefficient R^2 and the correlation slope

305 being 0.85 and 4.8×10^{11} s cm^{-3}, respectively (Fig. 6). Notably, the slopes were in the range of $(4.0\text{-}4.8)\times10^{11}$

306 s cm^{-3} for all the previous filed campaigns in NCP and PRD regions, for both summer and winter (Tan et al.,

307 2017;Tan et al., 2018c;Lu et al., 2012;Ma et al., 2019). It suggested that the atmospheric oxidation capacity

308 to sustain the radical concentrations was comparable under various chemical conditions in the three major

309 urban agglomerations. Besides, the intercept of the linear fit for this campaign was about 7.6×10^5 cm^{-3}, which

310 was comparable to the Wangdu campaign in 2014 (7.7×10^5 cm^{-3}) and lower than the Yufa and Backgarden

311 campaigns in 2006 (1.6×10^6 cm^{-3} and 2.4×10^6 cm^{-3}, respectively). It represented the non-photolytically

312 produced OH concentration.

3.3 Modelled OH reactivity

314 OH reactivity (k_{OH}) is the pseudo first-order loss rate coefficient of OH radical, and indicates the inverse of

315 the chemical lifetime of OH radical. It can be defined by the sum of the OH reactants concentrations

316 multiplied by their reaction rate constants versus OH radical (Fuchs et al., 2017;Yang et al., 2016;Yang et

317 al., 2019;Lou et al., 2010):

318 $k_{OH} = \sum_i k_{OH+X_i} [X_i]$ (Eq. 2)

319 In this study, the k_{OH} was calculated from measured NO, NO$_2$, CO, CH$_4$, SO$_2$, C2-C12 VOCs (including

320 isoprene and monoterpene), HCHO, acetaldehyde, glyoxal, and acetone and model-generated intermediate

321 species (mainly referred to the unconstrained oxygenated VOCs). The calculated k_{OH} ranged between 5 s^{-1}

322 and 40 s^{-1} (Fig. 3).

323 The typical mean diurnal variation of k_{OH} showed a peak in the early morning and then dropped by nearly

324 50% to a minimum in the afternoon (Fig. 7a). The averaged k_{OH} for periods with OH radical measurement

325 was 10.8 s^{-1} on daytime basis (08:00-16:00), and a total of 36% of the modelled k_{OH} could be attributed to

326 the inorganic compounds (Fig. 7b). CO was the single largest contributor to k_{OH}, with a campaign average

327 contribution of 19%. NO and NO$_2$ together contributed 15% of the modelled k_{OH}. Alkanes, alkenes, and

328 aromatics contributed additional 15% of the modelled k_{OH}. The reactivity from isoprene made a small

329 contribution (5%) to the modelled k_{OH} compared to other campaigns conducted in suburban China, where

330 isoprene typically contributed about 20% of the total k_{OH} (Lou et al., 2010;Fuchs et al., 2017). The

331 contributions that monoterpene made was 4%, which was a substantial faction considering that the daytime

332 monoterpene level was usually low in suburban and urban area.

333 The OVOCs made up a large portion, accounting for approximately 40% of the modelled k_{OH}. The model-

334 generated OVOCs made comparable contribution to the measured ones (22% vs. 18%), and the model-

335 generated contribution to OH reactivity was insensitive to the imposed physical loss rate (Fig. S3). This

336 characteristic was similar to what was observed in London and Wangdu (Whalley et al., 2016;Fuchs et al.,

337 2017), where major OVOCs including HCHO, acetaldehyde, and acetone were directly measured and the

338 measured OVOCs together with the modeled-generated OVOCs accounted for a large portion of the total

339 reactivity (44% and 25%, respectively). It was noteworthy that, in both campaigns, k_{OH} was directly

340 measured and the k_{OH} budget was largely closed. In some previous studies in urban and suburban areas,

341 however, missing k_{OH} ranging from less than 30% to over 50% of the total reactivity was often observed

342 (Kovacs et al., 2003;Lou et al., 2010;Shirley et al., 2006;Yang et al., 2016). The common feature of these

343 observations was that the measurement of OVOCs was completely missing. In fact, model simulations had

344 proved that the model-generated OVOCs from the photooxidation of measured VOCs could quantitatively

345 explain the missing k_{OH} in most of these campaigns during daytime, and the majority of the model-generated

346 OVOCs were HCHO, acetaldehyde, glyoxal, and the isoprene oxidation products. Therefore, in recent

347 studies, with the improved coverage of the measurement of major OVOCs species, together with the model-

348 generated secondary species, the calculated k_{OH} was largely in agreement with the measured k_{OH} in urban

349 and suburban areas during the daytime. However, significant difference could still be observed in areas

350 affected by dramatic anthropogenic influences, for instance in central Beijing (Whalley et al., 2021), 30% of

351 the measured k_{OH} remained unaccounted for, even if the measured and model-generated OVOCs were taken

352 into account, which only contributed 6.5% of the total reactivity, implying that the missing reactivity could

353 be attributed to the undetected or unrecognized species under complex environments.

354 **4. Discussion**

355 **4.1 Sources and sinks of RO_x radicals**

356 The sum of OH, HO_2, and RO_2 radicals are known as RO_x radical. The interconversion within the RO_x radical

357 family is relatively efficient via radical propagation reactions, in which the number of consumed and

358 produced radicals are equal and do not change the total RO_x concentrations. In this section, we concentrate

359 on the radical initiation processes that produce radicals from non-radical molecules, and chain termination

360 processes that destroy radicals. The radical primary production consists of photolysis reactions and alkene

361 ozonolysis. Radical termination processes include reactions with nitrogen oxides and recombination of

362 peroxy radicals.

363 Figure 8 presents the mean diurnal profiles of RO_x radical production and destruction rates based on the

364 model calculation. The $P(RO_x)$ and $L(RO_x)$ show distinct diurnal variation with maximum of 6.8 ppb h^{-1} at

365 noontime. In other campaigns (Table 3), diurnal maximum $P(RO_x)$ varies from 1.1 ppb h^{-1} at a suburban site

366 in Nashville to about 11.6 ppb h^{-1} at a rural site near London during a heatwave (Martinez, 2003;Emmerson

367 et al., 2007). The $P(RO_x)$ in EXPLORE-YRD campaign is comparable to those found in Mexico 2003,

368 Mexico 2006 and Yufa 2006 (Mao et al., 2010;Dusanter et al., 2009b;Lu et al., 2013) .

369 The daytime averaged radical chemistry production rate was 5.7 ppb h^{-1}, of which 83% was attributed to

370 photolytic process. HONO photolysis was the dominant primary source for the entire day and contributed

371 up to 42% of $P(RO_x)$ on daytime basis. Two recent winter campaigns in the same region also found HONO

372 photolysis dominated radical primary source, contributing 38% to 53% of the total radical sources, despite

373 the overall radical production rates were several times lower than that in summertime (Lou et al., 2022;Zhang

374 et al., 2022). In fact, the photolysis of HONO is one of the most important radical primary sources in

375 worldwide urban and suburban areas for both summer (Ren et al., 2003b;Dusanter et al., 2009b;Michoud et

376 al., 2012;Whalley et al., 2018;Tan et al., 2017) and winter time (Ren et al., 2006;Kanaya et al., 2007;Kim et

377 al., 2014;Tan et al., 2018c;Ma et al., 2019). Besides, carbonyl compounds (including HCHO) photolysis was

378 also an important contributor to radical primary sources under urban and suburban conditions (Kanaya et al.,

379 2007;Griffith et al., 2016;Emmerson et al., 2007). In this study, carbonyl compounds photolysis accounted

380 for on average 24% of $P(RO_x)$, in which 14% was from HCHO solely. The dominant primary radical source

381 in remote regions, ozone photolysis (generating O^{1}D and subsequently reacts with H_2O to produce OH), also

382 played a significant role in this study, contributing 17% to $P(RO_x)$. Besides, the non-photolytic radical source

383 alkene ozonolysis peaked at around 10:00 in the morning, and the most important O_3 reactant was

384 monoterpene (35% on daytime basis). It was worth noting that $P(RO_x)$ reduced significantly after sunset

385 while there was a small peak of 1.5 ppb h^{-1} appeared at dusk. The nighttime radical chemistry was mainly

386 initiated by NO_3 oxidation (82%) with monoterpene in the first half of the night, but the NO_3 chemistry was

387 suppressed from midnight to sunrise by the increasing NO concentration because of the efficient titration

388 effect (Wang et al., 2020a).

389   During the EXPLORE-YRD campaign, the RO_x termination processes were mainly dominated by the

390   OH+NO_2 reaction before 08:00 and by peroxy radical self-reaction in the afternoon (Fig. 8). On daytime

391   basis, nitrate formation and peroxy radical recombination both accounted for half of $L(RO_x)$. The peroxy

392   radical recombination including HO_2+RO_2, HO_2+HO_2, and RO_2+RO_2 reactions contributed 33%, 15%, and

393   1% to $L(RO_x)$, respectively. Because the HO_2 and RO_2 concentrations were usually similar, the different

394   contributions between three kinds of peroxy radical recombination were caused by different reaction rate

395   constants. In RACM2, the HO_2+RO_2 reaction rate varied from 5.1×10^{-12} cm^3 $molecule^{-1}$ s^{-1} (methyl peroxy

396   radical at 298 K) to 1.6×10^{-11} cm^3 $molecule^{-1}$ s^{-1} (isoprene derived RO_2 at 298K). In comparison, the effective

397   HO_2+HO_2 reaction rate constant was 3.5×10^{-12} cm^3 $molecule^{-1}$ s^{-1} assuming ambient H_2O mixing ratio of 2%.

398   The self-combination of methyl peroxy radicals rate constant was 3.5×10^{-13} cm^3 $molecule^{-1}$ s^{-1}, one order of

399   magnitude smaller than the other radical recombination reaction. The reversible reaction between peroxyacyl

400   radical and PANs became a net radical sink in the morning because relatively high-NO_2 and low-temperature

401   shifted the thermodynamic equilibrium to form PANs. The net formation of PANs followed by physical

402   losses contributed on average 12% of $L(RO_x)$. Besides, part of the RO_2 species reacts with NO to form

403   organic nitrate rather than recycle to HO_2 radical, resulting in 6% of the radical losses during the daytime.

404   As for the nighttime, since the radicals formed from NO_3 oxidation were dominantly OLND (peroxy radicals

405   of NO_3-alkene adduct reacting via deposition) and OLNN (peroxy radicals of NO_3-alkene adduct reacting to

406   form carbonitrates and HO_2) in RACM2, the nighttime radical losses were dominated by the formation of

407   organic nitrates from OLND and OLNN reaction with themselves and other peroxy radicals. The radical

408   termination processes in winter were quite different from that in summer. During wintertime, the peroxy

409   radical recombination was almost negligible, and the radical termination was almost all contributed by the

410   reactions with NOx (Zhang et al., 2022;Tan et al., 2018d;Ma et al., 2019;Slater et al., 2020).

4.2 OH and HO_2 measurement-model comparison

412   OH and HO_2 radical concentrations were simulated by a box model, which showed generally good

413   agreements with observations (Fig. 3). A significant discrepancy between observed and modelled HO_2

414   concentrations occurred on 12 and 13 June. On these two days, maximum HO_2 increased to 2.6×10^9 cm^{-3},

415   twice of the campaign averaged maximum, while modelled HO_2 concentration remained nearly the same as

416 the campaign averaged maximum. We investigated the discrepancy between observed and modelled HO_2

417 against different chemical compositions but could not identify the cause of elevated HO_2 concentration on

418 these two days. In the following analysis, the observation-model comparison mainly focused on the mean

419 diurnal average to extract the overall feature of the campaign.

420 4.2.1 OH underestimation in low NO regime

421 As shown in Fig. 4, the modelled OH concentration captured the increasing trend in the morning but

422 unpredicted the measurement since 10:00 with largest discrepancy occurred at noon. The HO_2 measurement-

423 model comparison showed similar diurnal variation but the largest discrepancy shifted to 1 hour later

424 together with the diurnal maximum. On daytime basis, the modelled OH and HO_2 radical concentrations

425 were on average 30% and 28% smaller than measurements, respectively. The discrepancies can be explained

426 by their respective combined 1σ uncertainties of measurement and model calculation (10% and 13% for

427 measurement and 32% and 40% for model calculation). In fact, the HO_2 discrepancy in the mean diurnal

428 profile was mainly caused by two outlier days, which disappeared in the median diurnal profile (Fig. S6).

429 However, the discrepancy of OH was also observed in median diurnal profile indicating a persistent OH

430 underestimation during afternoon.

431 The OH underestimation discrepancy showed dependence on the NO concentration. Figure 9 illustrates the

432 dependence of observed and modelled HO_x radicals on NO concentration. To remove the influence of

433 photolysis on OH radical, OH concentration was normalized to $j(O^1D)$ prior to NO dependence analysis.

434 The observed median OH_{norm} was almost constant over the whole NO regime, while the modelled value

435 tended to decrease towards lower NO (<0.3 ppb). The modelled OH_{norm} was 42% smaller than the observed

436 one at NO mixing ratio below 0.1 ppb (Fig. 9), which was beyond the measurement-model combined

437 uncertainty. This discrepancy was mainly caused by the data obtained in the afternoon. The observed and

438 modelled HO_2 agreed throughout the NO regime (Fig. 9), and was consistent with the median diurnal profiles.

439 Such OH-underestimation in low NO regime (typically with NO concentration less than 1 ppb) was

440 frequently found in environments with intense biogenic emission, especially isoprene (Tan et al., 2001;Ren

441 et al., 2008;Lelieveld et al., 2008;Whalley et al., 2011;Stone et al., 2011a;Lu et al., 2012;Hofzumahaus et al.,

442 2009;Lu et al., 2013). We included up-to-date chemical mechanisms related to H-shift processes to consider

443   the impact of additional OH source, such as the H-shift mechanism of isoprene derived peroxy radicals

444   (Peeters et al., 2014). However, during this campaign, isoprene concentration was only 0.2 ppb, contributing

445   5% of the modelled OH reactivity. The H-shift mechanism of isoprene derived peroxy radicals only increased

446   1.2% of the modelled OH concentration and thus play a minor role in OH chemistry. Therefore, other

447   processes should account for the OH underestimation in low NO conditions.

448   To resolve the OH underestimation, a genetic mechanism X was proposed for the Backgarden 2006 campaign,

449   in which X served as NO that converted RO_2 to HO_2 and then HO_2 to OH (Hofzumahaus et al., 2009).

450   Sensitivity tests demonstrated the requested amount of X was equivalent to 100 ppt NO for the EXPLORE-

451   YRD campaign (Fig. 9). Comparatively, the X concentration is the same as in Wangdu campaign (Tan et al.,

452   2017) but smaller than those identified in Backgarden (0.8 ppb (Hofzumahaus et al., 2009)) , Yufa (0.4 ppb

453   (Lu et al., 2013)), and Heshan (0.4 ppb (Tan et al., 2019a)), where the biogenic isoprene and OH reactivities

454   were three to five times and twice as high as during this campaign, respectively (Table 3).

455   It should be pointed out that the precedingly quantified X of 100 ppt equivalent NO was supposed to be the

456   lowest limit in this study, if missing reactivity existed. Therefore, we performed a series of sensitivity tests,

457   by adding a genetic reaction converting OH to RO_2 that equivalent to 30% of the total OH reactivity was

458   added to account for the possible missing reactivity in this study. The adopted degree of missing reactivity

459   was comparable to that was observed in central Beijing (Whalley et al., 2021), which represented a

460   significant portion of potential missing reactivity. Besides, the formed RO_2 species was varied to investigate

461   the influence of different RO_2 types on the modelled radical concentrations including the MO_2 (methyl

462   peroxy radical), ETEP (peroxy radical formed from ethene), and ACO_3 (acetyl peroxy radical). In these cases,

463   the modelled OH decreased by $1.1\sim1.7\times10^6$ cm^{-3} compared to the base case, and the requested amount of X

464   increased to be equivalent to 200~300 ppt of NO depending on the specific RO_2 types (Fig. S7).

465   On the other hand, the OH measurement-model discrepancy could be attributed to measurement artifacts

466   (Mao et al., 2012;Novelli et al., 2014;Novelli et al., 2017;Rickly and Stevens, 2018;Fittschen et al., 2019).

467   Previous studies proposed that stabilized Criegee intermediates (SCIs) produced from reaction of ozone with

468   alkenes and trioxides (ROOOH) produced from reaction of larger RO_2 with OH might cause artificial OH

469   signals using LIF techniques (Novelli et al., 2017;Fittschen et al., 2019). However, chemical modulation

470   tests on an ozone polluted day when both O_3 and ROOOH (modelled) concentrations were high (7 June)

471 indicated insignificant interference for OH measurement in this study (Fig. S8). Furthermore, little relevance

472 of ROOOH and the degree of disagreement between measurement and model was found in this study (Fig.

473 S9), and thus, there is no hint for significant OH measurement interference during the EXPLORE-YRD

474 campaign. However, one should note that the precision is not good enough to rule out the possibility.

4.2.2 Monoterpenes influence

476 The observed monoterpenes varied from 0.2 to 0.4 ppb showing a broad peak around noon (Fig. 2). The high

477 monoterpene concentration and daytime peak indicate a strong daytime source given its short lifetime due

478 to oxidation (24 minutes for α-pinene or 8.2 minutes for Limonene, OH=1.0×10^7 cm^{-3}, O$_3$=80 ppb). The

479 diurnal variation was different from forest environments where maxima usually appeared at night (Kim et

480 al., 2013;Wolfe et al., 2014;Hens et al., 2014). The relatively low nighttime monoterpenes could be related

481 the strong NO$_3$ chemistry in this study (Wang et al., 2020a).

482 In the base model run, observed monoterpenes concentrations were all allocated to α-pinene accounting for

483 0.5 s^{-1} of k_{OH} (Fig. 7). Detailed mechanism referred to α-pinene oxidation in RACM2 were listed in Table

484 S1. A sensitivity test without monoterpenes constrained showed the k_{OH} would decrease by 1.0 s^{-1}. Apart

485 from the decrease in monoterpene itself, half of the decrease of k_{OH} was attributed to the degradation products

486 of α-pinene oxidation. Consequently, the daytime OH and HO$_2$ concentrations would increase by 7% (5×10^5

487 cm^{-3}) and 4% (3×10^7 cm^{-3}), respectively (Fig. 4).

488 We also performed a sensitivity test to attribute the sum of monoterpenes to Limonene, another monoterpene

489 species in RACM2. In this case, the OH concentration would decrease by 11%, while the HO$_2$ concentration

490 would slightly increase by 1% relative to the base case. The reduced modelled OH concentration was resulted

491 from the three times faster reaction rate constant of Limonene with OH (1.6×10^{-10} cm^{-3} s^{-1} at 298K) than that

492 of α-pinene (5.3×10^{-11} cm^{-3} s^{-1} at 298K). It indicated that the different assumptions of monoterpenes

493 speciation had a minor impact on modelled OH and HO$_2$ concentrations in this study.

494 In recent studies, Whalley et al. (2021) highlighted that large RO$_2$ species, such as those derived from α-

495 pinene and ozone reaction, form RO species upon reaction with NO, and these RO species can isomerize to

496 form another RO$_2$ species rather than forming HO$_2$ directly, and thus might have impact on the modelled OH

497 and HO$_2$ concentration. We also performed a sensitivity test to substitute the reactions of α-pinene with ozone

498   in RACM2 by those considering RO isomerization in MCM3.3.1. The modelled OH and HO_2 concentrations

499   decreased by 2.0×10^4 cm^{-3} and 2.5×10^7 cm^{-3}, respectively compared to the base model (Fig. S3), indicating

500   that α-pinene derived RO isomerization had little impact on the modelled OH and HO_2 concentrations in this

501   study.

502   Other studies conducted in forested environments with a strong influence of monoterpenes from pine trees

503   emission found discrepancies of up to three times in HO_2 measurement-model comparison (Kim et al.,

504   2013;Wolfe et al., 2014;Hens et al., 2014). In present study, however, HO_2 concentration was well

505   reproduced by chemical model within combined uncertainty during daytime with high monoterpenes

506   concentrations. Nevertheless, we cannot draw solid conclusion that the monoterpenes oxidation chemistry

507   in environment with both strong anthropogenic and biogenic influences can be captured by the applied

508   chemical mechanisms with respect to HO_x concentration, since missing HO_2 sources and sinks might exist

509   simultaneously but cancel out each other. Given that there were no OH reactivity or RO_2 observations in this

510   study, we cannot rule out these possibilities.

511   4.2.3 HO_2 heterogeneous uptake

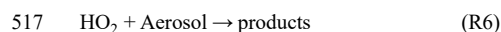
512   A recent model study proposed that HO_2 heterogeneous uptake processes play an important role in HO_x

513   radical chemistry and thus suppress ozone formation in China (Li et al., 2019). The RACM2-LIM1

514   mechanisms used in our study only consist gas phase reactions without heterogeneous chemistry. Therefore,

515   in this section, we performed a sensitivity test with HO_2 radical uptake considered to investigate the potential

516   impact on the modelled radical concentrations by adding a radical termination process (R6).

517   HO_2 + Aerosol $\rightarrow$ products   (R6)

518   The heterogeneous loss rate of HO_2 radical is limited by the free molecular collision because the aerosol

519   surface is mainly contributed by submicron particles. HO_2 radical uptake process can be simplified as a

520   pseudo first order reaction, and the first-order kinetics constant can be calculated by the Eq. 3:

521    $k_{HO_2} = \dfrac{V_{HO_2} \times S_a \times \gamma}{4}$ (Eq. 3)

522    $V_{HO_2} = \sqrt{\dfrac{8RT}{\pi \times 0.033}}$ (Eq. 4)

523   V_{HO2} represents the mean molecular velocity of HO_2 determined by Eq. 4. S_a is the humid aerosol surface

524   areas calculated by the SMPS measured particle number and size distribution in each size bin corrected by

525   the hygroscopic growth factor. γ is the effective HO_2 uptake coefficient on aerosol giving the probability of

526   HO_2 loss by impacting the aerosol surface.

527   The effective uptake coefficients vary from 10^{-5} to 0.82 from multiple laboratory studies (Thornton et al.,

528   2008;Taketani et al., 2009;Taketani and Kanaya, 2010;George et al., 2013;Lakey et al., 2015;Zou et al.,

529   2019). A relatively high value of 0.2 was found in aerosol samples collected in North China Plain, which

530   was attributed to the abundant dissolved copper ions in aqueous aerosol (Taketani et al., 2012). A study based

531   on radical experimental budget analysis determined the effective HO_2 uptake coefficient to be 0.08±0.13 in

532   North China Plain (Tan et al., 2020). In our sensitivity tests, both coefficients were applied and simulated

533   separately.

534   As shown in Fig. 4, the incorporation of HO_2 heterogeneous uptake process worsened the model-

535   measurement agreement with both OH and HO_2 radicals for both cases. The modelled OH and HO_2 radicals

536   were reduced by 10% and 20%, respectively, for the coefficient of 0.2, and by 5% and 10% for the coefficient

537   of 0.08. For the case the coefficient of 0.08, the increased radical loss rate from HO_2 uptake process was 0.4

538   ppb h^{-1} on daytime basis, which was smaller than that during the Wangdu campaign (0.6±1.3 ppb h^{-1}). The

539   discrepancy between two studies was caused by the lower aerosol surface areas during the EXPLORE-YRD

540   campaign (750 compared to 1600 μm^2 cm^{-3}). The measured and modelled HO_2 concentrations agreed within

541   33% on daytime basis, which was less than the 40% uncertainty of HO_2 simulation. However, this

542   discrepancy enlarged to 51% as the coefficient increased to 0.2 exceeding the uncertainty of HO_2 simulation.

543   The agreements between measurement and model calculation of OH and HO_2 indicated that the base model

544   without heterogenous reaction captured the key processes for OH and HO_2 radical chemistry in this study.

545   As discussed in Sect. 4.2.1, a series of sensitivity tests had been performed to test the effect of missing

546   reactivity on the modelled radical concentrations (Fig. S7). It turned out that when OH converted to MO_2,

547   the modelled HO_2 would increase by $6.2×10^7$ cm^{-3} compared to the base case which makes more room for

548   the HO_2 heterogeneous loss. However, considering the potential effect of missing reactivity on HO_2, the

549   measured and modelled HO_2 discrepancy (41%) would still be beyond the uncertainty of HO_2 simulation for

550   coefficient of 0.2. On the contrary, for cases that OH converted to ETEP and ACO_3, the modelled HO_2

551   decreased by $1.3×10^7$ cm^{-3} and $1.5×10^7$ cm^{-3}, respectively compared to the base cases, possibly due to the

552   faster radical termination rates through RO_2+HO_2 in both these cases compared to that of MO_2. Nevertheless,

553   the model sensitivity tests suggested that HO_2 uptake coefficient was less than 0.2, if the HO_2 heterogeneous

554   loss played a role during this campaign.

4.3 local Ozone production rate

556   Peroxy radical chemistry is intimately tied to the atmospheric ozone production. All peroxy radicals which

557   could react with NO to form NO_2 leading to ozone formation ($F(O_x)$), as expressed in Eq. 5. In this study,

558   the ozone formation contributing from RO_2 was derived from model calculation due to the absence of RO_2

559   measurement. The reaction rate constant between HO_2 and NO is approximately 8.5×10^{-12} cm^3 molecule^{-1} s^{-}

560   ^{1} at 298 K, while the rate constant for the reaction of RO_2 with NO varies significantly (ranging in fivefold)

561   depends on the specific speciation in RACM2. Besides, the NO_2 yield from RO_2 and NO reaction also differs

562   for different RO_2 groups in RACM2. Part of the RO_2 radicals reacts with NO forming organic nitrates rather

563   than producing NO_2 and recycling the peroxy radicals. The nitrate yield increases with higher carbon

564   numbers and branch structure. Therefore, the NO_2 production from RO_2+NO reaction is manipulated by the

565   effective reaction rate considering both reaction rate constant and NO_2 yield for different RO_2 species i (Eq.

566   5).

567    $F(O_x) = k_{HO_2+NO} [HO_2] [NO] + \sum_i k_{RO_2 i+NO} [RO_2]_i [NO]$ (Eq. 5)

568   On the other hand, formed O_3 could be involved and consumed in the radical chain reactions by initiating

569   the radicals from photolysis and reaction with alkenes and propagating the radicals from reaction with OH

570   and HO_2, and besides, part of the NO_2 would react with OH to generate nitric acid rather than photolysis

571   ($L(O_x)$). Additionally, NO_2 could also react with O_3 to form NO_3 radical, which could further combine with

572   another NO_2 to form N_2O_5 or oxidize VOCs to form organic nitrates, leading to 2 to 3 times faster O_x loss

573   than NO_3 radical formation. Considering the fact that NO_3 radical could be easily photolyzed to regenerate

574   NO_2 and O_3 or be titrated by NO to regenerate NO_2, the contribution from net NO_3 radical formation pathway

575   was taken into account by taking the largest O_x loss per NO_3 net formation of 3 in Eq. 6.

576    $L(O_x) = J(O^1D) [O_3] \times \varphi + k_{O_3+Alkenes} [Alkenes] [O_3] + k_{O_3+OH} [OH] [O_3] + k_{O_3+HO_2} [HO_2] [O_3] +$

577    $k_{OH+NO_2} [OH] [NO_2] + 3 \times (k_{NO_2+O_3} [NO_2] [O_3] - k_{NO+NO_3} [NO] [NO_3] - j_{NO_3} [NO_3])$ (Eq. 6)

578   Thus, the net ozone production rate ($P(O_x)$) could be deduced from the difference between O_x formation and

579   O_x loss rates as expressed in Eq. 7.

580    $P(O_x) = F(O_x) - L(O_x)$ (Eq. 7)

581   Figure 10a shows the mean diurnal profiles of the calculated $F(O_x)$ and $L(O_x)$ in this study. Fast ozone

582   formation rate of up to 20 ppb h^{-1} was observed at 09:00, while the maximum ozone loss rate of 4 ppb h^{-1}

583   shifted to two hours later at noon, when the ozone formation rate reduced to 11.4 ppb h^{-1}. This rate was

584   comparable to other campaigns conducted in rural areas, while the ozone production rates increased

585   significantly in urban areas, where the noontime ozone formation rates varied from 13.9 ppb h^{-1} in Tokyo to

586   65 ppb h^{-1} in Mexico (Table 3).

587   Fast ozone formation is the consequence of both strong primary source and efficient radical propagation.

588   The latter one can be evaluated by the ratio between $F(O_x)$ and $P(RO_x)$ and known as ozone production

589   efficiency (OPE). As discussed in Sect. 4.1, the radical primary source was relatively high during the

590   EXPLORE-YRD campaign, and thus, the OPE was only 1.7, which was smaller than or comparable to other

591   rural campaigns (Table 3). Urban campaigns in the U.S., Mexico and Tokyo showed significant higher OPE

592   varying from 6 to 10 (Table 3) probably benefit from the moderate NO_x level. In comparison, OPE was

593   smaller in four megacities in China (Beijing: 3.4, Shanghai: 3.1, Guangzhou: 2.2, Chongqing: 3.6) than in

594   the U.S. cities ranging from 3 to 7 because of the suppression of high NO_x in Chinese cities (Tan et al.,

595   2019b). However, during the EXPLORE-YRD campaign, the low OPE indicates that the radical propagation

596   chain length was relatively short due to low NO conditions.

597   As shown in Fig. 10b, the integrated net ozone production was 68.3 ppb d^{-1} over the entire daytime (08:00-

598   16:00). The daily integrated $P(O_x)$ calculated based on the modelled peroxy radicals was 6.9 ppb lower than

599   on derived from observation (Fig. 10b). The discrepancy for observation and model derived $P(O_x)$ mainly

600   appears at NO concentration larger than 1 ppb (Fig. 9). This behavior has been observed in a number of

601   previous urban radical measurement campaigns (Kanaya et al., 2008;Kanaya et al., 2012;Martinez, 2003;Ren

602   et al., 2003a;Ren et al., 2013;Elshorbany et al., 2012;Brune et al., 2016;Whalley et al., 2018;Tan et al., 2017),

603   which was caused by the model underprediction of the observed HO_2 concentrations under high NO

604   concentration (typically NO greater than 1 ppb). Although some of the previous HO_2 measurement might

605   suffer from unrecognized interference from RO_2 species, this kind of interference have been minimized by

606   lowering down the added NO concentration in recent studies (Griffith et al., 2016;Brune et al., 2016).

607   However, the underestimation of ozone production from HO_2 radical persist, indicating that the

608   photochemical production mechanism of ozone under polluted urban environment is still not well understood.

609   We also investigated the impact of different model scenarios on $P(O_x)$ by comparing integrated $P(O_x)$ in

610   different cases to that obtained in base model (Fig. 10b). Sensitivity test without α-pinene constrained

611   predicted 6.3 ppb less daily integrated net ozone production than base case. Meanwhile, the contribution of

612   α-pinene derived peroxy radicals (APIP) on $F(O_x)$ only accounted for 2.3 ppb O_3 formation (Fig. 10a). The

613   difference can be attributed to the degradation products of α-pinene which also contribute to ozone

614   production. For example, aldehyde (ALD) is an important daughter product from α-pinene oxidation, which

615   reacts with OH and forms acyl peroxy radicals. Acyl peroxy radicals have two advantages in ozone formation.

616   On one hand, acyl peroxy radicals have the fastest rate constants with NO among all the peroxy radicals

617   (2~5 times faster than others). On the other hand, acyl peroxy radicals react with NO to produce NO_2 and

618   methyl or ethyl peroxy radicals, which can further oxidize the NO to NO_2 and generate HO_2. Given that the

619   modelled HO_2 concentration increased by 4% in the sensitivity test, the smaller in $P(O_x)$ was mainly

620   attributed to significant reduction in modelled RO_2 concentration. In fact, the modelled RO_2 concentration

621   would reduce by 23% if α-pinene was not constrained to observation, which indicated α-pinene was an

622   important RO_2 precursor. It proved that monoterpene contributes significantly to the photochemical

623   production of O_3 in this study.

624   Moreover, we also investigated the impact of the α-pinene derived RO species which can isomerize to form

625   another RO_2 rather than forming HO_2 directly on the calculated ozone production rate. It turned out that

626   including α-pinene derived RO isomerization mechanism in the model run would reduce the daily net O_3

627   production by 1 ppb.

628   Additionally, HO_2 heterogeneous uptake process in the model run would reduce the daily net O_3 production

629   by 4.8 ppb by assuming the effective coefficient of 0.08. The reduction in $P(O_x)$ was only slightly smaller

630   than the relative change in modelled HO_2 concentration (10%) because 62% of the $F(O_x)$ was contributed by

631   the reaction of HO_2 with NO (Fig. 10a).

632   **4   Conclusion**

633   A comprehensive field campaign to elucidate the atmospheric oxidation capacity in Yangtze River Delta in

634   China was carried out in summer 2018, providing the first OH and HO_2 radicals observations in this region.

635   Daily maximum concentrations of OH and HO_2 radicals were in the range from 8 to 24×10^6 cm^{-3} and 4 to

636   28×10^8 cm^{-3}, with mean values of 1.0×10^7 cm^{-3} and 1.1×10^9 cm^{-3}, respectively. The OH radical was of the

637   second highest concentration among the observations in China, indicating the strong oxidation capacity in

638   YRD region from the perspective of OH radical concentration. The modelled k_{OH} varied from 5 s^{-1} to 40 s^{-1}

639   over the whole campaign, and 40% of which could be explained by OVOCs, in which measured and

640   modelled OVOCs made up comparable contributions.

641   The radical primary source was dominated by HONO photolysis during this campaign, contributing 42% of

642    $P(RO_x)$. The secondary contributor was the photolysis of carbonyl compounds (including HCHO),

643   accounting for 24% of the total radical primary source. Radical termination was dominated by the reactions

644   with NO_x in the morning and peroxy radical self-reactions in the afternoon. Specifically, $OH+NO_2$ reaction

645   and peroxy radical self-reaction from HO_2+RO_2 were the most important pathways, contributing 25% and

646   33% of the total radical loss rates, respectively.

647   The comparison between observation and box model simulation showed generally good agreement for both

648   OH and HO_2 radicals on average. However, the OH radical showed a tendency of underestimation towards

649   low NO regime (NO< 0.1 ppb), and the discrepancy (42%) was beyond the measurement-model combined

650   uncertainty. The up-to-date H-shift mechanism of isoprene derived peroxy radicals could not explain the

651   discrepancy due to the low isoprene concentration (0.2 ppb) during this campaign. A genetic OH recycling

652   process equivalent to 100 ppt NO was capable to fill the gaps, which was also found in previous campaigns

653   in Backgarden, Yufa, Heshan, and Wangdu in China. In addition, the good simulation in HO_2 radical was

654   different from other monoterpene-rich forest environments, where HO_2 underestimations were found.

655   Additional sensitivity tests were performed to investigate the impact of monoterpenes and HO_2

656   heterogeneous uptake on radical chemistry in this study. Model simulation without monoterpene input or

657   allocating monoterpene to a different isomer (α-pinene and Limonene in this study) showed that HO_x radical

658   concentrations were not sensitive to the monoterpene in this study. In fact, the modelled RO_2 radical

659   concentration would be reduced by 23% without monoterpene constrained. The reduced RO_2 radical offset

660   the enhancement of HO_x radicals. The combined influence caused the net daily integrated ozone production

661   to decrease by 6.3 ppb compared to the base model of 61.4 ppb, which demonstrated the importance of

662 monoterpene chemistry on the photochemical ozone production in this study. The role of HO_2 heterogeneous

663 uptake was tested by adding a pseudo first-order reaction loss of HO_2, and taking the effective uptake

664 coefficients of 0.2 and 0.08, respectively. The sensitivity test suggested the applied chemical mechanism

665 without HO_2 heterogeneous uptake could capture the key processes for HO_x radicals, and the effective uptake

666 coefficient should be less than 0.2, if the HO_2 heterogeneous loss played a role in this study, otherwise, the

667 HO_2 measurement-model discrepancy would be beyond the combined uncertainty. The daily integrated net

668 ozone production would reduce by 4.8 ppb, if the effective uptake coefficient was assumed to be 0.08.

669 Additionally, the noontime ozone production rate was 11.4 ppb h^{-1}, which was much slower than other

670 campaigns in urban and suburban areas varying from 13.9 to 65 ppb h^{-1}. Thus, the ozone production

671 efficiency calculated from the ratio of $P(O_x)$ and $P(RO_x)$ was only 1.7 in this study, which was comparable

672 to the values in rural campaigns but was 3 to 7 times lower than the values in other urban and suburban

673 campaigns, indicating the slow radical propagation rate and short chain length in this study.

674

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

677

678 ***Author contributions.*** YZ and KL organized the field campaign. KL and YZ designed the experiments. XM
679 and ZT analyzed the data. XM wrote the manuscript with input from ZT. All authors contributed to
680 measurements, discussing results, and commenting on the manuscript.

681

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

683

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1084 **Table 1. Measured species and performance of the instruments.**

Parameters	Techniques	Time resolutions	Limit of Detection[a]	Accuracy
OH	LIF[b]	30 s	6.0×10^5 cm^{-3}	±10%
HO$_2$	LIF[b,c]	30 s	1.0×10^7 cm^{-3}	±13%
Photolysis frequencies	Spectroradiometer	9 s	[d]	±10%
O$_3$	UV photometry	60 s	0.5 ppb	±5%
NO	Chemiluminescence	60 s	60 ppt	±20%
NO$_2$	Chemiluminescence[e]	60 s	0.3 ppb	±20%
HONO	LOPAP[f]	60 s	10 ppt	±20%
CO	Infrared absorption	60 s	1 ppb	±1 ppb
SO$_2$	Pulsed UV fluorescence	60 s	0.1 ppb	±5%
VOCs[g]	GC-FID/MS[h]	1 h	20-300 ppt	±15%
HCHO	Hantzsch fluorimetry	60 s	25 ppt	±5%
Glyoxal	CEAS	60 s	60 ppt	±10%
Monoterpene[i]	PTR-MS	10 s	20 ppt	±15%
PNSD	SMPS	5 min	14 nm-700 nm	±20%

1085 [a] Signal-to-noise ratio =1. [b] Laser Induced Fluorescence. [c] Chemical conversion to OH via NO reaction before detection. [d]

1086 Process-specific, 5 orders of magnitude lower than maximum at noon. [e] Photolytic conversion to NO before detection, home-

1087 built converter. [f] Long-path absorption photometry. [g] VOCs including C_2-C_{11} alkanes, C_2-C_6 alkenes, C_6-C_{10} aromatics. [h] Gas

1088 chromatography equipped with a mass spectrometer and a flame ionization detector. [i] the sum of monoterpene.

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1092 **Table 2. Assignment of measured and constrained VOCs in RAMC2 during this study.**

RACM	Measured hydrocarbons
ACE	acetylene
ETH	ethane
HC3	propane, *i*-butane, *n*-butane, 2,2-dimethylbutane
HC5	*i*-pentane, *n*-pentane, cyclopentane, 2,3-dimethylbutane, 2-methylpentane, 3-methylpentane, MTBE, *n*-hexane, 2,3-dimethylpentane, 2,4-dimethylpentane, methylcyclopentane, 2-methylhexane
HC8	cyclohexane, 3-methylhexane, 2,2,4-trimethylpentane, 2,3,4-trimethylpentane, *n*-heptane, methylcyclohexane, 2-methylheptane, 3-methylheptane, *n*-octane, *n*-nonane, *n*-decane, *n*-undecane
ETE	ethylene
OLI	*trans*-2-butene, *cis*-2-butene, *trans*-2-pentene, *cis*-2-pentene
OLT	propene, 1-butene, 1-pentene, 1-hexene, styrene
DIEN	1,3-butadiene
BEN	benzene
TOL	toluene, ethylbenzene, *i*-propylbenzene, *n*-propylbenzene
XYO	*o*-xylene, *o*-ethyltoluene
XYM	*m*-ethyltoluene, 1,3,5-trimethylbenzene, 1,2,4-trimethylbenzene, 1,2,3-trimethylbenzene, *m*-diethylbenzene
XYP	*m*,*p*-xylene, *p*-ethyltoluene, *p*-diethylbenzene
ISO	isoprene
API	sum of monoterpenes
HCHO	formaldehyde
ACD	acetaldehyde
GLY	glyoxal
ACT	acetone
MACR	methacrolein
MVK	methyl vinyl ketone
MEK	methyl ethyl ketone

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1096 **Table 3. Summary of filed measurements and model simulation for j(O^1D), O_3, NO_x, OH, HO_2, $P(RO_x)$, $F(O_x)$ and OPE at local noon in urban**

1097 **suburban environments.**

Location	Month Year	Type	j(O^1D) /10^{-5} s^{-1}	O_3 /ppb	NO_x /ppb	OH /10^6 cm^{-3}	HO_2 /10^8 cm^{-3}	$P(RO_x)$ /ppb/h	$F(O_x)$ /ppb/h	OPE[s]	References
Pabstthum, Germany, 52.85°N, 12.94°W, 50 km NW of Berlin	July-August 1998	Rural	1.5	42	1.55	3.5	2.2	1.7[a]	2.2[b]	1.3	(Holland et al., 2003;Volz-Thomas al., 2003;Platt et al., 2002)
Nashville, USA, 36°11.4′N, 86°42.0′W, 8 km NE of downtown area	June-July 1999	Suburban	3.0[a]	60[a]	4.4[a]	10	7.5	1.1	9[c]	8.2	(Martinez, 2003;Thornton et al 2002)
La Porte, USA, 29°40′N, 95°01′W, 40 km SE of Houston	August-September 2000	Suburban	3.0	70	6	20	7.5	4.9	25[d]	5.1	(Mao et al., 2010)
New York (Queens College), USA, 40°44′15″N, 73°49′18″W, in the Borough of Queens	June-August 2001	Urban	2.5	48	28	7.0[e]	1.0[e]	4.8	34[d]	7.1	(Mao et al., 2010;Re al., 2003b;Ren et al. 2003a)
Mexico City, Mexico, 19 °25′N, ~7 km SE of downtown area	April-May 2003	Urban	4.5	115	18	12[f]	15[f]	8.6	65[d]	7.6	(Mao et al., 2010;Shirley et al., 2006)
Essex (Writtle College), England, 51°44′12″N, 0°25′28″E, 25 miles NE of central London	July-August 2003	Rural	1.0[g]	46.5[g]	10.8[g]	2[g]	0.7[g]	11.6[g]	7.2[g,h]	0.6	(Emmerson et al., 2

Location	Date	Type									Reference
Tokyo (University of Tokyo), Japan, 35°39'N, 139°41'E, near city center	July-August 2004	Urban	2.5	32	12	6.3[e]	1.4[e]	2.2 (6.8)[i]	13.9[i]	6.3 (2.0)[i]	(Kanaya et al., 2007;Kanaya et al., 2008)
Backgardon, China, 23.487°N, 113.034°E, 60 km NW of downtown Guangzhou	July 2006	Rural	3.5	51	11.4	14	17[k]	10.7	18[l]	1.7	(Lu et al., 2012;Lou et al., 2010)
Yufa, China, 39.5145°N, 116.3055°E, ~40 km south of the Beijing downtown area	August-September 2006	Rural	1.8	71	8.8	5.5	7.2[k]	7.0	15[l]	2.1	(Lu et al., 2013)
Mexico City, Mexico, 19 °N, 100°W, ~7 km SE of downtown area	March 2006	Urban	4.0	90	49	4.6[e]	1.9[e]	7.5	31[c]	4.1	(Dusanter et al., 2009a;Dusanter et al., 2009b;Molina et al., 2010)
University of Houston (70 m above ground level), USA, 29.7176°N, 95.3413°W, 5 km SE of downtown Houston	August-September 2006	Urban (Tower)	3.1	68	4	15	12.5	5.3	45[d]	8.5	(Mao et al., 2010)
University of Houston (70 m above ground level), USA, 29.7176°N, 95.3413°W, 5 km SE of downtown Houston	April-May 2009	Urban (Tower)	-	47	2.5	8.8[e]	6.3[e]	3	18[i]	6	(Ren et al., 2013;Lee et al., 2013)
Paris, France, 48.718°N, 2.207°E, ~14 km SW of Paris	July 2009	Suburban	2.2	35	4.3	4.2	1.3[m]	0.75[n]	7.1[o]	9.5	(Michoud et al., 2012)

Location	Date	Type									Reference
Pasadena, USA, 34.1408°N, 118.1223°W, ~18 km NE of downtown	May-June 2010	Suburban	2.1 (2.5)[p]	45 (72)[p]	19 (9)[p]	3.5 (4.0)[p]	2.0 (5.0)[p]	4.0 (5.3)[p]	33 (23)[p,q]	8.3 (4.3)	(Griffith et al., 2016)
London, England, 51°31'16"N, 0°1'248"W, in central London	July-August 2012	Urban	-	24.2 (37.4)[r]	13.1 (24.3)[r]	2.1 (3.0)[r]	2.0 (0.6)[r]	4.9	5.6[g]	1.1	(Whalley et al., 2018;Whalley, 2016)
Wangdu, China, 38.71°N, 115.15°E, ~35 km SW of Baoding and 170 km SW of Beijing	June-July 2014	Rural	1.8	88	8.2	8.3	7.7	4.8	14.7[b]	3.1	(Tan et al., 2017)
Heshan, China, 22.728°N, 112.929°E, ~6 km SW of the city of Heshan and 50 km SW of Guangzhou and Foshan	October-November 2014	Suburban	1.3	51	26.9	4.8	2.3	5.1	18.1[b]	3.5	(Tan et al., 2019a)
Beijing, China, 39.97 °N, 116.38 °E, in central Beijing	May-June 2017	Urban	2.4	100	25	9.0	3.0	7.0	7.8[t]	2.4[t]	(Whalley et al., 2021;Shi et al., 2019)
Taizhou, China, 32.56°N, 119.99 °E, ~200 km NW of Shanghai	May-June 2018	Suburban	2.1	82	3.6	10.6	11.4	6.8	11.4[j]	1.7	This study

[a] Take from a typical day. [b] Calculated from measured peroxy radical with NO reaction. [c] Calculated from measured HO$_2$ to HO$_2$) with NO. [e] Median. [f] Median and revised. [g] 11:00-15:00 mean. [h] Calculated by summing all of the reaction rates for NO to NO$_2$ conversions. [i] For smog-free day and smog day (in parenthesis) separately. [j] Calculated from measured HO$_2$ and modelled RO$_2$ with NO. [k] HO$_2$*(HO$_2$ and partial RO$_2$). [l] Calculated from modelled HO$_2$ and RO$_2$ with NO. [m] Total peroxy radicals (HO$_2$+RO$_2$). [n] 8:00-16:00 mean. [o] Calculated by measured total peroxy radicals (HO$_2$+RO$_2$) with NO. [p] For week days and weekend days (in parenthesis) separately. [q] Calculated from measured HO$_2$* with NO. [r] For westerly flow and easterly flow (in parenthesis) separately. [s] Calculated by the ratio between F(O$_x$) and P(RO$_x$). [t] Daily mean.

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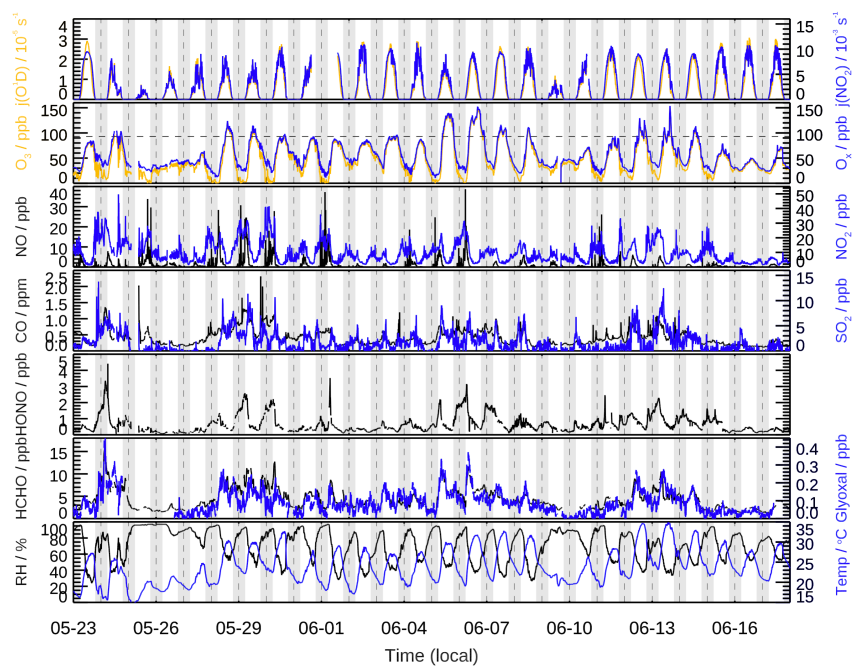
Figure 1. Time series of measured photolysis frequencies (j(O^{1}D), j(NO$_2$)), relative humidity (RH), ambient temperature (T), and concentrations of O$_3$, O$_x$ (=O$_3$+NO$_2$), NO, NO$_2$, CO, SO$_2$, HONO, formaldehyde (HCHO), and glyoxal (CHOCHO). The dotted horizontal line represents the Chinese national air quality standard level II of O$_3$ (hourly averaged limit 93 ppb). The grey areas denote nighttime.

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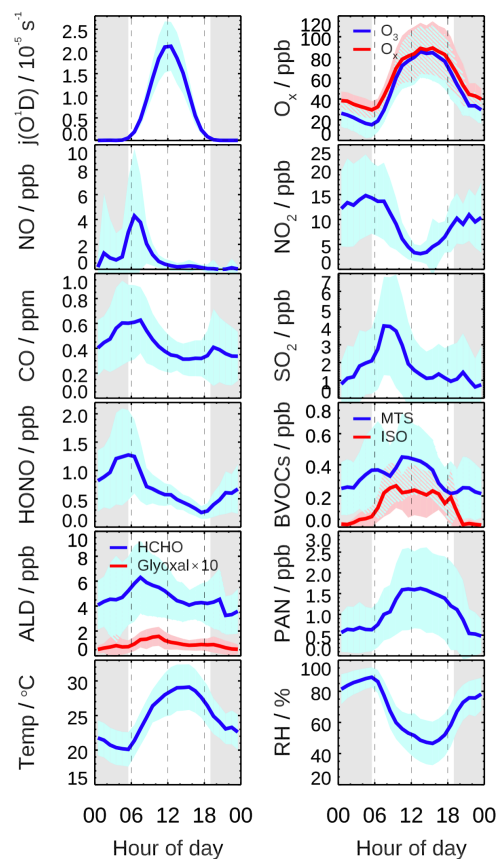
Figure 2. Mean diurnal profiles of measured photolysis frequencies (j(O¹D)), relative humidity (RH),

ambient temperature (T), and concentrations of O_3, O_x (=O_3+NO_2), NO, NO_2, CO, SO_2, HONO,

formaldehyde (HCHO), glyoxal (CHOCHO), biogenic VOCs (monoterpenes, isoprene), and PAN.

Data are averaged over the period with HO_x radical measurement. Colored areas denote the standard

deviation of variability (1σ). The grey areas denote nighttime.

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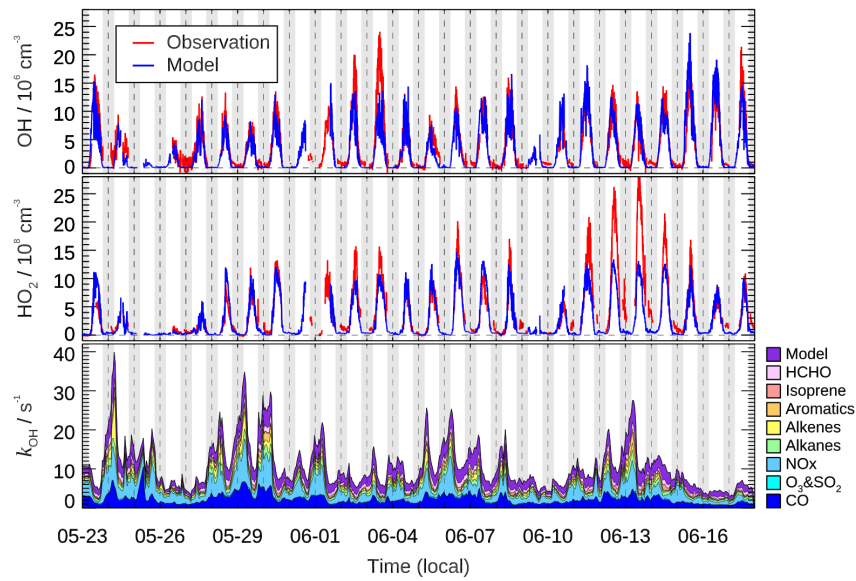
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Figure 3. Time series of observed and modelled OH and HO$_2$ concentrations, and the modelled grouped OH reactivity (k_{OH}). Vertical dash lines denote midnight. The grey areas denote nighttime.

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Figure 5. Summary of OH radical concentrations (noon time, 11:00-13:00) measured in five summer field campaigns in China. Yufa (YF) and Wangdu (WD) campaign in North China Plain, Heshan (HS) and Backgarden (BG) campaign in Pearl River Delta, and Taizhou (TZ, this study) campaign in Yangtze River Delta. The box-whisker plot shows the 90th, 75th, 50th, 25th, and 10th percentile values of noon OH radical concentrations in each campaign. The diamond shows the mean values of noon OH radical concentrations.

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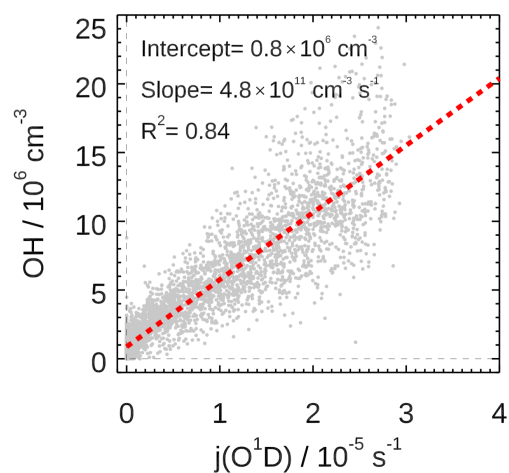
Figure 6. Correlation between measured OH and j(O^1D). Grey scatter plot represents the 5 min observation result for the EXPLORE-YRD campaign. A linear fit which takes both measurements error into account is applied. The linear fit lines and correlation slopes, intercept and coefficients are also shown.

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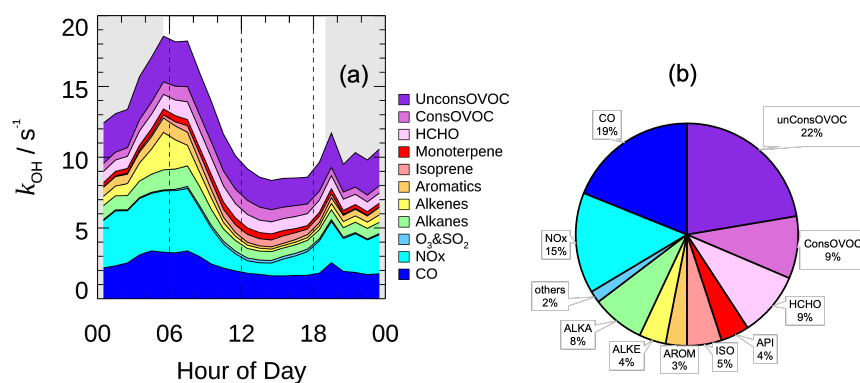
Figure 7. (a) The mean diurnal profiles of speciated OH reactivity. The grey areas denote nighttime. (b) Breakdown of modelled OH reactivity for daytime conditions (08:00-16:00).

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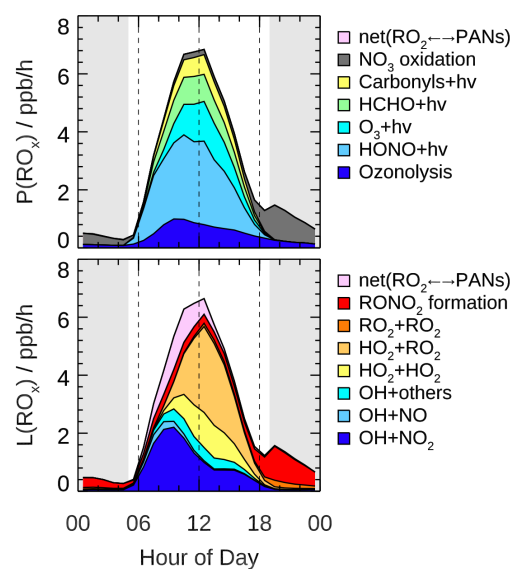
Figure 8. Hourly mean diurnal profiles of primary sources and sinks of RO$_x$ radicals from model

calculations. The grey areas denote nighttime.

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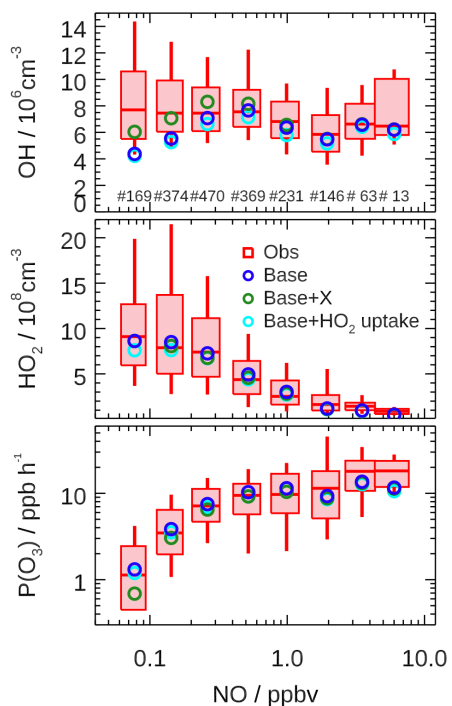
Figure 9. Dependence of measured and modelled OH, HO$_2$, and P(O$_x$) on NO concentrations for daytime condition (j(O^{1}D)> 0.5×10^{-5} s^{-1}). Box-whisker plot shows the median, the 75 and 25 percentiles, and the 90 and 10 percentiles of the measured results for each NO interval bins. Only median values are shown for modelled results. Numbers in upper panel represent the data points incorporated in each NO interval. Results from base case, with additional recycling process by a species *X* (equivalent to 100 ppt NO), and with additional HO$_2$ heterogeneous uptake process (γ assuming of 0.08) are all plotted.

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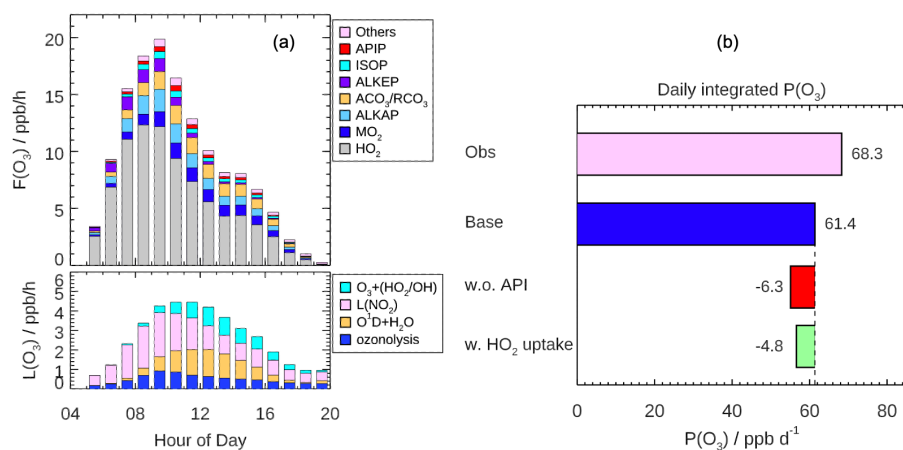
Figure 10. (a) Mean diurnal profiles of the speciation ozone formation rate (F(O$_x$)) from different

peroxy radical species (upper panel) and the speciation ozone destruction rate (L(O$_x$), lower panel)

calculated based on the measured OH and HO$_2$ and modelled RO$_2$ radicals. (b) Daily (08:00-16:00)

integrated net ozone production calculated from the observed and modelled radical concentration,

respectively. The discrepancies between two model scenarios run (Scenario1: without α-pinene

constrained; Scenario2: with HO$_2$ heterogeneous uptake considered by assuming γ of 0.08) from base

case are also shown.