



Supplement of

Why did ozone concentrations remain high during Shanghai's static management? A statistical and radical-chemistry perspective

Jian Zhu et al.

Correspondence to: Shanshan Wang (shanshanwang@fudan.edu.cn) and Bin Zhou (binzhou@fudan.edu.cn)

The copyright of individual parts of the supplement might differ from the article licence.

1 Text S1 meteorological conditions.

2 We evaluated whether there were significant changes in ground-level airflows in Shanghai during the static 3 management period compared to the same periods in 2020 and 2021. An analysis of the frequency distribution of 4 wind speed and wind direction (see Figure S7a-S7f) during the lockdown period shows that wind speeds were 5 primarily distributed in the range of 2-4 m s⁻¹, with the predominant wind direction between 0-180° (with 0° as true 6 north and counting clockwise). Compared to the same periods in 2020 and 2021, during the 2022 lockdown period, 7 there was an increase in the frequency of northerly winds and a decrease in the frequency of westerly winds. This 8 indicates that Shanghai was upwind of other cities in the Yangtze River Delta region for most of the time during the 9 static management period in 2022. From the mean diurnal profiles of wind speed and wind direction, it can be 10 observed that during the lockdown period, the predominant wind direction throughout the day was between 90-150°. 11 and higher wind speeds typically occurred in the afternoon, corresponding to a wind direction of around 100°.

From the rose diagrams of ozone and its precursors NO₂ and VOCs (see Figure S8), during the 2022 lockdown period, the predominant winds during high ozone levels were southerly winds with higher wind speeds and westerly winds with lower wind speeds. When NO₂ concentrations were high, wind speeds were generally lower, and the predominant wind direction during periods of high VOCs concentrations was southwest to south. Comparing the same period in 2020 and 2021, it is obvious that the transmission contribution of ozone and its precursors from other cities in the Yangtze River Delta in 2022 was limited.

18 We also analyzed the percentage change in meteorological conditions in Shanghai and its surrounding areas during 19 the 2022 lockdown period compared to the same periods in 2020 and 2021 as shown in Figure S9 and Figure S10. 20 The results indicate that in 2022, the 2-m temperature and relative humidity in the Shanghai area showed a slight 21 decrease compared to 2020 and 2021, with the changes being relatively small. surface net solar radiation in 2022 22 decreased compared to 2020 but was slightly higher than in 2021, while total precipitation in 2022 was significantly 23 higher than in 2020. During the static management period in Shanghai, the decrease in average temperature, 24 weakening of solar radiation, and increased precipitation may have contributed to the reduction in O_3 production by 25 slowing down chemical reaction rates. ERA5 reanalysis data also indicates that during the static management period, 26 there were minimal variations in 2-meter temperature, relative humidity, surface net solar radiation, boundary layer 27 height, and total cloud cover in the Shanghai area, whereas these parameters exhibited more significant changes in 28 the surrounding regions. The above results indicate that the increase in O₃ concentration in Shanghai during the 2022 29 static management period was not due to changes in meteorological conditions.

30

31 Text S2 Correlation analysis between the sources of radicals and ozone-related indices.

32 Regarding the impact of the sources of radicals in urban environments on air quality, we conducted a correlation 33 analysis between the sources of radicals and ozone-related indices, as shown in Figure R2. The production rates of 34 radicals P(ROx) had a strong positive correlation with the production rates of ozone $P(O_3)$, and both were 35 temperature-dependent. The higher the temperature, the higher $P(O_3)$ and P(ROx). Additionally, we defined daily net 36 ozone production O₃ net as the difference between the highest ozone value at noon and the lowest value in the 37 morning. The correlation analysis between daily O_3 net and the photolysis rates of HONO, O_3 , HCHO, and OVOCs, 38 as well as the total radical source, reveals a significant positive relationship. This implies that the strength of different 39 sources of modeled radicals positively contributes to ozone production. From the perspective of the slopes, the 40 contribution of HCHO photolysis to net ozone generation is evident. This may be attributed to the enhancement of 41 the NO₂-NO-O₃ cycle by the HO₂ radicals produced from HCHO photolysis.

42

43 Text S3 Review of radical observation and simulation research.

We have compiled observations and simulations of radical chemistry conducted by various research teams in different environments (see Table R1). It is evident that the primary sources of radicals vary in different regions and seasons. Compared to marine boundary layer environments, forest environments, and suburban environments, the primary sources of radicals in urban environments were complex. For example, simulation work conducted in urban 48 environments in Nashville, Houston, and Writtle indicates that the photolysis of ozone was a primary contributor to 49 the primary source of radicals (Kovacs et al., 2003; Martinez et al., 2003; Thornton et al., 2002; Mao et al., 2010; Lee 50 et al., 2006; Emmerson et al., 2007; Emmerson and Carslaw, 2009). And in locations like New York, Palaiseau, 51 Shenzhen, the photolysis of HONO played a significant role (Ren et al., 2003a; Ren et al., 2003b; Cai et al., 2008; 52 Dolgorouky et al., 2012; Michoud et al., 2012; Yang et al., 2022). It is noteworthy that within the same urban 53 environment, the dominant sources can vary across different seasons, time periods, and conditions. In Tokyo, the 54 primary sources of free radicals in winter were the reactions between ozone and alkenes, while in summer, they were 55 the photolysis of ozone and OVOCs (Kanaya et al., 2008; Kanaya et al., 2007a). In New York, during the daytime, 56 the primary source was the photolysis of HONO, while at night, it resulted from the reaction between O_3 and 57 alkenes(Cai et al., 2008; Ren et al., 2006). In Jülich, under high NOx conditions, the primary source was the 58 photolysis of HONO, whereas under low NOx conditions, it was the photolysis of O_3 (Kanaya et al., 2012). In marine 59 boundary layer environments, most studies indicated that the photolysis of ozone was the primary contributor to free 60 radicals during the day, while at night, it resulted from the reaction between O₃ and alkenes. In suburban and rural 61 environments, the primary contributor was the photolysis of HONO. Just as you mentioned the differences in radical 62 chemistry between urban and suburban environments, historical research has also indicated this, and it is a crucial 63 aspect of the simulation studies we conducted in Shanghai.

65 Text S4 Role of VOCs in ozone production.

66 Different VOC species display a range of reactivity and diverse potentials for O₃ formation, which can be assessed 67 using the maximum incremental reactivity (Carter, 2009). The calculated ozone formation potential (OFP) for each 68 VOC species illustrates the maximum contribution of the species to the formation of ozone. (Bufalini and Dodge, 69 1983). The OFP for each VOC species is calculated using the following equation (Ma et al., 2019; Zhu et al., 2020):

$$OFP_i = MIR_i \times [VOC_i] \times \frac{M_i}{M_{ozone}}$$
S1

where OFP_i (ppbv) represents the ozone formation potential of VOC species i, [VOCi] (ppbv) denotes the atmospheric concentration of VOC species i, and MIRi (g O₃/g VOC) is the ozone formation coefficient of VOCi in the maximum increment reactions of ozone. Mozone and Mi are the molar masses (g mol⁻¹) of O₃ and VOC species i, respectively.

74 In addition, another widely used indicator of atmospheric oxidative capacity is the OH reactivity, defined as the 75 reaction rate coefficient multiplied by the concentration of OH reactants, depending on the abundance and 76 composition of major pollutants. The OBM model can output the kOH for each VOCs, which reflects the reactivity 77 of VOCs.

78 The comparison of the mean concentration of the six VOCs groups and their OFP in 2020, 2021, and 2022 is 79 presented in Figure S11. It is obvious that the concentration of the VOC group was not proportional to its OFP. The 80 average proportions of each VOCs component in 2020 and 2021 are 47.2%, 6.7%, 9.2%, 4.8%, 13.8% and 18.4% 81 respectively, while the corresponding average proportions of OFP are 19.6%, 24.0%, 40.4%, 1.1%, 14.1% and 0.9%, 82 respectively. In 2022, with minimal changes in the concentration proportions of alkenes, the OFP proportion 83 increased by 11.3%. The proportion of aromatic hydrocarbons decreased by 4.2%, resulting in a 23.7% decrease in 84 their OFP proportion. The proportion of OVOCs increased by 3.7%, leading to an 8.5% increase in their OFP 85 proportion. In short, the primary contributors to OFP in 2020 and 2021 were aromatic hydrocarbons, followed by 86 alkenes, while in 2022, the main contributors were alkenes, followed by OVOCs.

We combined two indicators, OFP and *k*OH, to identify key VOCs in photochemical processes. Figure S11b clearly shows a significant positive correlation between the OFP and *k*OH for each VOC after logarithmic transformation. Therefore, VOCs that rank high in both indicators are sufficient to indicate that these VOCs are key contributors in photochemical processes. In 2020 and 2021, m/p-xylene, toluene, ethylene, and propylene were the top contributors to both OFP and *k*OH. However, in 2022, propylene and ethylene took the lead in OFP, while propylene, isoprene, and ethylene topped the *k*OH.

93



Figure S2. Performance comparisons of the stacking model and the five base models after 5-fold cross-validation with the indicators of the coefficient of determination (r2_score), root mean square error (RMSE), and slope between predicted and measured O₃.



101 Figure S3. Performance comparisons of the stacking model and the five base models after 5-fold cross-validation with the indicators of r2_score, RMSE, and slope between predicted and measured NO₂.



Figure S4. Performance comparisons of the stacking model and the five base models after 5-fold cross-validation with the indicators of r2_score, RMSE, and slope between predicted and measured HCHO.



107 Figure S5. Performance comparisons of the stacking model and the four base models after 5-fold cross-validation with the indicators of r2_score, RMSE, and slope between predicted and measured HONO.



110Figure S6. Performance comparisons of the stacking model and the four base models after 5-fold cross-validation with the indicators of
r2_score, RMSE, and slope between predicted and measured SO2.



Figure S7. The frequency (a-f) and the mean diurnal profiles (d, h, i) of wind speed and wind direction during the periods from April to May of 2020, 2021, and 2022.





117180°180°0118Figure S8. The polar plots of O3 (a, b, c), NO2 (d, e, f) and VOCs (g, h, i) during the periods from April to May of 2020, 2021, and 2022.



Figure S9. The percentage change in average meteorological parameters from the ERA5 data for Shanghai and its neighboring regions during the 2022 lockdown period compared to the same period in 2020. The 2-m temperature (t2m) (a), relative humidity calculated based on 2-m temperature and 2-m dewpoint temperature (b), surface net solar radiation (ssr) (c), boundary layer height (blh) (d), total cloud cover (tcc) (e), and total precipitation (tp) (f).



Figure S10. Same as Figure S9 but compared to the same period in 2021.



Figure S11. (a) The mean

concentration and OFP of six VOC groups and (b) Scatter plots of the average OFP and OH reactivity for individual VOCs during daytime hours between 06:00 and 18:00 for the periods of April to May in 2020, 2021, and 2022.



132

133Figure S12. (a) The mean diurnal profiles of VOCs for the periods of April to May in 2020, 2021, and 2022, as well as June 2023. (b)134The mean diurnal profiles of VOCs for weekdays and weekends in June 2023





1366912151869121518137Figure S13. The proportions (a, b, c) and the mean diurnal profiles (d, e, f) of primary sources of daytime radicals during the periods138from April to May of 2020, 2021, and 2022.

Cluster 1 O3+VOCs (a) (b) Cluster 2 (c) Cluster 3 (d) Cluster 4 0₁+VOCs O3+VOCs 03+VOCs HCHO+hv HCHO+hv HCHO+hv NO₃+VOC 13.8% HCHO+hv NO3+VOCs 14.3% 13.5% 13.9% 13.5% 14.3% 18.3% NO3+VOCs NO3+VOCs 12.0% 13.3% OVOCs+hv 15.2% OVOCs+hv 18.4% OVOCs+hv 13.7% OVOCs+hv 19.7% 24.5% HONO+hv 31.0% HONO+h HONO+h HONO+hv 15.4% 25.3% 20.6% 27.2% 4 (e) O3+hv O₃+hv 4 (f) 4 (g) (h) O₃+hv O₃+hv 4 P(ROx) [ppbv s⁻¹] τ ν ω 3 3 3 2 2 2 1 1 1 0 0 0 0 15 18 12 15 15 18 12 12 ģ 12 15 18 ģ 6 18 6 ģ 6 9

 $140 \\ 141 \\ 142$

Figure S14. The proportions (a, b, c, d) and the mean diurnal profiles (e, f, g, h) of primary sources of daytime radicals for Cluster 1, Cluster 2, Cluster 3, and Cluster 4



Figure S15. Correlation

143

144 145

analysis between the sources of radicals and ozone-related indices, (a) P(O₃) & P(ROx); (b) O₃_net & HONO+hv; (c) O₃_net & O₃+hv; (d) O₃_net & HCHO+hv; (e) O₃_net & HONO+hv; (f) O₃_net & P(ROx).



Figure S16. Time series of meteorological parameters (temp, RH, *j*(NO₂)) and air pollutants (O₃, NO₂, HONO, HCHO, SO₂, PM_{2.5}, VOCs) from April to May 2020. The data with the "+" symbol represents the predictions made by machine learning and is used to fill in missing values in the observations.



150 Figure S17. Same as Figure S11, but for the period between April and May 2021.



152 Figure S18. Same as Figure S11, but for the period between April and May 2022.

Trace gas	Fitting window (nm)	absorption cross sections	Polynomial degree	detection limits
O3	280.6-290.6	O ₃ (Voigt et al., 2001), SO ₂ (Vandaele et al., 2009), HCHO (Meller and Moortgat, 2000), and NO ₂ (Voight et al., 2002)	5	1.3 ppbv
NO ₂	365.3-380.4	NO ₂ (Voight et al., 2002), HONO (Stutz et al., 2000), HCHO (Meller and Moortgat, 2000), and solar spectrum (Kurucz, 1984)	5	0.5 ppbv
SO ₂	295.3-307.9	SO ₂ (Vandaele et al., 2009), O ₃ (Voigt et al., 2001), HCHO (Meller and Moortgat, 2000), NO ₂ (Voight et al., 2002), and solar spectrum (Kurucz, 1984)	5	0.1 ppbv
HONO	339.4-373.2	HONO (Stutz et al., 2000), NO ₂ (Voight et al., 2002), HCHO (Meller and Moortgat, 2000), and solar spectrum (Kurucz, 1984)	5	0.1 ppbv
НСНО	311.7-342.1	HCHO (Meller and Moortgat, 2000), NO ₂ (Voight et al., 2002), HONO (Stutz et al., 2000), O ₃ (Voigt et al., 2001), SO ₂ (Vandaele et al., 2009), and solar spectrum (Kurucz, 1984)	5	0.5 ppbv

154 Table S1. The configuration of spectral fitting of O₃, NO₂, SO₂, HONO and HCHO.

155

Table S2. Summary of the mean concentration of measured VOCs during the periods from April to May of 2020, 2021,

156 157

Species	Average concentration (mean \pm std, unit: ppbv)						
alkanes	2020	2021	2022				
Ethane	4.36 ± 3.73	4.30 ± 2.02	3.66 ± 2.57				
Propane	2.91 ± 2.91	2.96 ± 1.96	1.63 ± 1.28				
n-Butane	1.12 ± 1.04	1.23 ± 0.87	0.70 ± 0.67				
Isobutane	0.86 ± 0.96	1.00 ± 0.83	0.54 ± 0.53				
n-Pentane	0.46 ± 0.55	0.50 ± 0.44	0.32 ± 0.34				
Isopentane	0.82 ± 1.07	0.92 ± 0.99	0.66 ± 0.83				
Cyclopentane	0.04 ± 0.04	0.04 ± 0.07	0.03 ± 0.04				
n-Hexane	0.13 ± 0.16	0.14 ± 0.15	0.06 ± 0.06				
2,2-Dimethylbutane	0.02 ± 0.03	0.03 ± 0.02	0.01 ± 0.01				
Cyclohexane	0.05 ± 0.07	0.05 ± 0.07	0.02 ± 0.02				
2,3-Dimethylbutane	0.03 ± 0.03	0.05 ± 0.04					
2-Methylpentane	0.15 ± 0.16	0.21 ± 0.19	0.09 ± 0.09				
3-Methylpentane	0.12 ± 0.14	0.11 ± 0.12	0.04 ± 0.06				
Methylcyclopentane	0.04 ± 0.04	0.05 ± 0.04	0.02 ± 0.02				
n-Heptane	0.04 ± 0.04	0.05 ± 0.06	0.02 ± 0.03				
2,3-Dimethylpentane	0.01 ± 0.01	0.02 ± 0.02	0.00 ± 0.01				
2,4-Dimethylpentane	0.01 ± 0.01	0.01 ± 0.01	0.00 ± 0.00				
3-Methylhexane	0.03 ± 0.03	0.04 ± 0.04	0.02 ± 0.02				
2-Methylhexane	0.03 ± 0.02	0.03 ± 0.03	0.01 ± 0.01				
Methylcyclohexane	0.03 ± 0.04	0.04 ± 0.05	0.02 ± 0.02				
n-Octane	0.04 ± 0.05	0.03 ± 0.03	0.01 ± 0.01				
2,2,4-trimethylpentane	0.02 ± 0.02	0.02 ± 0.02	0.00 ± 0.01				
2,3,4-trimethylpentane	0.01 ± 0.01	0.01 ± 0.01	0.00 ± 0.01				
2-Methylheptane	0.01 ± 0.01	0.01 ± 0.01	0.01 ± 0.02				
3-Methylheptane	0.01 ± 0.01	0.01 ± 0.01	0.00 ± 0.01				
n-nonane	0.02 ± 0.02	0.02 ± 0.01	0.01 ± 0.01				

n-Decane	0.02 ± 0.01	0.02 ± 0.02	0.00 ± 0.01
n-undecane	0.01 ± 0.01	0.02 ± 0.01	0.00 ± 0.01
n-Dodecane	0.02 ± 0.01	0.02 ± 0.01	0.20 ± 0.36
alkenes			
Ethylene	0.91 ± 1.14	1.13 ± 1.06	0.60 ± 0.61
Propylene	0.26 ± 0.50	0.30 ± 0.36	0.30 ± 0.83
Isobutylene	0.04 ± 0.05	0.06 ± 0.04	0.04 ± 0.03
1-butene	0.06 ± 0.09	0.08 ± 0.08	0.06 ± 0.08
cis-2-butene	0.03 ± 0.04	0.13 ± 0.06	0.05 ± 0.03
trans-2-butene	0.02 ± 0.05	0.05 ± 0.07	0.03 ± 0.05
1,3-Butadiene	0.01 ± 0.04	0.02 ± 0.02	0.01 ± 0.04
1-pentene	0.02 ± 0.02	0.04 ± 0.03	0.02 ± 0.01
cis-2-pentene	0.00 ± 0.01	0.00 ± 0.01	0.00 ± 0.00
trans-2-pentene	0.00 ± 0.03	0.00 ± 0.01	0.00 ± 0.01
1-Hexene	0.01 ± 0.01	0.00 ± 0.01	0.00 ± 0.00
isoprene	0.04 ± 0.09	0.06 ± 0.11	0.03 ± 0.06
Alkyne			
Acetylene	0.96 ± 0.69	1.14 ± 0.78	0.75 ± 0.38
aromatic			
Benzene	0.34 ± 0.25	0.40 ± 0.38	0.24 ± 0.20
Toluene	0.57 ± 0.67	0.92 ± 1.56	0.18 ± 0.23
Ethylbenzene	0.20 ± 0.26	0.27 ± 0.39	0.05 ± 0.05
o-Xylene	0.16 ± 0.26	0.22 ± 0.34	0.04 ± 0.05
m-Xylene	0.28 ± 0.43	0.40 ± 0.58	0.06 ± 0.08
p-xylene	0.28 ± 0.43	0.40 ± 0.58	0.06 ± 0.08
Styrene	0.02 ± 0.03	0.03 ± 0.05	0.00 ± 0.01
1,2,3-Trimethylbenzene	0.01 ± 0.01	0.01 ± 0.01	0.00 ± 0.00
1,2,4-Trimethylbenzene	0.04 ± 0.05	0.04 ± 0.04	0.01 ± 0.01
1,3,5-Trimethylbenzene	0.01 ± 0.02	0.01 ± 0.02	0.00 ± 0.00
o-Ethyl toluene	0.01 ± 0.01	0.02 ± 0.01	0.00 ± 0.01
m-Ethyltoluene	0.02 ± 0.03	0.03 ± 0.03	0.01 ± 0.01
p-Ethyltoluene	0.01 ± 0.02	0.02 ± 0.02	0.00 ± 0.00
Isopropylbenzene	0.01 ± 0.01	0.01 ± 0.01	0.00 ± 0.01
n-propylbenzene	0.01 ± 0.01	0.01 ± 0.01	0.00 ± 0.00
m-diethylbenzene	0.00 ± 0.01	0.00 ± 0.00	0.00 ± 0.00
p-diethylbenzene	0.01 ± 0.01	0.01 ± 0.01	0.00 ± 0.00
OVOCs			
Acetone	1.81 ± 1.40	2.53 ± 2.08	1.94 ± 0.98
Propionaldehyde	0.17 ± 0.10	0.13 ± 0.11	0.11 ± 0.05
Acrolein	0.07 ± 0.06	0.05 ± 0.04	0.03 ± 0.02
2-Butanone	0.03 ± 0.02	0.03 ± 0.02	0.04 ± 0.02
Butyraldehyde	0.03 ± 0.02	0.03 ± 0.02	0.04 ± 0.02
2-Methylacrylaldehyde	0.03 ± 0.05	0.03 ± 0.04	0.01 ± 0.02
Methyl tert-butyl ether	0.22 ± 0.33	0.14 ± 0.16	0.07 ± 0.12
3-Pentanone	0.02 ± 0.01	0.01 ± 0.01	0.01 ± 0.01
Valeraldehyde	0.03 ± 0.02	0.03 ± 0.01	0.02 ± 0.02
2-Pentanone	0.02 ± 0.01	0.01 ± 0.01	0.02 ± 0.01

Benzyl chloride	0.00 ± 0.01	0.00 ± 0.00	0.00 ± 0.00
Hexanal	0.37 ± 0.37	0.24 ± 0.27	0.32 ± 0.35
Methyl vinyl ketone(butenone)	0.05 ± 0.06	0.03 ± 0.05	0.02 ± 0.02
halohydrocarbons			
Chloromethane	1.24 ± 0.81	0.64 ± 0.30	0.80 ± 0.25
Dichloromethane	1.16 ± 1.34	1.27 ± 1.11	0.57 ± 0.46
Chloroform	0.13 ± 0.17	0.11 ± 0.08	0.06 ± 0.03
Carbon tetrachloride	0.12 ± 0.03	0.10 ± 0.02	0.13 ± 0.02
Bromomethane	0.03 ± 0.04	0.02 ± 0.02	0.02 ± 0.01
Bromoform	0.01 ± 0.01	0.01 ± 0.01	0.00 ± 0.01
Monobromodichloromethane	0.00 ± 0.00	0.00 ± 0.00	0.00 ± 0.00
Trichloromonofluoromethane	0.53 ± 0.16	0.80 ± 0.88	0.58 ± 0.21
Chloroethane	0.05 ± 0.11	0.05 ± 0.10	0.02 ± 0.03
1,1-Dichloroethane	0.01 ± 0.01	0.01 ± 0.01	0.00 ± 0.01
1,2-Dichloroethane	0.41 ± 0.39	0.34 ± 0.29	0.20 ± 0.15
1,1,1-Trichloroethane	0.00 ± 0.00	0.00 ± 0.00	0.00 ± 0.00
1,1,2-Trichloroethane	0.03 ± 0.03	0.02 ± 0.02	0.01 ± 0.01
1,1,2,2-Tetrachloroethane	0.00 ± 0.01	0.00 ± 0.00	0.00 ± 0.00
1,2-dibromoethane	0.00 ± 0.00	0.00 ± 0.00	0.00 ± 0.00
Dichlorotetrafluoroethane	0.02 ± 0.01	0.02 ± 0.01	0.02 ± 0.00
Trichlorotrifluoroethane	0.10 ± 0.02	0.07 ± 0.02	0.07 ± 0.00
Vinyl chloride	0.02 ± 0.04	0.01 ± 0.04	0.00 ± 0.01
1,1-Dichloroethylene	0.00 ± 0.01	0.00 ± 0.01	0.00 ± 0.00
cis-1,2-dichloroethylene	0.00 ± 0.00	0.00 ± 0.00	0.00 ± 0.00
Trichloroethylene	0.04 ± 0.07	0.03 ± 0.05	0.01 ± 0.01
Tetrachloroethylene	0.04 ± 0.04	0.04 ± 0.04	0.02 ± 0.02
1,2-Dichloropropane	0.06 ± 0.06	0.10 ± 0.11	0.05 ± 0.06
cis-1,3-dichloropropene	0.00 ± 0.00	0.00 ± 0.00	0.00 ± 0.00
trans-1,3-dichloropropene	0.00 ± 0.00	0.00 ± 0.00	0.00 ± 0.00
Chlorobenzene	0.02 ± 0.02	0.01 ± 0.03	0.00 ± 0.01
1,2-Dichlorobenzene	0.01 ± 0.01	0.01 ± 0.01	0.00 ± 0.00
1,3-Dichlorobenzene	0.00 ± 0.01	0.00 ± 0.01	0.00 ± 0.00
1,4-Dichlorobenzene	0.04 ± 0.05	0.04 ± 0.04	0.02 ± 0.03
Iodomethane	0.00 ± 0.00	0.00 ± 0.00	0.00 ± 0.00
Acetonitrile	0.10 ± 0.10	0.13 ± 0.10	0.14 ± 0.08

60 Table S3. Summary of measurements and model comparisons for OH and HO2 in different typical environments, as well as OH reactivity and HOx primary

sources	sources									
campaign	year	location	Technique	OH measured	HO ₂ measured	OH reactivity	HOx primary sources	comments	Ref.	
					Urban environme	nt				
SOS	June-July 1999	Nashville, Tennessee,	LIF	0.8 pptv at noon	80 pptv at noon	11.3±4.8 s ⁻¹	O ₃ +hv	OH observed-to-modeled ratio: 1.33; OH observed-to-modeled ratio: 1.56; the	(Thornton et al., 2002; Martinez et	
		USA, 36°N, 88°W						times larger than modeled.	al., 2003; Kovacs et al., 2003)	
PUMA	June 1999 &	Birmingham,	LIF	$(2-9) \times 10^6$ molecule	$(1.5-10) \times 10^{8}$	-	O ₃ +alkenes:	OH modeled-to-measured ratio: 0.58 in	(Emmerson et al.,	
	January- February 2000	UK, 53°N, 2°W		cm ⁻³ in summer, (0.5- 4)×10 ⁶ molecule cm ⁻³ in summer,	molecule cm ⁻³ in summer, $\sim 4 \times 10^{6}$ molecule cm ⁻³ in summer,		46% in summer, 62% in winter	summer and 0.5 in winter; HO ₂ modeled-to-measured ratio: 0.56 in summer and 0.49 in winter.	2005a; Emmerson et al., 2005b; Heard et al., 2004; Harrison et al., 2006)	
TEXAQS	August- September 2000	Houston, Texas, USA, 29°N, 95°W	LIF	Maximum ~0.8 pptv	Maximum ~30 pptv	7-12 s ⁻¹	O ₃ +hv		(Mao et al., 2010)	
PMTACS- NY	June-August 2001	New York, USA, 41°N, 74°W	LIF	(2-20)×10 ⁶ molecule cm ⁻³	$(0.5-2) \times 10^{8}$ molecule cm ⁻³	15-25 s ⁻¹	HONO+hv	OH observed-to-modeled ratio: 1.10 ; HO ₂ observed-to-modeled ratio: 1.24 ; The OH reactivity measurements agree with the calculations to within 10%	(Cai et al., 2008; Ren et al., 2003b; Ren et al., 2003a)	
HOxComp	9-11 July 2005	2005 Julich, Germany LIF, DOAS, (50°54'33"N, CIMS	Maximum 9.4×10 ⁶ molecule cm ⁻³	Maximum 35 pptv		high-NOx: HONO+hv;	Good agreement between model and observations for OH under high isoprene low NOx (fresh iconrene emissions)	(Kanaya et al., 2012)		
		06°24'44"E)					low-NOx: O ₃ +hv	low NOX (fresh isoprene emissions)		
МСМА	April 2003	Mexico City, Mexico, 19°N,100°W	LIF	(5-8)×10 ⁶ molecule cm ⁻³	15-60 pptv	25-120 s ⁻¹	HCHO+hv	(OH)model= $1.2 \times$ (OH)-0.008 pptv R ² =0.80; (HO ₂)model= $0.90 \times$ (HO ₂)+0.98 pptv R ² =0.64; OH reactivity in the model is about 10-20% too low	(Volkamer et al., 2010; Sheehy et al., 2010; Shirley et al., 2006)	
TORCH-1	July-August 2003	Writtle, Essex, UK, 51°N, 0°E	LIF	$(1.2-7.5) \times 10^6$ molecule cm ⁻³ , with 2.6×10^6 molecule cm ⁻³ at night	$(0.16-3.3)\times10^8$ molecule cm ⁻³ , with 2.9×10 ⁷ molecule cm ⁻³ at night	2-10 s ⁻¹	O ₃ +hv	Daytime OH and HO ₂ Overpredicted by 24% and 7%, respectively; nighttime OH and HO ₂ unpredicted 41% and 16%, respectively	(Emmerson and Carslaw, 2009; Emmerson et al., 2007; Lee et al., 2006)	
IMPACT IV&L	January- February and July-August 2004	Tokyo, Japan, 35°N, 139°E	LIF	In winter, daytime median was 1.5×10 ⁶ molecule cm ⁻³ and night mean was 1.8×10 ⁵ molecule cm ⁻³ ; in summer, daytime median was 6.3×10 ⁶ molecule cm ⁻³ and night mean was 3.7×10 ⁵ molecule cm ⁻⁴	In winter, daytime median was 1.1 pptv and night mean was 0.7 pptv; in summer, daytime median was 5.7 pptv and night mean		the day and night in winter: O_3 +alkenes; in daytime during summer: O_3 +hv and OVOCs+hv, during the early morning in summer:	Daytime OH well reproduced by model for both periods; daytime HO ₂ underestimated in winter and overestimated in summer.	(Kanaya et al., 2008; Kanaya et al., 2007a)	

				3	was 2.6 pptv		HONO+hv		
PMTACS-2	January- February 2004	New York, USA, 41°N, 74°W	LIF	maximum 1.4×10 ⁶ molecule cm ⁻³	maximum 0.7 pptv	20-40 s ⁻¹	Daytime: HONO+hv; Nighttime: O ₃ +alkenes	OH observed to modelled ratio of 0.98; HO ₂ observed to modelled ratio of 6, with the greatest values at high NO; OH reactivity measured higher than calculated at rush hour in the morning and in the evening, possibly due to unmeasured or missing VOCs.	(Cai et al., 2008; Ren et al., 2006)
MILAGRO	March 2006	Mexico City, Mexico, 19°N, 100°W	LIF	maximum median 4.6×10^6 molecule cm ⁻ $_3$	maximum median 1.9×10 ⁸ molecule cm ⁻³		HCHO+hv	OH overpredicted by a factor of 1.7 at midday, well reproduced after 14:30; HO ₂ underpredicted in the morning, well reproduced after 11:30	(Dusanter et al., 2009b; Dusanter et al., 2009a)
TRAMP	August- September 2006	Houston, Texas, USA, 29°N, 95°W	LIF	Daytime: 0.33±0.23 pptv; Nighttime: 0.087±0.066 pptv	Daytime: 22±18 pptv; Nighttime: 11±7.8 pptv	10-20 s ⁻¹	morning rush hour: HONO+hv; daytime: O_3 +hv; nighttime: O_3 +alkenes	the measured OH was generally greater than the modeled OH for all mechanisms, especially during the afternoon; For HO ₂ , Good agreement was found in the morning for the models with most mechanisms, except for SAPRC-99 (slope=0.67); This good agreement between measured and calculated OH reactivity	(Chen et al., 2010; Mao et al., 2010)
MEGAPOLI	July 2009	Palaiseau, French 48.71°N,2.21°E	LIF	~5×10 ⁶ molecule cm ⁻³	~1.2×10 ⁸ molecule cm ⁻³		HONO+hv	Photo Stationary State calculations overestimate OH by 50 %, box model overestimated 12% and 5 %, for OH and (HO ₂ +RO ₂) respectively.	(Michoud et al., 2012; Dolgorouky et al., 2012)
STORM	September- October 2018	Peking University Shenzhen Graduate School, Shenzhen, China 22.60°N, 113.97°E	LIF	maximum of 4.5×10 ⁶ molecule cm ⁻³	Maximum of 4.2×10 ⁸ molecule cm ⁻³	18-22 s ⁻¹	HONO+hv	Good agreement between the observed and modeled kOH during the several days in Shenzhen	(Yang et al., 2022)
				Mari	ne boundary enviro	onment			
EASE97	April-May 1997	Mace Head, Ireland, 53°N, 10°W	LIF	(2.0-6.0)×10 ⁶ molecule cm ⁻³	$(0.5-3.5) \times 10^8$ molecule cm ⁻³		O ₃ +hv	average model-measurement ratios were 2.4 for OH, 3.6 for HO_2 between 11:00 and 15:00.	(Creasey et al., 2002; Carslaw et al., 2002)
OKIPEX	July-August 1998	Oki Dogo Island, Japan, 36°N, 133°E	LIF	Below the detection limit of the instrument (0.8 pptv)	Maximum of 17 pptv		O ₃ +hv	Model usually overestimated HO ₂ by a factor of 2	(Kanaya et al., 2000; Kanaya and Akimoto, 2002)
ORION99	August 1999	Cape Hedo, Okinawa Island, Japan, 27°N, 128°E	LIF	Maximum of 4×10 ⁶ molecule cm ⁻³	Daytime: maximum of 17 pptv; nighttime: 0.5-5.5 pptv		O ₃ +hv	OH was underestimated by model calculations but within a large uncertainty; Model underestimated daytime HO ₂ by only 20%	(Kanaya et al., 2001b; Kanaya et al., 2001a; Kanaya et al., 2002a)
SOAPEX-2	January- February 1999	Cape Grim, Tasmania, 41°S,	LIF	Maximum of 3.5×10 ⁶ molecule cm ⁻³	Maximum of 2×10^8 molecule		O ₃ +hv	Models overestimated OH by 10%-20%; Models overestimated HO ₂ by \sim 40%;	(Sommariva et al., 2004; Creasey et

		142°E			cm ⁻³				al., 2003)
RISOTTO	June 2000	Rishiri Island, Japan, 45°N, 141°E	LIF		~10 pptv at midday; mean of 4.2±1.2 pptv at night		Nighttime: O ₃ +alkenes	OH overestimated by \sim 36%; HO ₂ overestimated by \sim 70%, requiring 25 pptv IO to reconcile model with observations	(Kanaya et al., 2002c; Kanaya et al., 2002b)
RISFEX	September 2003	Rishiri Island, Japan, 45.07°N, 141.12°E	LIF	Daytime: maximum of 2.7×10^6 molecule cm ⁻³ ; Nighttime: $(0.07-0.55) \times 10^6$ molecule cm ⁻³	Daytime: maximum of 5.9 pptv; Nighttime: (0.5- 4.9) pptv		Daytime: O ₃ +hv; Nighttime: O ₃ +alkenes	OH overestimated by 35%; HO_2 overestimated by 89%; median nighttime modeled-to-observed ratios were 1.29 and 0.56 for HO_2 and OH, respectively	(Kanaya et al., 2007b; Qi et al., 2007)
RHaMBLe	May-June 2007	Cape Verde, Atlantic Ocean, 16.85°N, 24.87°W	LIF	Maximum of 9×10 ⁶ molecule cm ⁻³	Daytime: maximum of 6×10^8 molecule cm ⁻³ ; Nighttime: ~0.6 pptv		Daytime: O ₃ +hv; Nighttime: O ₃ +alkenes	under-predicted OH on average by 18%; under-predicted HO ₂ by 39%	(Lee et al., 2010; Whalley et al., 2010)
SOS	February-	Cape Verde,	LIF	Maximum of $\sim 9 \times 10^6$	maximum of		O ₃ +hv	Concentrations in summer (June,	(Carpenter et al.,
	March; June; September	Atlantic Ocean, 17°N, 25°W		molecule cm ⁻⁵	$4 \times 10^{\circ}$ molecule cm ⁻³ , $\sim 10^{7}$			September) almost double those	2010; Vaughan et al., 2012)
	2009				molecule cm ⁻³ at night			observed in winter (Feb, March)	
					Forest environmen	t			
AEROBIC	July-August 1997	Indigenous forest, North West Greece, 40°N, 21°E	LIF	(4-12)×10 ⁶ molecule cm ⁻³	$(0.4-9) \times 10^8$ molecule cm ⁻³		O ₃ +hv	Model underprediction of OH by ~50%. Modelled HO ₂ was typically higher than observations. But observations showed high variability	(Creasey et al., 2001; Carslaw et al., 2001)
PROPHET- 98	August 1998	Deciduous forest, North Michigan, USA, 45.6°N, 84.7°W	LIF	Daytime: 0.1-0.2 pptv; Nighttime: 0.04 pptv	Daytime: 10-25 pptv: Nighttime: 1-4 pptv		O ₃ +alkenes	OH observations 2.7 times greater than the model; HO_2 observations and model in good agreement	(Faloona et al., 2001; Tan et al., 2001)
GABRIEL	October 2005	Suriname, South America	LIF	0.25 pptv	~(50-55) pptv		O ₃ +hv	Observed to modelled ratio of 12.2 for OH and 4.1 for HO_2	(Kubistin et al., 2010; Butler et al., 2008; Lelieveld et al., 2008; Martinez et al., 2010)
OP3	April and July 2008	Sabah, Borneo, 5°N, 118°E	LIF	2.5×10^6 molecule cm ⁻ ³	2×10 ⁸ molecule cm ⁻	10-60 s ⁻¹	O ₃ +hv	Factor of 10 underprediction in OH when model constrained to OH reactivity. HO ₂ overpredicted at ground level	(Whalley et al., 2011; Stone et al., 2011; Pugh et al., 2010)
HUMPPA-	July and	boreal forest in	LIF, CIMS	3.5×10^6 molecule cm ⁻	37 pptv	12.4 s ⁻¹	O3+hv	$OH_{LIF}/OH_{CIMS} = (1.31 \pm 0.14);$	(Hens et al., 2014; Nölscher et al., 2012)
2010	August 2010	Hyytiälä, southern Finland		5				$OH_{mod.}/OH_{obs.}{=}1.00\pm0.16;$	
		61.9°N, 24.3°E						$HO_2{}^{mod.}/HO_2{}^{obs}{=}0.3\pm0.2;$	
								simulated OH reactivity does not match the observed OH reactivity	

				Suburt	oan & rural enviro	nments			
CAREBeijin g-2006	August- early September 2006	Suburban rural site, Beijing, China, 39.61°N, 116.30°E	LIF	(4-17)×10 ⁶ molecule cm ⁻³	$(2-24) \times 10^8$ molecule cm ⁻³	10-30 s ⁻¹	HCHO+hv	A large discrepancy of a factor 2.6 is found at the lowest NO concentration encountered (0.1 ppb)	(Lu et al., 2010)
PRIDE-PRD 2014	autumn 2014	Guangdong Atmospheric Supersite, China 22.73°N, 112.93°E	LIF	maximum median of 4.5×10^6 molecule cm ⁻ ₃	maximum median of 3×10^8 molecule cm ⁻³	22-32 s ⁻¹	HONO+hv	50 % was unexplained by the measured OH reactants	(Tan et al., 2019)
	June 2014	Wangdu, China	LIF	(5-15)×10 ⁶ molecule cm ⁻³	$(3.14) \times 10^{8}$ molecule cm ⁻³	10-20 s ⁻¹	HONO+hv	Model-measurement ratio was between 1.4 and 2; For HO ₂ , good agreement between modeled and observed concentrations during day and night	(Fuchs et al., 2017; Tan et al., 2017)
BEST-ONE	January- March 2016	suburban site Huairou, Beijing, China 40.41°N, 116.68°E	LIF	2.4×10 ⁶ molecule cm ⁻ ³ in severely polluted air; 3.6×10 ⁶ molecule cm ⁻³ in relatively clean air	0.52×10^8 molecule cm ⁻³ in severely polluted air; 0.93×10^8 molecule cm ⁻³ in relatively clean air	26.9 s ⁻¹ in severely polluted air; 10.1 in relatively clean air	HONO+hv	OH and HO ₂ observed to modelled ratio of 1.5 during clean days; underestimated HO ₂ concentrations by factors up to 5 during pollution episodes	(Tan et al., 2018)
CHOOSE- 2019	August- September 2019	Xinjin, Chengdu, China 30.40°N, 103.85°E	LIF	Mean of 9.5×10 ⁶ molecule cm ⁻³	Mean of 9×10 ⁸ molecule cm ⁻³		HONO+hv	OH observed to modelled ratio of 0.8, HO_2 observed to modelled ratio of 1.0	(Yang et al., 2021; Zhang et al., 2022)

		$HO_2+R \rightarrow OH$		HO ₂ ←OH+R		
R	NO	O ₃	NO ₃	СО	НСНО	
2020	3.911	0.052	0.014	1.904	0.309	
2021	4.074	0.062	0.015	1.773	0.221	
2022	3.435	0.125	0.019	2.086	0.274	
2022/2020	0.9	2.6	1.4	1.1	0.9	
2022/2021	0.8	2.1	1.3	1.2	1.2	

163 Table S4. The reaction rates of the main processes in the OH-HO₂ cycle for the three years.

165 **References:**

- Bufalini, J. J. and Dodge, M. C.: Ozone-forming potential of light saturated hydrocarbons, Environmental
 Science & Technology, 17, 308-311, <u>https://doi.org/10.1021/es00111a013</u>, 1983.
- 168 Butler, T., Taraborrelli, D., Brühl, C., Fischer, H., Harder, H., Martinez, M., Williams, J., Lawrence, M.,
- and Lelieveld, J.: Improved simulation of isoprene oxidation chemistry with the ECHAM5/MESSy chemistry-climate model: lessons from the GABRIEL airborne field campaign, Atmospheric Chemistry
- 171 and Physics, 8, 4529-4546, <u>https://doi.org/10.5194/acp-8-4529-2008</u>, 2008.
- 172 Cai, C., Hogrefe, C., Katsafados, P., Kallos, G., Beauharnois, M., Schwab, J. J., Ren, X., Brune, W. H.,
- 173 Zhou, X., and He, Y.: Performance evaluation of an air quality forecast modeling system for a summer and
- winter season-Photochemical oxidants and their precursors, Atmospheric Environment, 42, 8585-8599,
 https://doi.org/10.1016/j.atmosenv.2008.029, 2008.
- 176 Carpenter, L., Fleming, Z. L., Read, K., Lee, J., Moller, S., Hopkins, J., Purvis, R., Lewis, A., Müller, K.,
- 177 and Heinold, B.: Seasonal characteristics of tropical marine boundary layer air measured at the Cape Verde
- Atmospheric Observatory, Journal of Atmospheric Chemistry, 67, 87-140, <u>https://doi.org/10.1007/s10874-</u>
 011-9206-1, 2010.
- 180 Carslaw, N., Creasey, D., Harrison, D., Heard, D., Hunter, M., Jacobs, P., Jenkin, M., Lee, J., Lewis, A.,
 181 and Pilling, M.: OH and HO₂ radical chemistry in a forested region of north-western Greece, Atmospheric
- 182 Environment, 35, 4725-4737, <u>https://doi.org/10.1016/S1352-2310(01)00089-9</u>, 2001.
 183 Carslaw, N., Creasey, D., Heard, D., Jacobs, P., Lee, J., Lewis, A., McQuaid, J., Pilling, M., Bauguitte, S.,
- and Penkett, S.: Eastern Atlantic Spring Experiment 1997 (EASE97) 2. Comparisons of model concentrations of OH, HO₂, and RO₂ with measurements, Journal of Geophysical Research: Atmospheres, 107, ACH 5-1-ACH 5-16, <u>https://doi.org/10.1029/2001JD001568</u>, 2002.
- 187 Carter, W. P.: Updated maximum incremental reactivity scale and hydrocarbon bin reactivities for 188 regulatory applications, California Air Resources Board Contract, 339, 2009, 2009.
- 189 Chen, S., Ren, X., Mao, J., Chen, Z., Brune, W. H., Lefer, B., Rappenglück, B., Flynn, J., Olson, J., and
- 190 Crawford, J. H.: A comparison of chemical mechanisms based on TRAMP-2006 field data, Atmospheric
- 191 Environment, 44, 4116-4125, <u>https://doi.org/10.1016/j.atmosenv.2009.05.027</u>, 2010.
- 192 Creasey, D., Heard, D., and Lee, J.: OH and HO₂ measurements in a forested region of north-western 193 Greece, Atmospheric Environment, 35, 4713-4724, <u>https://doi.org/10.1016/S1352-2310(01)00090-5</u>, 2001.
- 194 Creasey, D., Heard, D., and Lee, J.: Eastern Atlantic Spring Experiment 1997 (EASE97) 1. Measurements
- of OH and HO₂ concentrations at Mace Head, Ireland, Journal of Geophysical Research: Atmospheres, 107,
 ACH 3-1-ACH 3-15, <u>https://doi.org/10.1029/2001JD000892</u>, 2002.
- 197 Creasey, D., Evans, G., Heard, D., and Lee, J.: Measurements of OH and HO₂ concentrations in the 198 Southern Ocean marine boundary layer, Journal of Geophysical Research: Atmospheres, 108, 199 <u>https://doi.org/10.1029/2002JD003206</u>, 2003.
- 200 Dolgorouky, C., Gros, V., Sarda-Esteve, R., Sinha, V., Williams, J., Marchand, N., Sauvage, S., Poulain, L.,
- Sciare, J., and Bonsang, B.: Total OH reactivity measurements in Paris during the 2010 MEGAPOLI winter
 campaign, Atmospheric Chemistry and Physics, 12, 9593-9612, <u>https://doi.org/10.5194/acp-12-9593-2012</u>,
 2012.
- 204 Dusanter, S., Vimal, D., Stevens, P., Volkamer, R., and Molina, L.: Measurements of OH and HO₂ 205 concentrations during the MCMA-2006 field campaign-Part 1: Deployment of the Indiana University laser-206 induced fluorescence instrument, Atmospheric Chemistry and Physics, 9. 1665-1685. 207 https://doi.org/10.5194/acp-9-1665-2009, 2009a.
- 208 Dusanter, S., Vimal, D., Stevens, P., Volkamer, R., Molina, L., Baker, A., Meinardi, S., Blake, D., Sheehy,
- 209 P., and Merten, A.: Measurements of OH and HO₂ concentrations during the MCMA-2006 field campaign-210 Part 2. Model and model and had be determined by the field of the second s
- 210 Part 2: Model comparison and radical budget, Atmospheric Chemistry and Physics, 9, 6655-6675,
- 211 <u>https://doi.org/10.5194/acp-9-6655-2009</u>, 2009b.

- Emmerson, K. and Carslaw, N.: Night-time radical chemistry during the TORCH campaign, Atmospheric Environment, 43, 3220-3226, https://doi.org/10.1016/j.atmosenv.2009.03.042, 2009.
- 214 Emmerson, K., Carslaw, N., and Pilling, M.: Urban atmospheric chemistry during the PUMA campaign 2:
- 215 Radical budgets for OH, HO₂ and RO₂, Journal of atmospheric chemistry, 52, 165-183, 216 <u>https://doi.org/10.1007/s10874-005-1323-2</u>, 2005a.
- Emmerson, K., Carslaw, N., Carpenter, L., Heard, D., Lee, J., and Pilling, M.: Urban atmospheric chemistry during the PUMA campaign 1: Comparison of modelled OH and HO₂ concentrations with measurements, Journal of Atmospheric Chemistry, 52, 143-164, <u>https://doi.org/10.1007/s10874-005-1322-</u> 3, 2005b.
- <u>3</u>, 2005b.
 Emmerson, K. M., Carslaw, N., Carslaw, D., Lee, J. D., McFiggans, G., Bloss, W. J., Gravestock, T., Heard,
 D. E., Hopkins, J., and Ingham, T.: Free radical modelling studies during the UK TORCH Campaign in
 Summer 2003, Atmospheric Chemistry and Physics, 7, 167-181, <u>https://doi.org/10.5194/acp-7-167-2007</u>,
- 224 2007.
- 225 Faloona, I., Tan, D., Brune, W., Hurst, J., Barket Jr, D., Couch, T. L., Shepson, P., Apel, E., Riemer, D.,
- and Thornberry, T.: Nighttime observations of anomalously high levels of hydroxyl radicals above a
 deciduous forest canopy, Journal of Geophysical Research: Atmospheres, 106, 24315-24333,
 <u>https://doi.org/10.1029/2000JD900691</u>, 2001.
- Fuchs, H., Tan, Z., Lu, K., Bohn, B., Broch, S., Brown, S. S., Dong, H., Gomm, S., Häseler, R., and He, L.: OH reactivity at a rural site (Wangdu) in the North China Plain: contributions from OH reactants and experimental OH budget, Atmospheric Chemistry and Physics, 17, 645-661, <u>https://doi.org/10.5194/acp-</u>
- <u>17-645-2017</u>, 2017.
- Harrison, R., Yin, J., Tilling, R., Cai, X., Seakins, P., Hopkins, J., Lansley, D., Lewis, A., Hunter, M., and
- Heard, D.: Measurement and modelling of air pollution and atmospheric chemistry in the UK West
 Midlands conurbation: Overview of the PUMA Consortium project, Science of the Total Environment, 360,
 5-25, <u>https://doi.org/10.1016/j.scitotenv.2005.08.053</u>, 2006.
- Heard, D., Carpenter, L., Creasey, D., Hopkins, J., Lee, J., Lewis, A., Pilling, M., Seakins, P., Carslaw, N.,
 and Emmerson, K.: High levels of the hydroxyl radical in the winter urban troposphere, Geophysical
 research letters, 31, <u>https://doi.org/10.1029/2004GL020544</u>, 2004.
- Hens, K., Novelli, A., Martinez, M., Auld, J., Axinte, R., Bohn, B., Fischer, H., Keronen, P., Kubistin, D., and Nölscher, A.: Observation and modelling of HO x radicals in a boreal forest, Atmospheric Chemistry
- 241 and Noisener, A.: Observation and moderning of 110 X fadicals in a borear forest, Au 242 and Physics, 14, 8723-8747, https://doi.org/10.5194/acp-14-8723-2014, 2014.
- Kanaya, Y. and Akimoto, H.: Direct measurements of HOx radicals in the marine boundary layer: Testing
 the current tropospheric chemistry mechanism, The Chemical Record, 2, 199-211,
 <u>https://doi.org/10.1002/tcr.10019</u>, 2002.
- 246 Kanaya, Y., Matsumoto, J., and Akimoto, H.: Photochemical ozone production at a subtropical island of
- Okinawa, Japan: Implications from simultaneous observations of HO₂ radical and NOx, Journal of
 Geophysical Research: Atmospheres, 107, ACH 2-1-ACH 2-14, <u>https://doi.org/10.1029/2001JD000858</u>,
 2002a.
- Kanaya, Y., Matsumoto, J., Kato, S., and Akimoto, H.: Behavior of OH and HO₂ radicals during the
 Observations at a Remote Island of Okinawa (ORION99) field campaign: 2. Comparison between
 observations and calculations, Journal of Geophysical Research: Atmospheres, 106, 24209-24223,
 <u>https://doi.org/10.1029/2000JD000179</u>, 2001a.
- 254 Kanaya, Y., Sadanaga, Y., Nakamura, K., and Akimoto, H.: Behavior of OH and HO₂ radicals during the
- 255 Observations at a Remote Island of Okinawa (ORION99) field campaign: 1. Observation using a laser -
- induced fluorescence instrument, Journal of Geophysical Research: Atmospheres, 106, 24197-24208,
 https://doi.org/10.1029/2000JD000178, 2001b.

- Kanaya, Y., Nakamura, K., Kato, S., Matsumoto, J., Tanimoto, H., and Akimoto, H.: Nighttime variations
 in HO₂ radical mixing ratios at Rishiri Island observed with elevated monoterpene mixing ratios,
 Atmospheric Environment, 36, 4929-4940, <u>https://doi.org/10.1016/S1352-2310(02)00401-6</u>, 2002b.
- Kanaya, Y., Sadanaga, Y., Matsumoto, J., Sharma, U. K., Hirokawa, J., Kajii, Y., and Akimoto, H.:
 Daytime HO₂ concentrations at Oki Island, Japan, in summer 1998: Comparison between measurement and
 theory, Journal of Geophysical Research: Atmospheres, 105, 24205-24222,
 https://doi.org/10.1029/2000JD900308, 2000.
- Kanaya, Y., Fukuda, M., Akimoto, H., Takegawa, N., Komazaki, Y., Yokouchi, Y., Koike, M., and Kondo,
 Y.: Urban photochemistry in central Tokyo: 2. Rates and regimes of oxidant (O₃+ NO₂) production, Journal
 of Geophysical Research: Atmospheres, 113, https://doi.org/10.1029/2007JD008671, 2008.
- Kanaya, Y., Yokouchi, Y., Matsumoto, J., Nakamura, K., Kato, S., Tanimoto, H., Furutani, H., Toyota, K.,
 and Akimoto, H.: Implications of iodine chemistry for daytime HO₂ levels at Rishiri Island, Geophysical
 research letters, 29, 45-41-45-44, <u>https://doi.org/10.1029/2001GL014061</u>, 2002c.
- Kanaya, Y., Cao, R., Akimoto, H., Fukuda, M., Komazaki, Y., Yokouchi, Y., Koike, M., Tanimoto, H.,
- Takegawa, N., and Kondo, Y.: Urban photochemistry in central Tokyo: 1. Observed and modeled OH and
 HO₂ radical concentrations during the winter and summer of 2004, Journal of Geophysical Research:
 Atmospheres, 112, https://doi.org/10.1029/2007JD008670, 2007a.
- Kanaya, Y., Cao, R., Kato, S., Miyakawa, Y., Kajii, Y., Tanimoto, H., Yokouchi, Y., Mochida, M.,
 Kawamura, K., and Akimoto, H.: Chemistry of OH and HO₂ radicals observed at Rishiri Island, Japan, in
- September 2003: Missing daytime sink of HO₂ and positive nighttime correlations with monoterpenes,
 Journal of Geophysical Research: Atmospheres, 112, <u>https://doi.org/10.1029/2006JD007987</u>, 2007b.
- Kanaya, Y., Hofzumahaus, A., Dorn, H.-P., Brauers, T., Fuchs, H., Holland, F., Rohrer, F., Bohn, B.,
 Tillmann, R., and Wegener, R.: Comparisons of observed and modeled OH and HO₂ concentrations during
 the ambient measurement period of the HOx Comp field campaign, Atmospheric Chemistry and Physics,
 12, 2567-2585, <u>https://doi.org/10.5194/acp-12-2567-2012</u>, 2012.
- Kovacs, T., Brune, W., Harder, H., Martinez, M., Simpas, J., Frost, G., Williams, E., Jobson, T., Stroud, C.,
 and Young, V.: Direct measurements of urban OH reactivity during Nashville SOS in summer 1999,
 Journal of Environmental Monitoring, 5, 68-74, <u>https://doi.org/10.1039/B204339D</u>, 2003.
- Kubistin, D., Harder, H., Martinez, M., Rudolf, M., Sander, R., Bozem, H., Eerdekens, G., Fischer, H.,
 Gurk, C., and Klüpfel, T.: Hydroxyl radicals in the tropical troposphere over the Suriname rainforest:
 comparison of measurements with the box model MECCA, Atmospheric Chemistry and Physics, 10, 97059728, <u>https://doi.org/10.5194/acp-10-9705-2010</u>, 2010.
- Kurucz, R. L.: Solar Flux Atlas from 296 to 1300 nm, National Solar Observatory Atlas, 1,
 <u>https://doi.org/10.1017/S0074180900035427</u>, 1984.
- Lee, J., McFiggans, G., Allan, J., Baker, A., Ball, S., Benton, A., Carpenter, L., Commane, R., Finley, B.,
- and Evans, M.: Reactive halogens in the marine boundary layer (RHaMBLe): the tropical North Atlantic
- 294 experiments, Atmospheric Chemistry and Physics, 10, 1031-1055, <u>https://doi.org/10.5194/acp-10-1031-</u> 295 <u>2010</u>, 2010.
- Lee, J. D., Lewis, A. C., Monks, P. S., Jacob, M., Hamilton, J. F., Hopkins, J. R., Watson, N. M., Saxton, J.
 E., Ennis, C., and Carpenter, L. J.: Ozone photochemistry and elevated isoprene during the UK heatwave of
- August 2003, Atmospheric Environment, 40, 7598-7613, <u>https://doi.org/10.1016/j.atmosenv.2006.06.057</u>,
 2006.
- 300 Lelieveld, J. a., Butler, T., Crowley, J., Dillon, T., Fischer, H., Ganzeveld, L., Harder, H., Lawrence, M.,
- 301 Martinez, M., and Taraborrelli, D.: Atmospheric oxidation capacity sustained by a tropical forest, Nature,
- 302 452, 737-740, <u>https://doi.org/10.1038/nature06870</u>, 2008.

- Lu, K., Zhang, Y., Su, H., Brauers, T., Chou, C. C., Hofzumahaus, A., Liu, S. C., Kita, K., Kondo, Y., and Shao, M.: Oxidant (O₃+ NO₂) production processes and formation regimes in Beijing, Journal of Geophysical Research: Atmospheres, 115, <u>https://doi.org/10.1029/2009JD012714</u>, 2010.
- Ma, Z., Liu, C., Zhang, C., Liu, P., Ye, C., Xue, C., Zhao, D., Sun, J., Du, Y., and Chai, F.: The levels,
 sources and reactivity of volatile organic compounds in a typical urban area of Northeast China, Journal of
 Environmental Sciences, 79, 121-134, <u>https://doi.org/10.1016/j.jes.2018.11.015</u>, 2019.
- 309 Mao, J., Ren, X., Chen, S., Brune, W. H., Chen, Z., Martinez, M., Harder, H., Lefer, B., Rappenglück, B.,
- and Flynn, J.: Atmospheric oxidation capacity in the summer of Houston 2006: Comparison with summer
 measurements in other metropolitan studies, Atmospheric Environment, 44, 4107-4115,
 https://doi.org/10.1016/j.atmosenv.2009.01.013, 2010.
- 313 Martinez, M., Harder, H., Kovacs, T., Simpas, J., Bassis, J., Lesher, R., Brune, W., Frost, G., Williams, E.,
- and Stroud, C.: OH and HO₂ concentrations, sources, and loss rates during the Southern Oxidants Study in
 Nashville, Tennessee, summer 1999, Journal of Geophysical Research: Atmospheres, 108,
 <u>https://doi.org/10.1029/2003JD003551</u>, 2003.
- 317 Martinez, M., Harder, H., Kubistin, D., Rudolf, M., Bozem, H., Eerdekens, G., Fischer, H., Klüpfel, T.,
- 318 Gurk, C., and Königstedt, R.: Hydroxyl radicals in the tropical troposphere over the Suriname rainforest:
- airborne measurements, Atmospheric Chemistry and Physics, 10, 3759-3773, <u>https://doi.org/10.5194/acp-</u>
 <u>10-3759-2010</u>, 2010.
- 321 Meller, R. and Moortgat, G. K.: Temperature dependence of the absorption cross sections of formaldehyde
- between 223 and 323 K in the wavelength range 225-375 nm, Journal of Geophysical Research:
 Atmospheres, 105, 7089-7101, 2000.
- Michoud, V., Kukui, A., Camredon, M., Colomb, A., Borbon, A., Miet, K., Aumont, B., Beekmann, M., Durand-Jolibois, R., and Perrier, S.: Radical budget analysis in a suburban European site during the MEGAPOLI summer field campaign, Atmospheric Chemistry and Physics, 12, 11951-11974,
- $\frac{526}{\text{MEGAPOLI summer field campaign, Atmospheric Chemistry and Physics, 12, 11951-119}}{\frac{\text{https://doi.org/10.5194/acp-12-11951-2012}}{2012}, 2012.$
- Nölscher, A., Williams, J., Sinha, V., Custer, T., Song, W., Johnson, A., Axinte, R., Bozem, H., Fischer, H.,
 and Pouvesle, N.: Summertime total OH reactivity measurements from boreal forest during HUMPPACOPEC 2010, Atmospheric chemistry and Physics, 12, 8257-8270, <u>https://doi.org/10.5194/acp-12-8257-</u>
 2012, 2012.
- 332 Pugh, T., MacKenzie, A., Hewitt, C., Langford, B., Edwards, P., Furneaux, K., Heard, D., Hopkins, J.,
- Jones, C., and Karunaharan, A.: Simulating atmospheric composition over a South-East Asian tropical rainforest: performance of a chemistry box model, Atmospheric Chemistry and Physics, 10, 279-298, <u>https://doi.org/10.5194/acp-10-279-2010</u>, 2010.
- Qi, B., Kanaya, Y., Takami, A., Hatakeyama, S., Kato, S., Sadanaga, Y., Tanimoto, H., and Kajii, Y.:
 Diurnal peroxy radical chemistry at a remote coastal site over the sea of Japan, Journal of Geophysical
 Research: Atmospheres, 112, <u>https://doi.org/10.1029/2006JD008236</u>, 2007.
- 339 Ren, X., Harder, H., Martinez, M., Lesher, R. L., Oliger, A., Shirley, T., Adams, J., Simpas, J. B., and
- Brune, W. H.: HOx concentrations and OH reactivity observations in New York City during PMTACS-NY2001, Atmospheric Environment, 37, 3627-3637, <u>https://doi.org/10.1016/S1352-2310(03)00460-6</u>,
- 342 2003a.
- Ren, X., Brune, W. H., Mao, J., Mitchell, M. J., Lesher, R. L., Simpas, J. B., Metcalf, A. R., Schwab, J. J.,
- Cai, C., and Li, Y.: Behavior of OH and HO₂ in the winter atmosphere in New York City, Atmospheric Environment, 40, 252-263, https://doi.org/10.1016/j.atmosenv.2005.11.073, 2006.
 - 346 Ren, X., Harder, H., Martinez, M., Lesher, R. L., Oliger, A., Simpas, J. B., Brune, W. H., Schwab, J. J.,
 - 347 Demerjian, K. L., and He, Y.: OH and HO₂ chemistry in the urban atmosphere of New York City,
- 348 Atmospheric Environment, 37, 3639-3651, <u>https://doi.org/10.1016/S1352-2310(03)00459-X</u>, 2003b.

- Sheehy, P., Volkamer, R., Molina, L. T., and Molina, M. J.: Oxidative capacity of the Mexico City atmosphere-Part 2: A RO x radical cycling perspective, Atmospheric Chemistry and Physics, 10, 6993-7008, https://doi.org/10.5194/acp-10-6993-2010, 2010.
- Shirley, T., Brune, W., Ren, X., Mao, J., Lesher, R., Cardenas, B., Volkamer, R., Molina, L., Molina, M. J., and Lamb, B.: Atmospheric oxidation in the Mexico city metropolitan area (MCMA) during April 2003,
- Atmospheric Chemistry and Physics, 6, 2753-2765, <u>https://doi.org/10.5194/acp-6-2753-2006</u>, 2006.
- 355 Sommariva, R., Haggerstone, A.-L., Carpenter, L., Carslaw, N., Creasey, D., Heard, D., Lee, J., Lewis, A.,
- Pilling, M., and Zádor, J.: OH and HO₂ chemistry in clean marine air during SOAPEX-2, Atmospheric
 Chemistry and Physics, 4, 839-856, <u>https://doi.org/10.5194/acp-4-839-2004</u>, 2004.
- 358 Stone, D., Evans, M. J., Edwards, P., Commane, R., Ingham, T., Rickard, A., Brookes, D., Hopkins, J.,
- Leigh, R., and Lewis, A.: Isoprene oxidation mechanisms: measurements and modelling of OH and HO₂ over a South-East Asian tropical rainforest during the OP3 field campaign, Atmospheric Chemistry and
- 361 Physics, 11, 6749-6771, <u>https://doi.org/10.5194/acp-11-6749-2011</u>, 2011.
- Stutz, J., Kim, E., Platt, U., Bruno, P., Perrino, C., and Febo, A.: UV visible absorption cross sections of
 nitrous acid, Journal of Geophysical Research: Atmospheres, 105, 14585-14592, 2000.
- Tan, D., Faloona, I., Simpas, J., Brune, W., Shepson, P., Couch, T., Sumner, A., Carroll, M., Thornberry, T.,
 and Apel, E.: HOx budgets in a deciduous forest: Results from the PROPHET summer 1998 campaign,
 Journal of Geophysical Research: Atmospheres, 106, 24407-24427, <u>https://doi.org/10.1029/2001JD900016</u>,
 2001.
- Tan, Z., Fuchs, H., Lu, K., Hofzumahaus, A., Bohn, B., Broch, S., Dong, H., Gomm, S., Häseler, R., and
 He, L.: Radical chemistry at a rural site (Wangdu) in the North China Plain: observation and model
 calculations of OH, HO₂ and RO₂ radicals, Atmospheric Chemistry and Physics, 17, 663-690,
 <u>https://doi.org/10.5194/acp-17-663-2017</u>, 2017.
- 372 Tan, Z., Lu, K., Hofzumahaus, A., Fuchs, H., Bohn, B., Holland, F., Liu, Y., Rohrer, F., Shao, M., and Sun, 373 K.: Experimental budgets of OH, HO₂, and RO₂ radicals and implications for ozone formation in the Pearl 374 Atmospheric chemistry River Delta in China 2014. and physics, 19. 7129-7150, 375 https://doi.org/10.5194/acp-19-7129-2019, 2019.
- Tan, Z., Rohrer, F., Lu, K., Ma, X., Bohn, B., Broch, S., Dong, H., Fuchs, H., Gkatzelis, G. I., and
 Hofzumahaus, A.: Wintertime photochemistry in Beijing: observations of ROx radical concentrations in the
 North China Plain during the BEST-ONE campaign, Atmospheric Chemistry and Physics, 18, 1239112411, https://doi.org/10.5194/acp-18-12391-2018, 2018.
- Thornton, J., Wooldridge, P., Cohen, R., Martinez, M., Harder, H., Brune, W., Williams, E., Roberts, J., Fehsenfeld, F., and Hall, S.: Ozone production rates as a function of NOx abundances and HOx production
- rates in the Nashville urban plume, Journal of Geophysical Research: Atmospheres, 107, ACH 7-1-ACH 7-17, https://doi.org/10.1029/2001JD000932, 2002.
- Vandaele, A. C., Hermans, C., and Fally, S.: Fourier transform measurements of SO₂ absorption cross
 sections: II.: Temperature dependence in the 29000-44000 cm⁻¹ (227-345 nm) region, Journal of
 Quantitative Spectroscopy and Radiative Transfer, 110, 2115-2126,
 https://doi.org/10.1016/j.jqsrt.2009.05.006, 2009.
- Vaughan, S., Ingham, T., Whalley, L., Stone, D., Evans, M., Read, K., Lee, J., Moller, S., Carpenter, L.,
 and Lewis, A.: Seasonal observations of OH and HO₂ in the remote tropical marine boundary layer,
 Atmospheric Chemistry and Physics, 12, 2149-2172, https://doi.org/10.5194/acp-12-2149-2012, 2012.
- 391 Voight, S., Orphal, J., and Burrows, J.: The temperature and pressure dependence of the absorption cross-
- 392 sections of NO₂ in the 250-800 nm region measured by Fourier-transform spectroscopy, Journal of
- 393 Photochemistry and Photobiology A: Chemistry, 149, 1-7, 2002.

- Voigt, S., Orphal, J., Bogumil, K., and Burrows, J.: The temperature dependence (203-293 K) of the absorption cross sections of O₃ in the 230-850 nm region measured by Fourier-transform spectroscopy, Journal of Photochemistry and Photobiology A: Chemistry, 143, 1-9, 2001.
- Volkamer, R., Sheehy, P., Molina, L. T., and Molina, M. J.: Oxidative capacity of the Mexico City
 atmosphere-Part 1: A radical source perspective, Atmospheric Chemistry and Physics, 10, 6969-6991,
 <u>https://doi.org/10.5194/acp-10-6969-2010</u>, 2010.
- 400 Whalley, L., Edwards, P., Furneaux, K., Goddard, A., Ingham, T., Evans, M. J., Stone, D., Hopkins, J.,
- 401 Jones, C. E., and Karunaharan, A.: Quantifying the magnitude of a missing hydroxyl radical source in a
- 402 tropical rainforest, Atmospheric Chemistry and Physics, 11, 7223-7233, https://doi.org/10.5194/acp-11-
- 403 <u>7223-2011</u>, 2011.
- Whalley, L., Furneaux, K., Goddard, A., Lee, J., Mahajan, A., Oetjen, H., Read, K., Kaaden, N., Carpenter,
 L., and Lewis, A.: The chemistry of OH and HO₂ radicals in the boundary layer over the tropical Atlantic
 Ocean, Atmospheric Chemistry and Physics, 10, 1555-1576, <u>https://doi.org/10.5194/acp-10-1555-2010</u>,
 2010.
- 408 Yang, X., Lu, K., Ma, X., Gao, Y., Tan, Z., Wang, H., Chen, X., Li, X., Huang, X., and He, L.: Radical
- 409 chemistry in the Pearl River Delta: observations and modeling of OH and HO₂ radicals in Shenzhen in
- 410 2018, Atmospheric Chemistry and Physics, 22, 12525-12542, <u>https://doi.org/10.5194/acp-22-12525-2022</u>,
 411 2022.
- Yang, X., Lu, K., Ma, X., Liu, Y., Wang, H., Hu, R., Li, X., Lou, S., Chen, S., and Dong, H.: Observations
 and modeling of OH and HO₂ radicals in Chengdu, China in summer 2019, Science of The Total
 Environment, 772, 144829, https://doi.org/10.1016/j.scitotenv.2020.144829, 2021.
- Zhang, G., Hu, R., Xie, P., Lu, K., Lou, S., Liu, X., Li, X., Wang, F., Wang, Y., and Yang, X.:
 Intercomparison of OH radical measurement in a complex atmosphere in Chengdu, China, Science of the
 Total Environment, 838, 155924, https://doi.org/10.1016/j.scitotenv.2022.155924, 2022.
- 418 Zhu, J., Wang, S., Wang, H., Jing, S., Lou, S., Saiz-Lopez, A., and Zhou, B.: Observationally constrained
- 419 modeling of atmospheric oxidation capacity and photochemical reactivity in Shanghai, China, Atmospheric
- 420 Chemistry and Physics, 20, 1217-1232, <u>https://doi.org/10.5194/acp-20-1217-2020</u>, 2020.
- 421