

1 **Atmospheric reactivity and oxidation capacity during summer at a suburban site**
2 **between Beijing and Tianjin**

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30 **Abstract**

31 Hydroxyl (OH) radicals, nitrate (NO₃) radicals, and ozone (O₃) play central roles in the
32 troposphere because they control the lifetimes of many trace gases that result from anthropogenic
33 and biogenic origins. To estimate the air chemistry, the atmospheric reactivity and oxidation
34 capacity were comprehensively analyzed based on a parameterization method at a suburban site in
35 Xianghe in the North China Plain from 6 July 2018 to 6 August 2018. The total OH, NO₃ and O₃
36 reactivities at the site varied from 9.2 s⁻¹ to 69.6 s⁻¹, 0.7 s⁻¹ to 27.5 s⁻¹ and 3.3×10⁻⁴ s⁻¹ to 1.8×10⁻²
37 s⁻¹ with campaign-averaged values of 27.5±9.7 s⁻¹, 2.2±2.6 s⁻¹ and 1.2±1.7×10⁻³ s⁻¹ (± standard
38 deviation), respectively. NO_x (NO+NO₂) was by far the main contributor to the reactivities of the
39 three oxidants, with average values of 43-99%. Alkenes dominated the OH, NO₃ and O₃ reactivities
40 towards total nonmethane volatile organic compounds (NMVOCs), accounting for 42.9%, 77.8%
41 and 94.0%, respectively. The total OH, NO₃ and O₃ reactivities displayed similar diurnal variations
42 with the lowest values during the afternoon but the highest values during rush hours, and the diurnal
43 profile of NO_x appears to be the major driver for the diurnal profiles of the reactivities of the three
44 oxidants. A box model (a model to Simulate the concentrations of Organic vapors, Sulfuric Acid
45 and Aerosols, SOSAA) derived from a column chemical transport model was used to simulate
46 OH and NO₃ concentrations during the observation period. The calculated atmospheric oxidation
47 capacity (AOC) reached 4.5×10⁸ molecules cm⁻³ s⁻¹ with a campaign-averaged value of 7.8×10⁷
48 molecules cm⁻³ s⁻¹ dominated by OH (7.7×10⁷ molecules cm⁻³ s⁻¹, 98.2%), O₃ (1.2×10⁶ molecules
49 cm⁻³ s⁻¹, 1.5%) and NO₃ (1.8×10⁵ molecules cm⁻³ s⁻¹, 0.3%). Overall, the integration of OH, NO₃
50 and O₃ reactivity analysis could provide useful insights for NMVOCs pollution control in the North
51 China Plain. We suggest that further studies, especially direct observations of OH and NO₃ radical
52 concentrations and their reactivities, are required to better understand trace gas reactivity and AOC.

53 **Keywords:**

54 VOCs, atmospheric oxidant reactivity, atmospheric oxidation capacity, North China Plain

55

56 **1 Introduction**

57 In the planetary boundary layer, high concentrations of primary pollutants, such as carbon
58 monoxide (CO), nitrogen oxides (NO_x=NO+NO₂) and volatile organic compounds (VOCs) from

59 both biogenic and anthropogenic origins, are transformed by reactions with atmospheric oxidants,
60 such as hydroxyl (OH) radicals, nitrate (NO₃) radicals, [chlorine atoms](#) and ozone (O₃) on local to
61 global scales (Atkinson and Arey, 2003; Heard and Pilling, 2003; Lu et al., 2018; Wang et al., 2020),
62 with the dominant reaction depending on the time of day and specific trace gases. Ultimately, these
63 processes lead to the formation of a series of important secondary pollutants, including tropospheric
64 O₃ and secondary organic [aerosols](#) (SOA) (Goldstein and Galbally, 2007).

65 OH radicals control the daytime oxidation capacity of the atmosphere (Heard and Pilling, 2003),
66 initiating and participating in many oxidation reaction processes. [OH can react by adding OH groups](#)
67 [to or abstracting H from trace gases](#), such as CO, NO_x, methane (CH₄), [nonmethane](#) volatile organic
68 compounds (NMVOCs) (Kovacs et al., 2003; Sadanaga et al., 2005). The total OH reactivity, which
69 is equivalent to the inverse chemical OH lifetime, is the sum of the products of the concentrations
70 and respective reaction rate coefficients for all gases that react with OH. The online techniques used
71 to determine OH reactivity include [a flow tube](#) with sliding injector method (Kovacs et al., 2003),
72 a comparative rate method (Sinha et al., 2008) and a laser flash photolysis pump probe technique
73 (Whalley et al., 2016). Based on these online methods, [total OH reactivity values](#) have been
74 measured in urban, suburban, remote and forest areas during the last decade. The urban areas
75 investigated [include](#) Nashville, USA (SOS) (Kovacs et al., 2003), New York, USA (PMTACS-
76 NY2004) (Ren et al., 2006a), Mexico City, Mexico (MCMA-2003) (Shirley et al., 2006), Houston,
77 USA (TRAMP2006) (Mao et al., 2010), Paris, France (MEGAPOLI) (Dolgorouky et al., 2012),
78 London, UK (ClearfLo) (Whalley et al., 2016), Helsinki, Finland (Praplan et al., 2017), Seoul, South
79 Korea (Kim et al., 2016) and Beijing, China (Yang et al., 2017). [The total OH reactivity](#) in these
80 urban areas ranged from 1 s⁻¹ in clean air to 200 s⁻¹ in extremely polluted air, and NO_x, CO,
81 formaldehyde (HCHO) and [nonmethane hydrocarbons](#) (NMHCs) were the main contributors
82 (Ferracci et al., 2018). The suburban areas investigated [include](#) Whiteface Mountain, USA
83 (PMTACS-NY2002) (Ren et al., 2006b), Weybourne, UK (TORCH-2) (Lee et al., 2010), Yufa,
84 China (CAREBeijing-2006) (Lu et al., 2010), Backgarden, China (PRIDE-PRD) (Lou et al., 2010),
85 Jülich, Germany (HO_x Comp) (Elshorbany et al., 2012), Ersa, Corsica (CARBOSOR-ChArMeX)
86 (Zannoni et al., 2017), Po Valley, Italy (Kaiser et al., 2015), [the Indo-Gangetic Plain](#), India (Kumar
87 et al., 2018) and Heshan, China (Yang et al., 2017). [The total OH reactivity](#) in these suburban areas

88 ranged from 4.6 to 64 s⁻¹. OH reactivity was also modeled by a global model by (Ferracci et al.,
89 2018) and by a box model based on the Master Chemical Mechanism (MCM) (Whalley et al.,
90 2016). The calculated total OH reactivity is the sum of the OH reactivities that are attributed to
91 measured trace gases. The concentrations (in molecules cm⁻³) of trace gases and the reaction rate
92 constants (in cm³ molecule⁻¹ s⁻¹) of these trace gases with the OH radical are the key factors for
93 computing OH reactivity (Mogensen et al., 2011; Mogensen et al., 2015). In general, the trace gases
94 considered in calculating OH reactivity include NMVOCs, CH₄, CO, NO_x, SO₂ and O₃. As reported,
95 the contribution from NO_x exceeds 50% for the cities of Paris, Tokyo, New York and Beijing,
96 showing the large influence of traffic-related emissions on OH reactivity (Dolgorouky et al.,
97 2012; Ren, 2003; Yang et al., 2017; Yoshino et al., 2006), but the contribution from NMVOCs reaches
98 50% in Mexico and Houston due to the large quantity of biomass fuel being burned and high
99 industrial solvent emissions (Mao et al., 2010; Shirley et al., 2006).

100 As OH levels are vastly reduced during the nighttime due to the absence of photolysis, NO₃
101 formed by the slow reaction NO₂ + O₃ → NO₃ + O₂ is the main initiator of nighttime oxidation
102 chemistry in the troposphere (Asaf et al., 2009; Geyer et al., 2001). NO₃ reacts effectively with
103 unsaturated NMVOCs, such as certain alkenes or aromatics via additions to >C=C< double bonds,
104 which can initiate the formation of peroxy radicals (HO₂ and RO₂) and even OH (Geyer et al.,
105 2001). High NO₃ mixing ratios and large reaction rate constants with several unsaturated NMVOCs
106 result in NO₃ being the dominant sink of many unsaturated NMVOCs during the nighttime. The
107 role of NO₃ as an oxidizing agent can be assessed via its total reactivity towards trace gases. The
108 total NO₃ reactivity is an indication of nighttime oxidation rates of trace gases with direct impacts
109 on NO_x levels and indirect impacts on heterogeneous NO_x losses and ClNO₂ formation (Liebmann
110 et al., 2017). As frequently reported for total OH reactivity, total NO₃ reactivity can be measured
111 online or calculated by summing the loss rates for a set of reactive trace gases. Previous work on
112 measured total NO₃ reactivity has revealed strong diel variation. For instance, the total NO₃
113 reactivity obtained in Hyytiälä, Finland, displayed strong diel variation, with a campaign-averaged
114 nighttime value of 0.11 s⁻¹ and daytime value of 0.04 s⁻¹ (Liebmann et al., 2018a), but values varied
115 from 0.005 to 0.1 s⁻¹ during the nighttime and reached values as high as 1.4 s⁻¹ in the daytime in
116 Taunus, Germany (Liebmann et al., 2017).

117 Along with reactions with OH and NO₃ radicals, trace gases are also oxidized in the
118 troposphere by reactions with O₃. Although most NMVOCs have reaction rates with O₃ that are
119 much lower than those with either OH or NO₃, O₃ is very important because it is present at elevated
120 mixing ratios in clean or contaminated atmospheres (Wang et al., 2013). The rate constants of the
121 reactions for some alkenes with O₃ are even comparable to those with NO₃ (Atkinson and Arey,
122 2003). The total reactivity of O₃ with trace gases can reflect the role of O₃ as an oxidizing agent.
123 Direct measurements of total O₃ reactivity were not available until very recently (Geyer, 2003);
124 hence, the reactivity of O₃ has traditionally been calculated by summing the reactivities due to
125 individual reactive trace gases. The calculated O₃ reactivity obtained in Pabstthum, Germany,
126 revealed that terpenes (20%), isoprene (20%) and other alkenes (60%) were the dominant
127 contributors during the night of 20 and 21 July but arose mainly (83%) from nonbiogenic alkenes
128 during the night of 4 and 5 August (Geyer, 2003).

129 As mentioned above OH radicals, NO₃ radicals and O₃ react with trace gases via different rate
130 coefficients and mechanisms, resulting in profoundly different reactivities. Therefore,
131 comprehensive evaluations of OH, NO₃ and O₃ reactivities are key to understanding atmospheric
132 oxidation capacity and identifying the controlling active species of secondary pollution in the
133 atmosphere. However, comprehensive evaluations of the total calculated OH, NO₃ and O₃
134 reactivities are scarce in China. In this study, we calculated the OH, O₃ and NO₃ reactivities at a
135 suburban site (Xianghe) in the North China Plain during an intensive measurement campaign in the
136 summer of 2018. By combining simulated OH and NO₃ concentrations using a box model (a model
137 to Simulate the concentrations of Organic vapors, Sulfuric Acid and Aerosols, SOSAA), we
138 calculated the oxidation capacities of OH, NO₃ and O₃ and estimated their relative contributions.

139 2 Methodology

140 2.1 Site description

141 The sampling site is located at the Xianghe Atmospheric Observatory (39.798 °N, 116.958 °E;
142 15 m above sea level), which is operated by the Institute of Atmospheric Physics (IAP)/Chinese
143 Academy of Sciences (CAS). The sampling site is a typical suburban site in the seriously polluted
144 Beijing-Tianjin-Hebei large urban region, which is approximately 50 km southeast of Beijing, 75
145 km northwest of Tianjin, and 35 km northeast of Langfang in Hebei Province. The sampling site is

146 approximately 4 km west of the downtown center and is surrounded by residential areas and
147 agricultural land (see Figure 1).

148 **2.2 Experimental method**

149 Ambient NMVOCs were collected and analyzed continuously and automatically with a time
150 resolution of 1 h using a custom-built gas chromatography-mass spectrometry/flame ionization
151 detector (GC-MS/FID) instrument. The suitability of this system for NMVOC measurements is well
152 verified, and it has been used in several large field campaigns (Chen et al., 2014; Yuan et al.,
153 2013; Wu et al., 2016). Detailed descriptions of the configuration of the GC-MS/FID system, the
154 detection limits, and the precision of NMVOC measurements can be found in our previous paper
155 (Yang et al., 2019). CH₄ was analyzed by an Agilent 7890A gas chromatography (GC) instrument
156 with a flame ionization detector (FID). HCHO was measured by Hantzsch fluorimetry with a
157 commercial instrument (AL4021, Aerolaser GmbH, Germany) (Lu et al., 2019). Air-quality-related
158 trace gases, including O₃, NO-NO₂-NO_x, SO₂ and CO were measured by analyzers from Thermo-
159 Fisher Scientific, United States. High-resolution (5 min averages) data sets of O₃, NO, NO-NO₂-
160 NO_x, SO₂ and CO were obtained, and hourly averaged data were used after applying strict data
161 quality control measures. HONO mixing ratios were determined using a custom-made HONO
162 analyzer (Zhang et al., 2019; Tong et al., 2015). The photolysis frequencies, JO¹D, JNO₂ and JNO₃,
163 in the atmosphere were measured by a PFS-100 photolysis spectrometer (Juguang Technology
164 (Hangzhou) Co., Ltd, Hangzhou, China). Further details of the measurements of NMVOCs, CH₄,
165 HCHO, trace gases, HONO and photolysis frequencies can be found in the Supporting Information.
166 The meteorological parameters, including wind speed, wind direction, temperature and relative
167 humidity, were obtained from the National Meteorological Information Center (<http://data.cma.cn/>).
168 The sensors are approximately 3000 meters away from the measurement area.

169 **2.3 Atmospheric chemical transport model: SOSAA**

170 SOSAA is a column (or one-dimensional) chemical transport model that was first developed
171 by (Boy et al., 2011). A more detailed description of its newest version can be found in (Zhou et al.,
172 2017a; Zhou et al., 2017b). In this study, a box model version of SOSAA was used, in which the
173 meteorological variables, including air temperature, air pressure, relative humidity and incoming
174 global radiation, were directly read from the measurement data. The chemistry scheme was

175 generated by MCM v3.3.1 (<http://mcm.leeds.ac.uk/MCMv3.3.1>) (Jenkin et al., 1997; Jenkin et al.,
176 2015; Saunders et al., 2003) and then converted to Fortran code with kinetic pre-processor (KPP)
177 (Damian et al., 2002). The mixing ratios of chemical species included in the chemistry scheme, e.g.,
178 O₃, NO, NO₂, SO₂, CO, HONO, HCHO, isoprene and acetone, were read from the measured data
179 when available. Ten OVOCs (acrolein (ACR), C₂H₃CHO, methacrolein (MACR), C₃H₇CHO,
180 methylvinylketone (MVK), methylethylketone (MEK), 2-pentanone (MPRK), C₄H₉CHO,
181 diethylketone (DIEK), C₅H₁₁CHO) were excluded from the input list, despite also being measured,
182 because their simulated concentrations were compared with the measurement data to validate the
183 model performance. Seven photolysis rates (J_O¹D, J_HCHO_M, J_NO₂, J_H₂O₂, J_HONO,
184 J_NO₃_M and J_NO₃_R) were also read from the measurement data, and the related photochemical
185 reactions are shown below:



193 The other photolysis rates were calculated using the incoming global radiation. The deposition
194 velocities of all noninput species were set to 0.01 m s⁻¹ and the boundary layer height was assumed
195 to be 1 km (Lu et al., 2013; Zhu et al., 2020). The simulated OVOCs were also assumed to condense
196 onto pre-existing aerosols. Their condensation sinks were set to make their simulated concentrations
197 approach the measurement data. The model time step was set to 10 s, and the data were output every
198 half an hour. All the input data were interpolated to the model time step.

199 2.4 Speciated oxidant reactivity

200 Atmospheric oxidant reactivity is a measure of the strength of the reaction of trace gases with
201 an oxidant (OH, O₃ or NO₃) (Kovacs et al., 2003; Mogensen et al., 2015). High oxidant reactivity
202 values correspond to short lifetimes and long-lived species have low reactivities. The total OH, NO₃
203 and O₃ reactivities can be calculated by Eq. (1)-(3), respectively.

204 The total OH reactivity = $\sum k_{OH+NMVOC_i} [NMVOC_i] + k_{OH+CH_4} [CH_4] + k_{OH+CO} [CO] +$
 205 $k_{OH+NO} [NO] + k_{OH+NO_2} [NO_2] + k_{OH+SO_2} [SO_2] + k_{OH+O_3} [O_3] + \dots$ (1)

206 The total NO₃ reactivity = $\sum k_{NO_3+NMVOC_i} [NMVOC_i] + k_{NO_3+CH_4} [CH_4] + k_{NO_3+NO} [NO] +$
 207 $k_{NO_3+NO_2} [NO_2] + k_{NO_3+SO_2} [SO_2] + \dots$ (2)

208 The total O₃ reactivity = $\sum k_{O_3+NMVOC_i} [NMVOC_i] + k_{O_3+CH_4} [CH_4] + k_{O_3+NO} [NO] +$
 209 $k_{O_3+NO_2} [NO_2] + \dots$ (3)

210 In the above equations, the temperature-dependent reaction rate coefficients (in cm³ molecule⁻¹ s⁻¹) for OH-NMVOC_i ($k_{OH+NMVOC_i}$), OH-CO (k_{OH+CO}), NO₃-NMVOC_i ($k_{NO_3+NMVOC_i}$) and O₃-
 211 NMVOC_i ($k_{O_3+NMVOC_i}$) are from (Atkinson and Arey, 2003; Atkinson et al., 2006; Atkinson et al.,
 212 1983; Salgado et al., 2008) and MCM v3.3.1 via the website: <http://mcm.leeds.ac.uk/MCM> (last
 213 accessed: 25 March 2020). OH-NO (k_{OH+NO}), OH-NO₂ (k_{OH+NO_2}), OH-SO₂ (k_{OH+SO_2}), OH-O₃
 214 (k_{OH+O_3}), NO₃-NO (k_{NO_3+NO}), NO₃-NO₂ ($k_{NO_3+NO_2}$), NO₃-SO₂ ($k_{NO_3+SO_2}$), O₃-NO (k_{O_3+NO}) and
 215 O₃-NO₂ ($k_{O_3+NO_2}$) are from (Atkinson et al., 2004). The temperature-dependent reaction rate
 216 coefficients are listed in Table S1 in the Supplementary Materials. [NMVOC_i], [CH₄], [CO], [NO],
 217 [NO₂], [SO₂] and [O₃] are the corresponding number concentrations (in molecules cm⁻³).

219 2.5 Atmospheric oxidation capacity (AOC)

220 The term "oxidation capacity" of an oxidant X (NO₃, OH and O₃) is defined as the sum of the
 221 respective oxidation rates of the molecules Y_i (NMVOCs, CH₄ and CO) (Geyer et al., 2001).

222
$$AOC = \sum_{i=1} k_{Y_i-X} [Y_i] [X] = \sum_{i=1} R_X^{Y_i} [X]$$
 (4)

223 Here, [Y_i] and [X] are number concentrations of molecule Y_i and oxidant X, respectively.

224 k_{Y_i-X} is the temperature-dependent reaction rate coefficient of molecule Y_i with oxidant X. $R_X^{Y_i}$

225 is the oxidant X reactivity of molecule Y_i.

226 3 Results and discussion

227 3.1 Overview of measurements

228 For the data evaluation, all measurements were averaged over 1-hour time intervals. The
 229 measured concentrations of major pollutants and meteorological parameters at Xianghe are depicted
 230 in Figure 2, while the mean diurnal profiles are shown in Figure S1. During the campaign, sunny
 231 weather conditions prevailed with temperatures ranging from 25°C to 31°C during the daytime.
 232 Wind data suggested that the prevailing wind was from the eastern sampling site with a mean wind

233 speed of 1.0 m s^{-1} ranging from 0.3 m s^{-1} to 1.4 m s^{-1} , and the average relative humidity was 85%,
234 reaching up to 96% during the night (Figure 2). Campaign-averaged maximum and minimum SO_2
235 mixing ratios of 3.6 ppb at approximately 14:00 h and 2.3 ppb during the nighttime were obtained
236 (Figure S1a). For JO^1D , JNO_2 and JNO_3 , a similar maximum at $\sim 14:00$ h was observed, with
237 maximum values of $2.1 \times 10^{-5} \text{ s}^{-1}$, $5.3 \times 10^{-3} \text{ s}^{-1}$ and $1.3 \times 10^{-1} \text{ s}^{-1}$, respectively (Figure S1k-m). The
238 maximum JO^1D at this site was comparable with those in Shanghai and Chongqing but higher than
239 that in Guangzhou and lower than that in Beijing (Tan et al., 2019; Wang et al., 2019). The observed
240 mean daily maxima of JNO_2 at this site were higher than those observed in the eastern Mediterranean
241 (Gerasopoulos et al., 2012) but lower than those in Beijing (Wang et al., 2019).

242 The diurnal maximum O_3 concentration was 72 ppb at this site (Figure S1d), which was in line
243 with that observed in Beijing (72 ppb) but higher than those measured in Guangzhou (65 ppb) and
244 Chongqing (56 ppb) and lower than that observed in Shanghai (80 ppb) (Tan et al., 2019). The O_3
245 precursors, CO, NO_x , CH_4 and NMVOCs, are shown in Figure 2 and Figure S1. The trend of
246 NMVOCs was inversely related to that of O_3 . When the NMVOCs concentrations in the atmosphere
247 accumulates to a certain level, as photochemical reactions progress, the O_3 concentration gradually
248 increases, and the NMVOCs concentrations gradually decreases (Kansal, 2009; Song et al., 2018).
249 CO and NO_x showed a similar diurnal profile with a maximum during rush hour and a minimum in
250 the afternoon (Figure S1b and c), suggesting that both CO and NO_x originated from the same source
251 (enhanced traffic emission), and/or were manipulated by the same factor (e.g., poor dilution
252 conditions). During the campaign, the average mixing ratio of total NMVOC was 32.4 ppb, with
253 the highest contributions from alkanes (13.2 ppb, 40.6%), followed by OVOCs (12.0 ppb, 37.0%),
254 aromatics (4.3 ppb, 13.2%) and alkenes (3.0 ppb, 9.2%). The top 10 NMVOC species (Figure 3a),
255 in terms of emissions, consisted of HCHO (7.0 ppb), propane (3.7 ppb), acetone (3.2 ppb), ethane
256 (3.2 ppb), n-butane (1.9 ppb), m/p-xylene (1.6 ppb), iso-pentane (1.3 ppb), ethylene (1.3 ppb), iso-
257 butane (1.1 ppb) and isoprene (1.0 ppb), accounting for 78.4% of the total NMVOC concentration.
258 As typical tracers of vehicle-related emissions, propane, ethane, ethene, butanes and pentanes were
259 present in high concentrations, suggesting that vehicle-related emissions were likely to be the
260 dominant source of NMVOCs at this site. In addition, the shape of the diurnal variations in total
261 NMVOCs backed the presence of vehicle-related emissions, presenting higher mixing ratios during

262 the early morning and from evening to midnight, which may be related to enhanced traffic emissions
263 during rush hours and poor dilution conditions (Yuan et al., 2009;He et al., 2019;Tan et al., 2019).
264 On the other hand, the mixing ratios of total NMVOCs began to decrease at 10:00 h and maintained
265 a broad trough during daytime hours, probably due to increased photochemical removal processes
266 favoring the destruction of NMVOCs, the elevated planetary boundary layer (PBL) promoting the
267 dispersion of NMVOCs and/or reduced NMVOC emissions reducing the levels of NMVOCs (He
268 et al., 2019;Zheng et al., 2018). In contrast, the OVOC concentrations (Figure S1i) increased from
269 a minimum near sunrise and reached a maximum in the late afternoon, reflecting the accumulation
270 of OVOCs during the photochemically active period of the day and illustrating the time profile of
271 the formation of secondary species (Yuan et al., 2012).

272 3.2 Reactivities of OH, NO₃ and O₃

273 3.2.1 OH reactivity

274 The OH reactivity of trace gases was categorized into SO₂, CO, O₃, NO_x, CH₄ and total
275 NMVOCs, which were grouped into alkanes, alkenes, aromatics and OVOCs (Table S1 lists the
276 NMVOCs included in each group), as shown in Figure 4a and 4b. The total OH reactivity was
277 between 9.2 and 69.6 s⁻¹, with an average of 27.5±9.7 s⁻¹ (± standard deviation). Statistically, the
278 average total OH reactivity was much higher than those determined in Beijing (16.4 s⁻¹ and 20±11
279 s⁻¹) (Tan et al., 2019;Yang et al., 2017), Shanghai (13.5 s⁻¹) (Tan et al., 2019), Chongqing (17.8 s⁻¹)
280 (Tan et al., 2019), Jinan (19.4±2.1 s⁻¹) (Lyu et al., 2019), Wangdu (10-20 s⁻¹) (Fuchs et al., 2017),
281 Houston (9-22 s⁻¹) (Mao et al., 2010), London (18.1 s⁻¹) (Whalley et al., 2016) and Nashville (11.3
282 ± 4.8 s⁻¹) (Kovacs et al., 2003), but was comparable to or lower than those in Heshan (31±20 s⁻¹)
283 (Yang et al., 2017), Backgarden (mean maximum value of 50 s⁻¹) (Lou et al., 2010) and New York
284 (25 s⁻¹) (Ren et al., 2006b). The OH reactivity towards SO₂, CO and NO_x was higher than the values
285 reported in various Chinese cities (Xu et al., 2011;Zhu et al., 2020;Liu et al., 2009) (Table 1). It
286 should be noted that the OH reactivity in this study was calculated from the sum of the products of
287 measured species and their rate coefficients for reactions with OH, and does not involve species that
288 were not measured, such as monoterpenes and alcohols. Previous studies have shown that there are
289 some discrepancies between the actual measured values and the calculated values of OH reactivity,
290 which may be attributed to missing OH reactivity that originates from VOC oxidation products of

291 both biogenic and anthropogenic origin (Di Carlo et al., 2004; Dolgorouky et al., 2012; Yoshino et
292 al., 2006; Zhu et al., 2020). Therefore, the OH reactivity calculated in this study is somewhat
293 underestimated.

294 The total OH reactivity was mainly contributed by NO_x (12.0±7.1 s⁻¹, 43.7%), followed by
295 NMVOCs (7.9±4.8 s⁻¹, 28.5%), CO (7.2±2.6 s⁻¹, 26.0%) and CH₄ (0.3±0.1 s⁻¹, 1.3%) and to a lesser
296 extent by SO₂ and O₃ (0.2±0.1 s⁻¹, 0.6%), indicating the strong influence of anthropogenic emissions
297 in Xianghe. The majority of total OH reactivity values were below 30 s⁻¹, as seen in the frequency
298 distribution, which was dominated by the sum of low-OH-reactivity contributions and less
299 influenced by single compounds with high OH reactivity (Figure S2a-f). Specifically, the
300 cumulative frequency distribution (Figure S3a) clearly showed that the OH reactivity at values >40
301 s⁻¹ was dominated entirely by OH reactivity towards NO_x, and the OH reactivity at values from 20-
302 40 s⁻¹ was nearly completely dominated by OH reactivity towards NO_x and total NMVOCs. In
303 general, the frequency distributions and cumulative frequency distributions of OH reactivity
304 highlighted the necessity of considering a large number of species to obtain a better understanding
305 of OH reactivity.

306 The OH reactivity towards total NMVOCs was 7.9±4.8 s⁻¹, which was much lower than those
307 in Beijing (11.2 s⁻¹) and Heshan (18.3 s⁻¹) (Yang et al., 2017) due to the higher content of reactive
308 hydrocarbons (e.g., alkenes and aromatics) in Beijing and Heshan and due to the unmeasured species
309 (e.g., acetaldehyde) in this study. Alkenes (3.4±3.7 s⁻¹, 42.9%) dominated over OVOCs (2.4±1.5
310 s⁻¹, 30.2%), aromatics (1.5±1.7 s⁻¹, 18.6%) and alkanes (0.7±0.5 s⁻¹, 8.3%) in the OH reactivity
311 towards total NMVOCs. The majority of the values of OH reactivity towards total NMVOCs were
312 below 13 s⁻¹ (Figure S4a-d). The cumulative frequency distribution showed that the OH reactivity
313 towards total NMVOCs at values of > 6 s⁻¹ was dominated by OH reactivity towards alkenes,
314 aromatics and OVOCs, and that the OH reactivity towards total NMVOCs at values of <6 s⁻¹ was
315 dominated by OH reactivity towards alkanes (Figure S5). Alkanes accounted for >50% of the
316 mixing ratio of NMVOCs, but only 8.3% of the OH reactivity towards total NMVOCs. In contrast,
317 aromatics, alkenes and OVOCs accounted for 44.6% of the mixing ratio of NMVOCs, providing
318 91.7% of the OH reactivity towards total NMVOCs. Significantly, isoprene accounted for only 4%
319 of the mixing ratio of NMVOCs but provided 31.2% of the OH reactivity towards total NMVOCs.

320 This result was explained by (1) the relatively low concentration of aromatics, alkenes and OVOCs
321 measured during the campaign, (2) the relatively high concentration of isoprene and (3) the
322 generally large isoprene reaction rate coefficient with OH ($101 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) (Atkinson
323 et al., 2006). The top 10 species, in terms of OH reactivity towards total NMVOCs, consisted of
324 isoprene, HCHO, m/p-xylene, ethylene, hexanal, o-xylene, propylene, styrene, MACR and cis-2-
325 butene (Figure 3b). These species contributed only 39.1% to NMVOC emissions but accounted for
326 80.3% of OH reactivity towards total NMVOCs. As shown in Table 1, the OH reactivity towards
327 the speciated NMVOCs in this study was basically within the values reported in various Chinese
328 cities (Tan et al., 2019; Xu et al., 2011; Yang et al., 2017; Zhu et al., 2020).

329 The mean diurnal profiles of the OH reactivity of trace gases and NMVOCs are presented in
330 Figure 5a-f and Figure 6a-d, respectively. In general, the total OH reactivity was the lowest in the
331 afternoon and the highest during rush hours, reaching a maximum of 33.0 s^{-1} during the morning
332 rush hour and a night-time peak of 30.5 s^{-1} (Figure 5a). Most campaigns have also reported slightly
333 higher OH reactivity in the morning traffic rush hour, which can be explained by higher levels of
334 reactive gases such as NO and NMVOCs due to heavy traffic, as well as slower reactions (Fuchs et
335 al., 2017; Yang et al., 2016). A similar diurnal profile was also observed for contributions from NO_x,
336 CO, alkane and aromatic species, which are typically connected to emissions from anthropogenic
337 activities. The shape of the total OH reactivity diurnal pattern was slightly shifted in the direction
338 of OH reactivity towards NO_x, strengthening the idea that the local pollution in Xianghe was
339 possibly impacted by traffic emissions. However, a different diurnal behavior to that of the above
340 species was observed for alkenes (Figure 6b) and OVOCs (Figure 6d), which are emitted by plants
341 or produced photochemically. The OH reactivity from OVOCs increased by a factor of
342 approximately 2 from nighttime to daytime, suggesting that during the daytime, dilution or chemical
343 removal had a weaker influence on the observed OVOCs than fresh production by photochemistry.
344 The opposite diurnal variation was reported in Wangdu, which showed a weak diurnal variation with
345 a decrease by a factor of approximately 2 from the morning to the evening (Fuchs et al., 2017). The
346 diurnal profile of OH reactivity towards isoprene appears to be the major driver for the diurnal
347 profile of OH reactivity towards alkenes. Biogenic isoprene is dependent on temperature and light
348 intensity (Chang et al., 2014), and anthropogenic isoprene is predominantly emitted by road traffic

349 (Ye et al., 1997); hence, the OH reactivity from alkenes increased during the daytime, with a
350 morning peak of 4.1 s^{-1} at 9:00 h and a night-time peak of 7.4 s^{-1} at 18:00 h. Many rainforest
351 campaigns have also reported a significant diurnal pattern with higher OH reactivity from alkenes
352 and OVOCs at **noontime or a maximum** at the beginning of the night (Yang et al., 2016). Notably,
353 the large amplitude **of the standard** deviation bars highlighted the large diel variability.

354 **3.2.2 NO₃ reactivity**

355 The NO₃ reactivity of trace gases was categorized into SO₂, NO_x, CH₄ and NMVOCs, as shown
356 in Figure 4c and d. **The campaign-averaged** values of total NO₃ reactivity were $2.2 \pm 2.6 \text{ s}^{-1}$, ranging
357 from 0.7 s^{-1} to 27.5 s^{-1} . The average total NO₃ reactivity was much higher than those determined
358 during the IBairn campaign (Liebmann et al., 2018a) and at a rural mountain site (988 m a.s.l.) in
359 southern Germany in 2017 (Liebmann et al., 2018b) **due to higher** contributions from NO_x. We noted
360 that NO_x was by far the main **contributor** to the total NO₃ reactivity, representing 99% of the total
361 NO₃ reactivity on average. NO exhibited the most prominent contribution to the total NO₃ reactivity
362 and represented an average of 78.0% of the total NO₃ reactivity. **In contrast to** NO, NO₂ had a
363 maximum contribution during **the** night-time and represented, on average, 27% of the total NO₃
364 reactivity. The NO₃ reactivity towards CH₄, NMVOCs and SO₂ was very minor, **accounting for** no
365 more than 1% of the total NO₃ reactivity over the whole campaign. The majority of **the** total NO₃
366 reactivity values were below 3 s^{-1} , but **values** below $5.5 \times 10^{-5} \text{ s}^{-1}$, 0.1 s^{-1} , 3 s^{-1} **and** $1 \times 10^{-8} \text{ s}^{-1}$ **were**
367 **observed** for NO₃ reactivity towards CH₄, total NMVOCs, NO_x and SO₂, respectively, as seen in
368 the frequency distribution (Figure S2g-k). The cumulative frequency distribution clearly showed
369 that the total NO₃ reactivity at low and high values was entirely dominated by NO₃ reactivity towards
370 SO₂ and NO_x, respectively (Figure S3b). **In total, the frequency distributions and cumulative**
371 **frequency distributions of NO₃ reactivity highlighted the necessity of considering a large number of**
372 **species to obtain a complete picture of NO₃ reactivity.**

373 The NO₃ reactivity towards total NMVOCs was $2.4 \pm 3.0 \times 10^{-2} \text{ s}^{-1}$ on average with a minimum
374 of $1.1 \times 10^{-3} \text{ s}^{-1}$ and a maximum of 0.3 s^{-1} . The largest fraction of attributed NO₃ reactivity towards
375 total NMVOCs was provided by alkenes (77.8%), followed by aromatics (20.7%) and OVOCs
376 (1.3%). The measured alkanes played virtually no **role in NO₃** reactivity towards total NMVOCs,
377 although they accounted for more than 50% of the mixing ratio of NMVOCs. **This result can be**

378 largely explained by the fact that the reaction rate coefficients of alkenes, aromatics and OVOCs
379 with NO₃ are 1-5 orders of magnitude higher than the alkane reaction rate coefficients with NO₃
380 (Atkinson and Arey, 2003; Atkinson et al., 2006). The majority of the NO₃ reactivity values towards
381 alkanes, alkenes, aromatics and OVOCs were below $5.0 \times 10^{-5} \text{ s}^{-1}$, 0.1 s^{-1} , $1.0 \times 10^{-2} \text{ s}^{-1}$ and 1.0×10^{-3}
382 s^{-1} , respectively (Figure S4e-f). The cumulative frequency distribution showed that the NO₃
383 reactivity towards total NMVOCs at values of $> 0.1 \text{ s}^{-1}$ was entirely dominated by NO₃ reactivity
384 towards alkenes, the NO₃ reactivity towards total NMVOCs at values from 0.01-0.1 s^{-1} was
385 dominated by NO₃ reactivity towards alkenes and aromatics, and the NO₃ reactivity towards total
386 NMVOCs at values of $< 1.0 \times 10^{-5} \text{ s}^{-1}$ was entirely dominated by NO₃ reactivity towards alkanes
387 (Figure S6). The top ten species in terms of NO₃ reactivity towards total NMVOCs consisted of
388 isoprene, styrene, cis-2-butene, trans-2-butene, cis-2-pentene, hexanal, HCHO, propylene, 1,3-
389 butadiene and trans-2-pentene (Figure 3c). These species contributed only 27.7% to NMVOC
390 emissions but accounted for 99.2% of the NO₃ reactivity towards total NMVOCs.

391 Total NO₃ reactivity displayed a weak diel variation with a campaign-averaged morning peak
392 value of 4.0 s^{-1} at 6:00-7:00 h (Figure 5g). The diurnal profile of NO₃ reactivity towards NO_x
393 (Figure 5i) appears to be the major driver for the diurnal profile of total NO₃ reactivity. The morning
394 peak value of total NO₃ reactivity could be explained by the accumulation of NO_x due to traffic
395 emissions that are released into the shallow nocturnal boundary layer during the morning rush hours.
396 In contrast, the average diurnal profile of NO₃ reactivity towards total NMVOCs (Figure 5k) had a
397 maximum at 18:00 h, which was slightly shifted in the direction of NO₃ reactivity towards alkenes
398 (Figure 6j). The evening peak value of NO₃ reactivity towards total NMVOCs could be accounted
399 for by the accumulation of alkenes due to vegetation emissions and traffic emissions that are
400 released into the shallow nocturnal boundary layer. NO₃ reactivity towards alkanes (Figure 6e),
401 alkenes (Figure 6f), aromatics (Figure 6g), OVOCs (Figure 6h) and SO₂ (Figure 5h) played virtually
402 no role in the diurnal variations in total NO₃ reactivity and NO₃ reactivity towards total NMVOCs
403 but exhibited a more distinct diurnal profile.

404 3.2.3 O₃ reactivity

405 The O₃ reactivity of trace gases was categorized into NO_x, CH₄ and total NMVOCs, as shown
406 in Figure 4e and f. The total O₃ reactivity at the site varied between a minimum of $3.3 \times 10^{-4} \text{ s}^{-1}$ and

407 a maximum of $1.8 \times 10^{-2} \text{ s}^{-1}$ and was $1.2 \pm 1.7 \times 10^{-3} \text{ s}^{-1}$ on average. NO exhibited the most prominent
408 contribution to the total O_3 reactivity and represented >99% of the total O_3 reactivity on average,
409 whereas nearly all other contributions were < 1%. This result can be largely accounted for by the
410 generally large NO reaction rate coefficients with O_3 ($1.8 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) (Atkinson et
411 al., 2006), which are several orders of magnitude higher than the reaction rate coefficients of NO_2 ,
412 alkanes, alkenes, aromatics and OVOCs with NO_3 (Atkinson et al., 2006; Atkinson and Arey,
413 2003; Yuan et al., 2013; Ferracci et al., 2018; Jenkin et al., 2015). The majority of the total O_3
414 reactivity values were below $2 \times 10^{-3} \text{ s}^{-1}$, but values below $5.5 \times 10^{-10} \text{ s}^{-1}$, $2 \times 10^{-6} \text{ s}^{-1}$ and $2 \times 10^{-3} \text{ s}^{-1}$
415 were observed for the O_3 reactivity towards CH_4 , total NMVOCs and NO_x , respectively, as seen in
416 the frequency distribution (Figure S21-o). The cumulative frequency distribution clearly showed that
417 the total O_3 reactivity at low and high values was entirely dominated by O_3 reactivity towards CH_4
418 and NO_x , respectively (Figure S3c). Generally, the frequency distributions and cumulative
419 frequency distributions of O_3 reactivity highlight the necessity of considering a large number of
420 species to obtain a complete picture of O_3 reactivity.

421 The O_3 reactivity towards total NMVOCs was $1.1 \pm 0.8 \times 10^{-6} \text{ s}^{-1}$ on average, ranging from a
422 minimum of $2.5 \times 10^{-7} \text{ s}^{-1}$ to a maximum of $1.0 \times 10^{-5} \text{ s}^{-1}$. Alkenes clearly dominated the O_3 reactivity
423 towards total NMVOCs, with a campaign-averaged contribution of 94.0%. Aromatics were the
424 second largest contributor, comprising an average of 5.2% of the O_3 reactivity towards total
425 NMVOCs. In comparison, OVOCs accounted for only 0.8% of the O_3 reactivity towards total
426 NMVOCs. In contrast, the measured alkanes played nearly no role in the O_3 reactivity towards total
427 NMVOCs due to their small reaction rate coefficients with O_3 ($< 1.0 \times 10^{-23} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$)
428 (Atkinson and Arey, 2003; Atkinson et al., 2006). The majority of the O_3 reactivity values towards
429 alkanes, alkenes, aromatics and OVOCs were below $5.0 \times 10^{-12} \text{ s}^{-1}$, $3.0 \times 10^{-6} \text{ s}^{-1}$, $2.0 \times 10^{-7} \text{ s}^{-1}$ and
430 $2.0 \times 10^{-8} \text{ s}^{-1}$, respectively (Figure S4i-l). The cumulative frequency distribution (Figure S7) clearly
431 showed that the O_3 reactivity towards total NMVOCs at $> 1.0 \times 10^{-7} \text{ s}^{-1}$ was dominated by O_3
432 reactivity towards alkenes and aromatics, the O_3 reactivity towards total NMVOCs between 1.0×10^{-9}
433 s^{-1} and $1.0 \times 10^{-7} \text{ s}^{-1}$ was dominated by O_3 reactivity towards alkenes, aromatics and OVOCs, and
434 the O_3 reactivity towards NMVOCs $< 1.0 \times 10^{-11} \text{ s}^{-1}$ was entirely dominated by O_3 reactivity towards
435 alkanes. In terms of individual species, isoprene, cis-2-butene, trans-2-butene, cis-2-pentene,

436 propylene, styrene, ethylene, 1-butene, trans-2-pentene and 1-pentene were the top ten species
437 (Figure 3d), accounting for 28%, 25%, 20%, 8%, 7%, 5%, 5%, 3%, 2% and 1%, respectively, of the
438 O₃ reactivity towards total NMVOCs and 3.1%, 0.3%, 0.1%, 0.1%, 1%, 0.4%, 4.1%, 0.4%, 0.1%
439 and 0.1%, respectively, of the total NMVOC emissions.

440 Compared with the OH and NO₃ reactivities, O₃ reactivity displayed a much weaker diel
441 variation, especially the O₃ reactivity towards alkenes and aromatics, as shown in Figure 5 and
442 Figure 6. This weakness can be explained by the following reasons. First, for a given species, the
443 reaction rate coefficients with O₃ were much smaller than the corresponding reaction rate
444 coefficients with OH and NO₃. For example, the ethylene reaction rate coefficients with OH
445 ($8.52 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) and NO₃ ($2.05 \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) are 6 and 2 orders of
446 magnitude higher, respectively, than the ethylene reaction rate coefficient with O₃ ($1.59 \times 10^{-18} \text{ cm}^3$
447 $\text{molecule}^{-1} \text{ s}^{-1}$) (Atkinson and Arey, 2003; Atkinson et al., 2006). Second, the high-emission species
448 reaction rate coefficients with O₃ are smaller than the low-emission species reaction rate coefficients
449 with O₃. For instance, the m/p-xylene (one of the top five species in terms of emissions) reaction
450 rate coefficient with O₃ ($< 1.0 \times 10^{-20} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) are much smaller than the 1-hexene (one of
451 the bottom five emissions species) reaction rate coefficients with O₃ ($1.13 \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$)
452 (Atkinson and Arey, 2003; Atkinson et al., 2006). The above two factors largely weaken the diurnal
453 variation in O₃ reactivity.

454 3.3 Implications for OH, NO₃ and O₃ reactivity-based NMVOC control strategies

455 Table 2 lists the top 10 NMVOC species (excluding isoprene) in terms of concentration, OH,
456 NO₃ and O₃ reactivities, and their corresponding contributions to concentrations, and OH, NO₃ and
457 O₃ reactivities. The order of the major OH, NO₃ and O₃ reactivity-contributing species differed
458 significantly from that of concentration-contributing species. Therefore, NMVOC control strategies
459 based on OH, NO₃ and O₃ reactivities differ significantly from those based on concentrations.

460 From the perspective of concentration, HCHO, propane, acetone, ethane, n-butane, m/p-xylene,
461 iso-pentane, ethylene, iso-butane and n-pentane should be targeted. If these 10 species were fully
462 controlled, it would lead to an NMVOC concentration reduction of 79.9% with OH, NO₃ and O₃
463 reactivity reductions of only 58.4%, 2.1% and 6.4%, respectively. These species are mainly from
464 fuel combustion and vehicle exhaust (Song et al., 2018; Liu et al., 2017); hence, from the perspective

465 of the current emission-based limits, we recommend that the priorities for the control of NMVOC
466 sources include fuel combustion and vehicle exhaust.

467 From the perspective of OH reactivity, HCHO, m/p-xylene, ethylene, hexanal, o-xylene,
468 propylene, styrene, MACR, cis-butene and MVK were the key species. If the releases of these
469 compounds were reduced to zero without any offset, OH reactivity would be reduced by 73.3% with
470 an NMVOC concentration reduction of 38.1%, a NO₃ reactivity reduction of 86.4% and O₃
471 reactivity reduction of 55.7%. From the perspective of NO₃ reactivity, the top 10 NMVOC species
472 consisted of styrene, cis-2-butene, trans-2-butene, cis-2-pentene, hexanal, HCHO, propylene, 1,3-
473 butadiene, trans-2-pentene and 1-butene. If the concentrations of these species were completely
474 eliminated, it would reduce NO₃ reactivity by 97.8% with an NMVOC concentration reduction of
475 25.8%, an OH reactivity reduction of 49.7% and an O₃ reactivity reduction of 91.8%. From the
476 perspective of O₃ reactivity, cis-2-butene, trans-2-butene, cis-2-pentene, propylene, styrene,
477 ethylene, 1-butene, trans-2-pentene, 1-pentene and MACR should be the key targets for control. If
478 the concentrations of these compounds were reduced to zero without any offset, it would lead to an
479 O₃ reactivity reduction of 98.9% with an NMVOC concentration reduction of 7.3%, an OH
480 reactivity reduction of 22.3% and a NO₃ reactivity reduction of 94.2%. The top ten species
481 associated with OH, NO₃ and O₃ reactivities are mainly from traffic-related emissions, industry and
482 solvent usage (Song et al., 2018; Liu et al., 2017; Chen et al., 2014). Therefore, in terms of reactivity-
483 based limits, we recommend that the priorities for the control of NMVOC sources include traffic-
484 related emissions, industry and solvent usage.

485 Clearly, species with large concentrations do not necessarily have high OH, NO₃ and O₃
486 reactivities, and a small concentration reduction can result in a maximum reduction in reactivity.
487 The key NMVOC species in terms of OH, NO₃ and O₃ reactivities also differed from each other.
488 However, reducing the concentrations of propylene, styrene and cis-2-butene may likely achieve a
489 win-win-win situation. Although the above comparisons were made under the assumption that
490 concentrations would be significantly reduced, it is obvious that OH, NO₃ and O₃ reactivity-based
491 control strategies are more efficient than concentration-based policies in terms of reducing NMVOC
492 pollution. Overall, the combined integration and comparison of OH, NO₃ and O₃ reactivities towards
493 NMVOCs could provide useful suggestions for VOC pollution control in the North China Plain.

494 3.4 AOC

495 3.4.1 Modeling OVOCs, OH, HO₂, RO₂ and NO₃ by SOSAA

496 With the appropriate [setup](#) of the condensation sinks for [the](#) ten calculated OVOCs (ACR,
497 C₂H₅CHO, MACR, C₃H₇CHO, MVK, MEK, MPRK, C₄H₉CHO, DIEK [and](#) C₅H₁₁CHO), the
498 modeled diurnal mean pattern generally [followed the measured pattern within 1 standard deviation](#)
499 [of the measurement data, although the model underestimated measurements, predicting values of](#)
500 [less than 1 ppb from 19:00 to 24:00h](#) (Figure S8a). With the inclusion of input MTBE and
501 CH₃COCH₃ (acetone) which constituted more than 50% of the total OVOCs, the modeled total
502 [OVOC](#) concentration agreed better with the [measurements](#) than expected (Figure S8b). The modeled
503 diurnal median number concentrations of OH, HO₂ and RO₂ showed an apparent diurnal pattern
504 with peaks during [midday and values](#) approaching zero during night, which resulted from the
505 [dependence](#) of their chemical production reactions [on incoming](#) solar radiation (Figure S9a, b and
506 c). The [midday time \(12:00-16:00 h\) median number concentrations](#) of OH, HO₂ and RO₂ were
507 1.2×10^7 , 5.9×10^8 and 3.7×10^8 [molecules cm⁻³, respectively](#), which were comparable to previous
508 studies (Tan et al., 2017). [The diurnal variation of in the hourly median NO₃ concentration showed](#)
509 [two peaks which were consistent with the high chemical production from NO₂ + O₃ \(Figure S9d\).](#)
510 Figure S10 shows the relationship between [the](#) modeled OH number concentration and the measured
511 J_O¹D. The coefficient of determination (R²) was 0.86, and the linear regression fit showed [that](#) the
512 slope was 6.1×10^{11} cm⁻³ s⁻¹ and the intercept was 0.9×10^6 cm⁻³. These values were comparable to
513 Tan et al. (2017), except the slope [here](#) was [approximately](#) 36% higher than the [observed](#) fit in Tan
514 et al. (2017).

515 3.4.2 Overall characteristics of AOC

516 The loss [rates](#) of NMVOCs, CH₄ and CO via reactions with OH, O₃ and NO₃ [were](#) calculated.
517 The calculated AOC was up to 4.5×10^8 molecules cm⁻³ s⁻¹ with [a](#) campaign-averaged [value](#) of
518 7.8×10^7 molecules cm⁻³ s⁻¹, daytime [average](#) (06:00-18:00 h) of 1.4×10^8 molecules cm⁻³ s⁻¹ and
519 nighttime [average](#) of 6.7×10^6 molecules cm⁻³ s⁻¹. As such, the total number of NMVOCs, CH₄ and
520 CO molecules depleted during [the](#) daytime and nighttime were 6.0×10^{12} and 2.9×10^{11} , respectively,
521 per cm⁻³ of air. [These](#) AOC levels were higher than those determined at the Tung Chung air quality
522 monitoring station (Xue et al., 2016), a polluted area in Santiago, Chile (Elshorbany et al., 2009)

523 and the Hong Kong Polytechnic University's air monitoring station at Hok Tsui (Li et al., 2018).

524 Comparisons of the AOC values calculated from OH, O₃ and NO₃ and the corresponding
525 oxidation concentrations are shown in Figure 7. The OH and NO₃ radical concentrations were
526 simulated by the SOSAA box model. The AOC calculated from OH, O₃ and NO₃ correlated well
527 with the corresponding oxidation concentrations, with correlation coefficients (r) of 0.91, 0.83 and
528 0.57, respectively, suggesting that the parameterized AOC here was consistent with that obtained
529 using radical concentration to indicate AOC. Specifically, the average oxidation capacities of OH,
530 O₃ and NO₃ radicals throughout the entire campaign were 7.7×10^7 , 1.2×10^6 and 1.8×10^5 molecules
531 $\text{cm}^{-3} \text{ s}^{-1}$, representing 98.2%, 1.5% and 0.3% of the total oxidation capacity, respectively. The total
532 number of depleted molecules per day due to oxidation by OH, O₃ and NO₃ was 6.6×10^{12} , 1.0×10^{11}
533 and 1.5×10^{10} molecules cm^{-3} , respectively; these values were slightly higher than those assessed in
534 a polluted area in Santiago, Chile (Elshorbany et al., 2009). Accordingly, OH radicals are the driving
535 force of AOC in Xianghe, especially during the daytime. Figure 8 shows a comparison of the
536 oxidation capacities of OH, O₃ and NO₃. On average, the relative contribution of O₃ and NO₃
537 oxidation capacities when integrated over 24 hours was less than 4% (Figure 8a-c). OH is the only
538 oxidant of CO in the troposphere. As expected, OH was responsible for 99% of the oxidation
539 capacity regarding NMVOCs, CH₄ and CO during the daytime (Figure 8d). The relative contribution
540 of OH to oxidation capacity decreased to 98% when restricting the calculation to NMVOC families
541 alone (Figure 8e). Focusing on the oxidation of unsaturated NMVOCs, OH was the dominant
542 oxidant with a relative proportion of approximately 97% (Figure 8f). Note that the influence of NO₃
543 and O₃ on the oxidation of CO and VOCs can be neglected during the daytime. However, elevated
544 relative contributions of O₃ and NO₃ to oxidation capacity can be observed during the nighttime. As
545 expected, O₃ and NO₃ accounted for 10% and 2%, respectively, of the oxidation capacity with
546 respect to NMVOCs, CH₄ and CO (Figure 9g), but 19% and 3% of NMVOC families alone (Figure
547 8h) occurred at night. Focusing on the oxidation of unsaturated NMVOCs, O₃ and NO₃ accounted
548 for 20% and 4%, respectively, of the oxidation capacity (Figure 8i). This quantitative
549 intercomparison of the oxidation capacities of OH, O₃ and NO₃ confirms the important role of OH
550 in the degradation of NMVOCs, CH₄ and CO. Compared with OH and O₃, NO₃ had a lower
551 contribution during both the daytime and nighttime, which was mainly caused by high NO

552 concentrations (Liebmann et al., 2018b).

553 **4. Summary and conclusions**

554 In the summer of 2018, a comprehensive field campaign was conducted at a suburban site in
555 the North China Plain. Based on simultaneous measurements of O₃, CO, SO₂, NO, NO₂, JO¹D,
556 JNO₂, JNO₃, HONO, HCHO, CH₄ and 65 NMVOCs, the reactivities (OH, NO₃ and O₃ reactivities)
557 towards trace gases and AOC were comprehensively analyzed. The main findings are summarized
558 as follows.

559 The total OH reactivity was between 9.2 and 69.6 s⁻¹ with an average of 27.5±9.7 s⁻¹, which
560 was mainly contributed by NO_x (43.7%), followed by NMVOCs (28.5%), CO (26.0%) and CH₄
561 (1.3%) and SO₂ and O₃ (0.5%). OH reactivity towards total NMVOCs was 7.9±4.8 s⁻¹ and
562 dominated by alkenes (42.9%). The campaign-averaged value of total NO₃ reactivity was 2.2±2.6
563 s⁻¹, ranging from 0.7 s⁻¹ to 27.5 s⁻¹. NO_x was the main contributor to the total NO₃ reactivity,
564 representing 99% of the total NO₃ reactivity on average. NO₃ reactivity towards total NMVOCs was
565 2.4±3.0×10⁻² s⁻¹, on average, and it was dominated by alkenes (77.8%). The total O₃ reactivity
566 varied between a minimum of 3.3×10⁻⁴ s⁻¹ and a maximum of 1.8×10⁻² s⁻¹ with an average of
567 1.2±1.7×10⁻³ s⁻¹. NO exhibited the most prominent contribution to the total O₃ reactivity and
568 represented an average of >99% of the total O₃ reactivity. The O₃ reactivity towards total NMVOCs
569 was 1.1±0.8×10⁻⁶ s⁻¹ on average, ranging from 2.5×10⁻⁷ s⁻¹ to 1.0×10⁻⁵ s⁻¹ and dominated by alkenes
570 (94.0%). The total OH, NO₃ and O₃ reactivities displayed a similar diel variation with the lowest
571 value in the afternoon and the highest value during rush hours, and the diurnal profile of NO_x appears
572 to be the major driver for the diurnal profiles of total OH, NO₃ and O₃ reactivities. Compared with
573 the OH and NO₃ reactivities, O₃ reactivity displayed a much weaker diel variation, especially the
574 O₃ reactivity towards alkenes and aromatics due to 1) the rate coefficients with O₃ being much
575 smaller than the corresponding reaction rate coefficients with OH and NO₃ for the same species and
576 2) the high-emission species reaction rate coefficients with O₃ being smaller than the low-emission
577 species reaction rate coefficients with O₃.

578 The relative OH reactivity towards NO_x and VOCs and the scatter plots of CO-NO_y color-
579 coded with O₃ concentrations indicated a VOC-limited regime of O₃ formation in Xianghe,
580 suggesting that control of VOCs would be most effective for controlling O₃ in Xianghe. OH, NO₃

581 and O₃ reactivity-based control strategies are more efficient than concentration-based policies in
582 terms of reducing NMVOC pollution. We suggest that policy makers shift the current concentration
583 -based limits to reactivity-based policies.

584 The loss rates of NMVOCs, CH₄ and CO via reactions with OH, O₃ and NO₃ were calculated;
585 these loss rates were up to 4.5×10⁸ molecules cm⁻³ s⁻¹ with a campaign-averaged value of 7.8×10⁷
586 molecules cm⁻³ s⁻¹, daytime average (06:00-18:00 h) of 1.4×10⁸ molecules cm⁻³ s⁻¹ and nighttime
587 average of 6.7×10⁶ molecules cm⁻³ s⁻¹. AOC was dominated by OH radicals (7.7×10⁷ molecules
588 cm⁻³ s⁻¹, 98.2%), O₃ (1.2×10⁶ molecules cm⁻³ s⁻¹, 1.5%) and NO₃ radicals (1.8×10⁵ molecule cm⁻³
589 s⁻¹, 0.3%), suggesting that the OH radical is the driving force of the oxidation capacity in the
590 atmosphere in Xianghe, especially during the daytime. The reaction with OH radical was the
591 dominant contributor to the loss rate for NMVOCs except for trans-2-butene, cis-2-butene and trans-
592 2-pentene, where the reaction with O₃ was more important for their loss rates during the nighttime.
593 Oxidation by NO₃ radicals was more important than oxidation by anthropogenic hydrocarbons for
594 the nighttime averaged loss rate of isoprene.

595 Our study provides useful insights for VOC pollution control in a typical suburban site in the
596 North China Plain. Further studies, especially direct observations of OH and NO₃ radicals, OH and
597 NO₃ reactivity measurements and speciated measurements, are required to further explore trace gas
598 reactivity and AOC.

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608 **Competing financial interests**

609 The authors declare no competing financial interests.

610 **Author contributions**

611 Y.W designed the research. Y.Y and D.Y, S.Z, D.J, Y.W conducted the measurements. Y.Y and Y.W
612 interpreted the data and write the paper. P.Z and D.C conducted SOSAA simulation. All the authors
613 contributed to discussing results and commenting on the paper.

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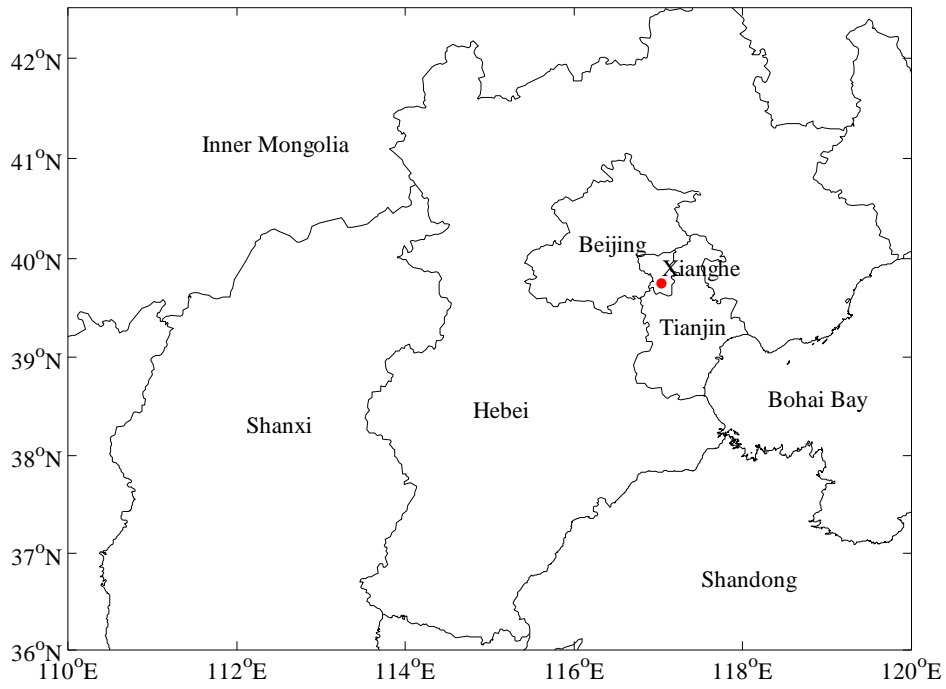
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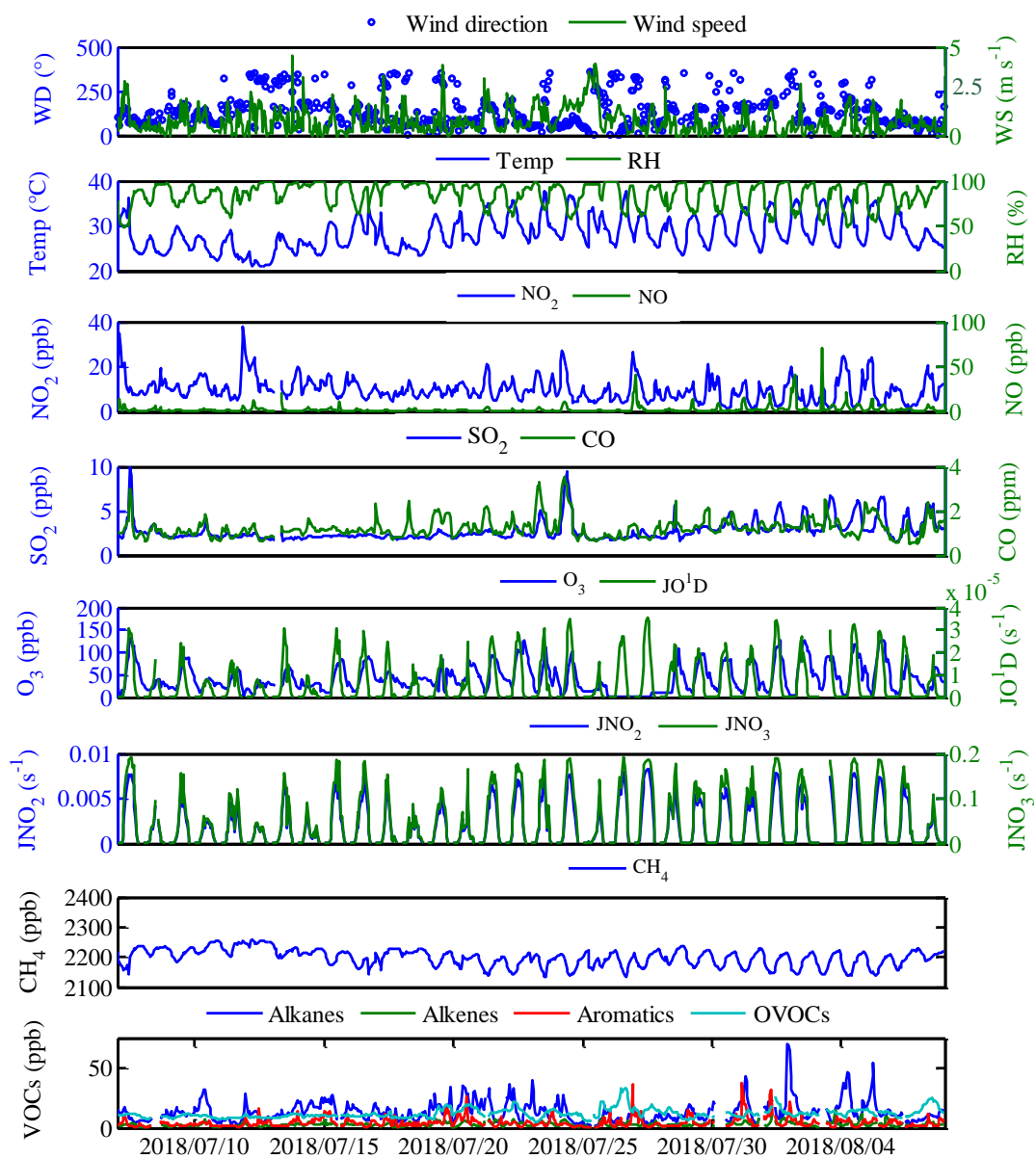
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Figure captions



903 Figure 1. The location of the sampling site, which is marked with a red dot. The blacklines are
904 provincial boundary lines of each province. (The figure was produced by MATLAB 2017a).

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914 Figure 2. Time series of meteorology parameters, trace gases, photolysis rates and VOCs

915 concentrations during the field campaign at Xianghe from 6 July to 6 August 2018.

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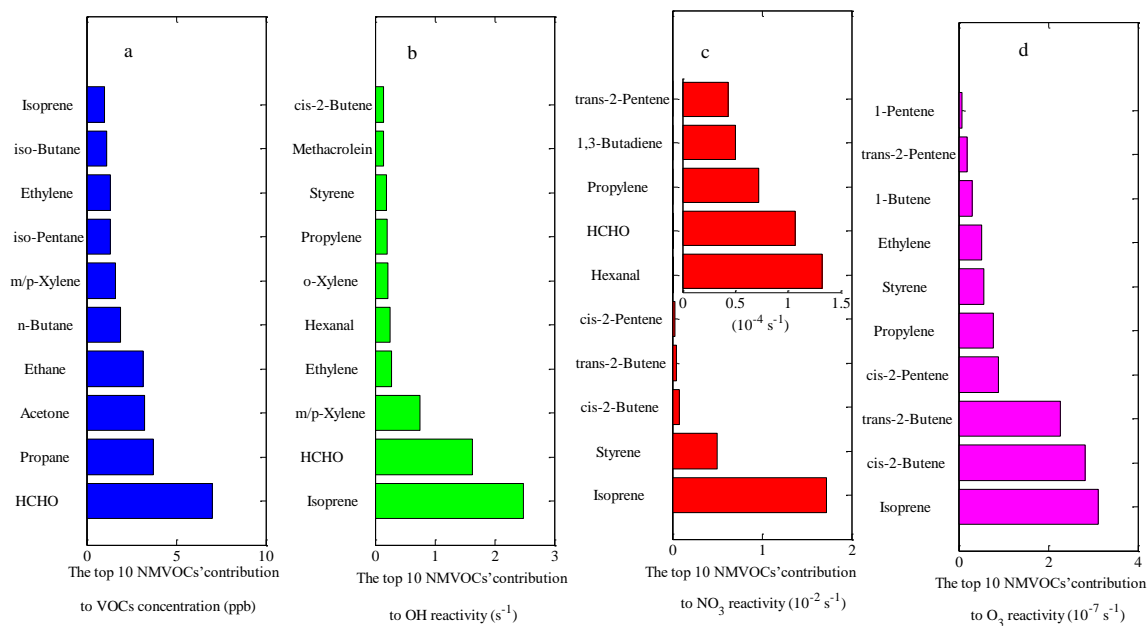
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926 Figure 3. The top 10 NMVOCs' contribution to total NMVOCs concentration (a),
927 OH reactivity (b),
928 NO_3 reactivity (c) and O_3 reactivity (d) during the field campaign at Xianghe from 6 July to 6 August
929 2018.

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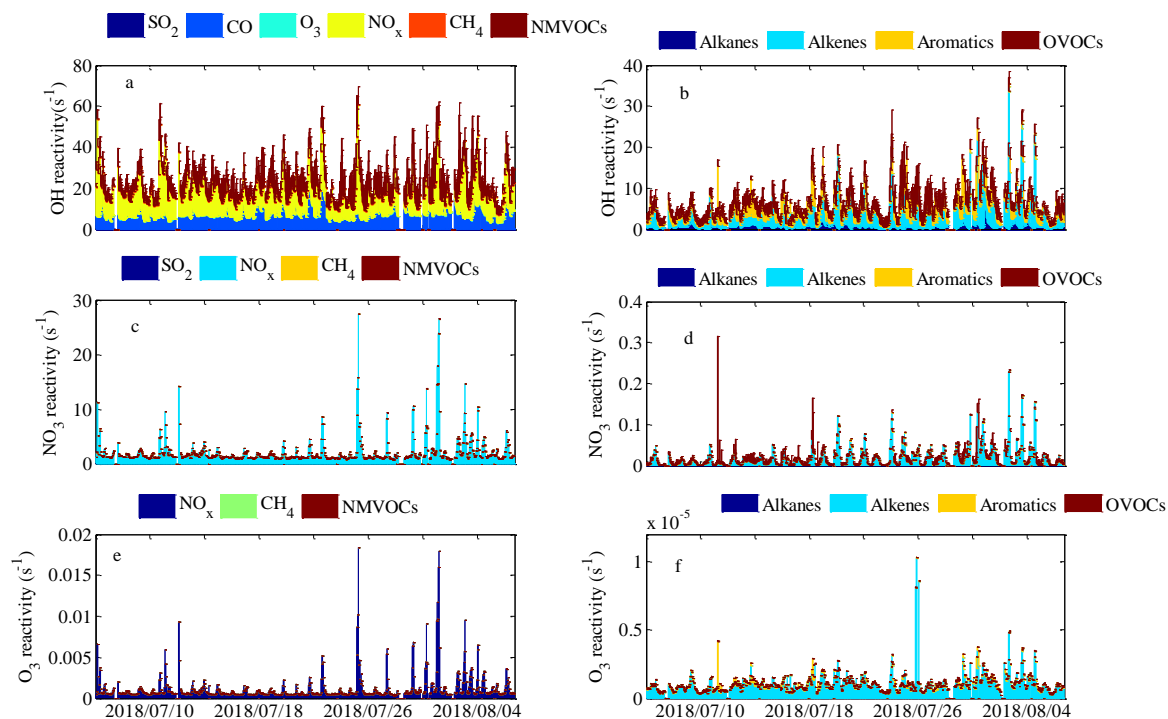
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946 Figure 4. The time series of OH reactivity (a,b), NO₃ reactivity (c,d) and O₃ reactivity (e,f) during

947 the field campaign at Xianghe from 6 July to 6 August 2018.

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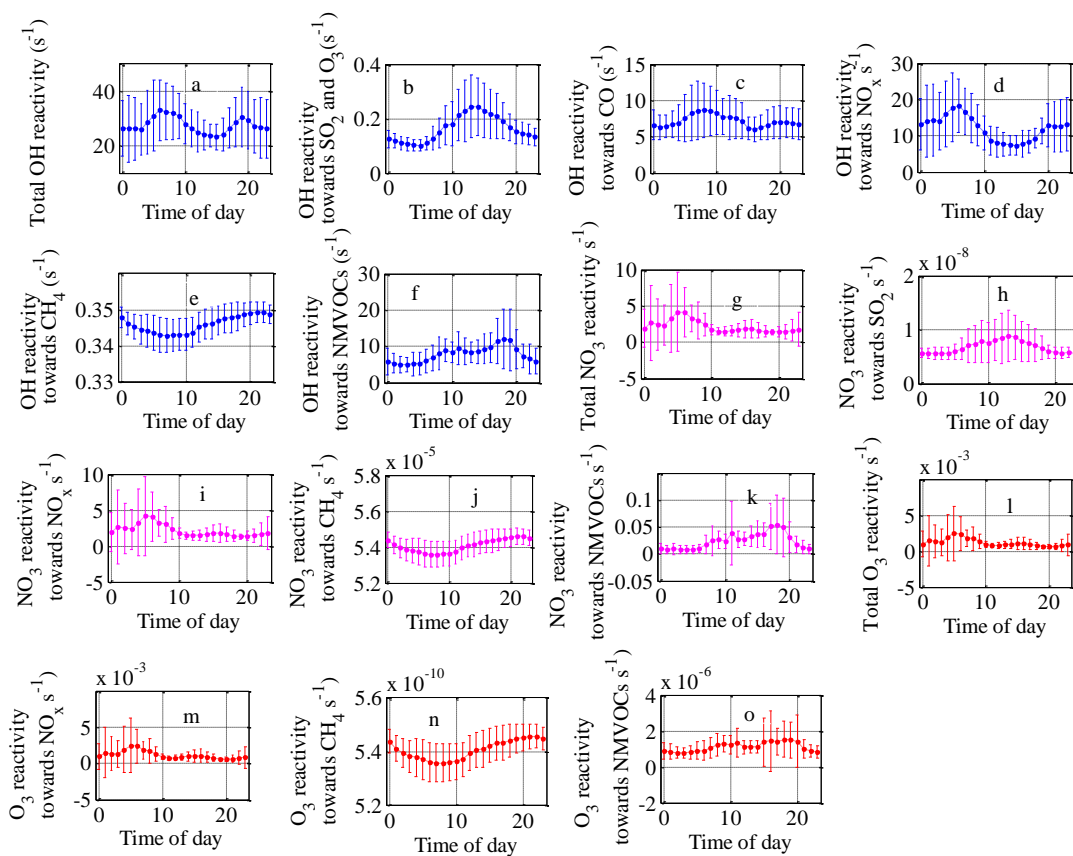
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961 Figure 5. Mean diurnal variations of OH reactivity (a-f), NO_3 reactivity (g-k) and O_3 reactivity (l-o)

962 of trace gases during the field campaign at Xianghe from 6 July to 6 August 2018.

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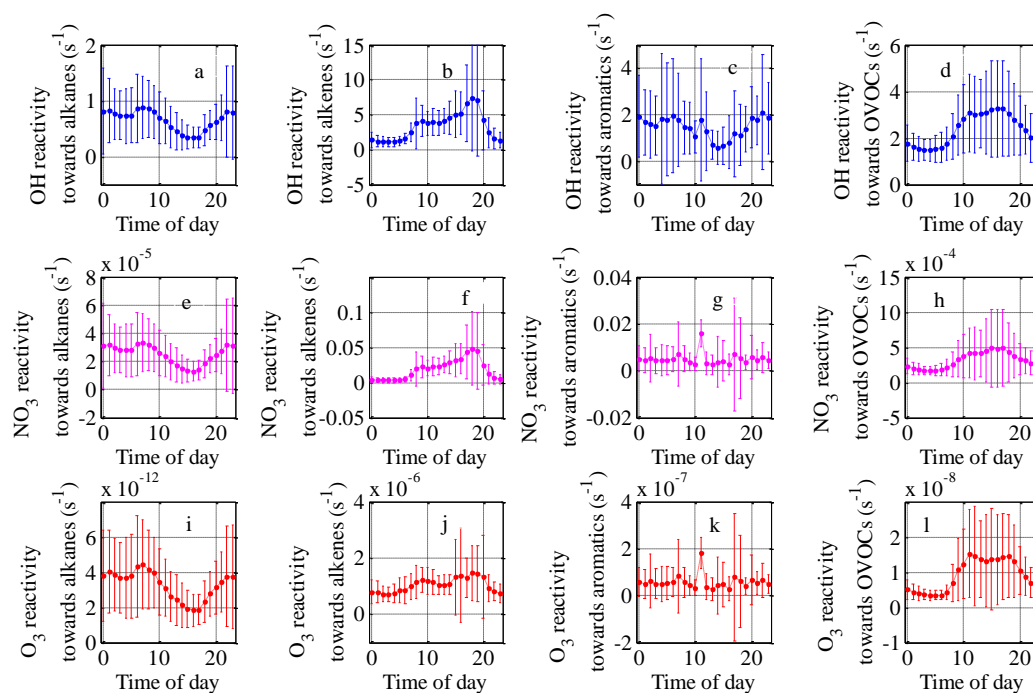
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970 Figure 6. Mean diurnal variations of OH reactivity (a-d), NO₃ reactivity (e-h) and O₃ reactivity (i-l)
 971 of NMVOCs groups during the field campaign at Xianghe from 6 July to 6 August 2018.

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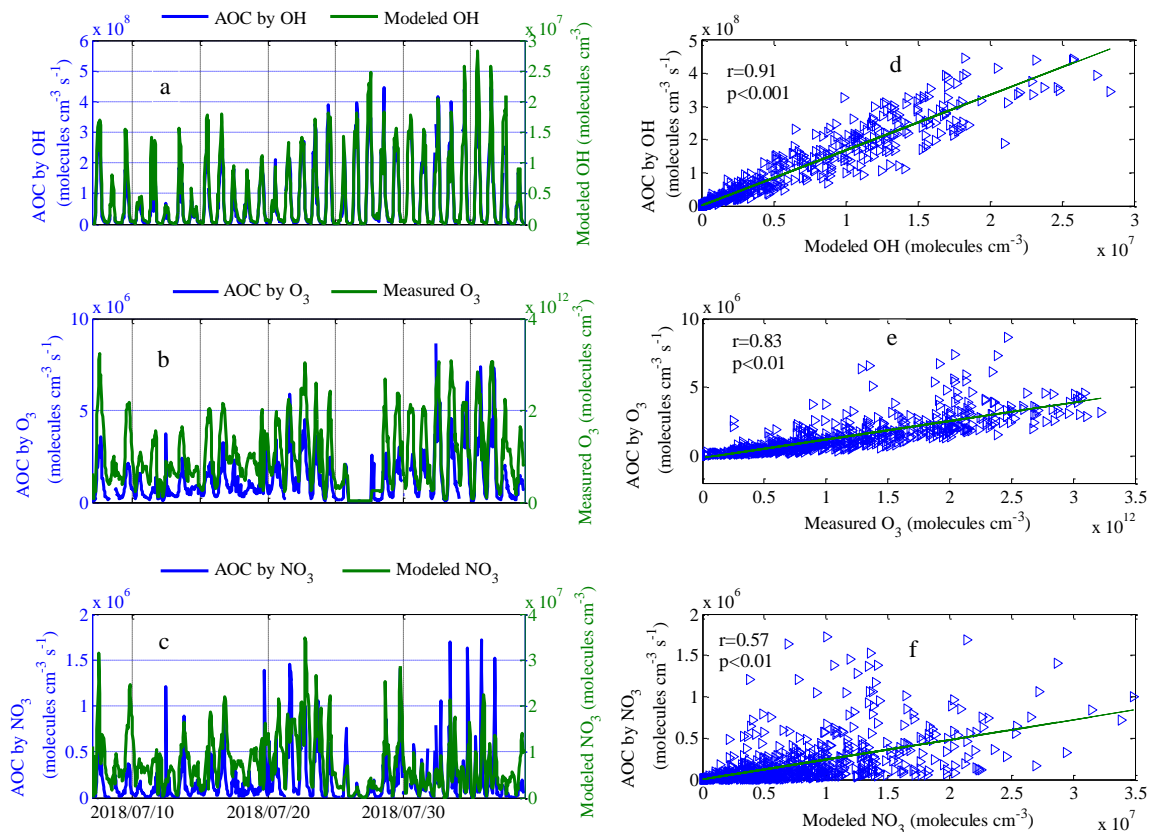
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987 Figure 7. Comparisons of calculated AOC by modeled OH (a), measured O₃ (b) and modeled NO₃
 988 (c), and corresponding oxidation concentrations. The left column shows the time series and the right
 989 column shows scatterplots of calculated AOC and corresponding oxidation concentrations. Note: r
 990 and p are the correlation coefficient and the significance level, respectively.

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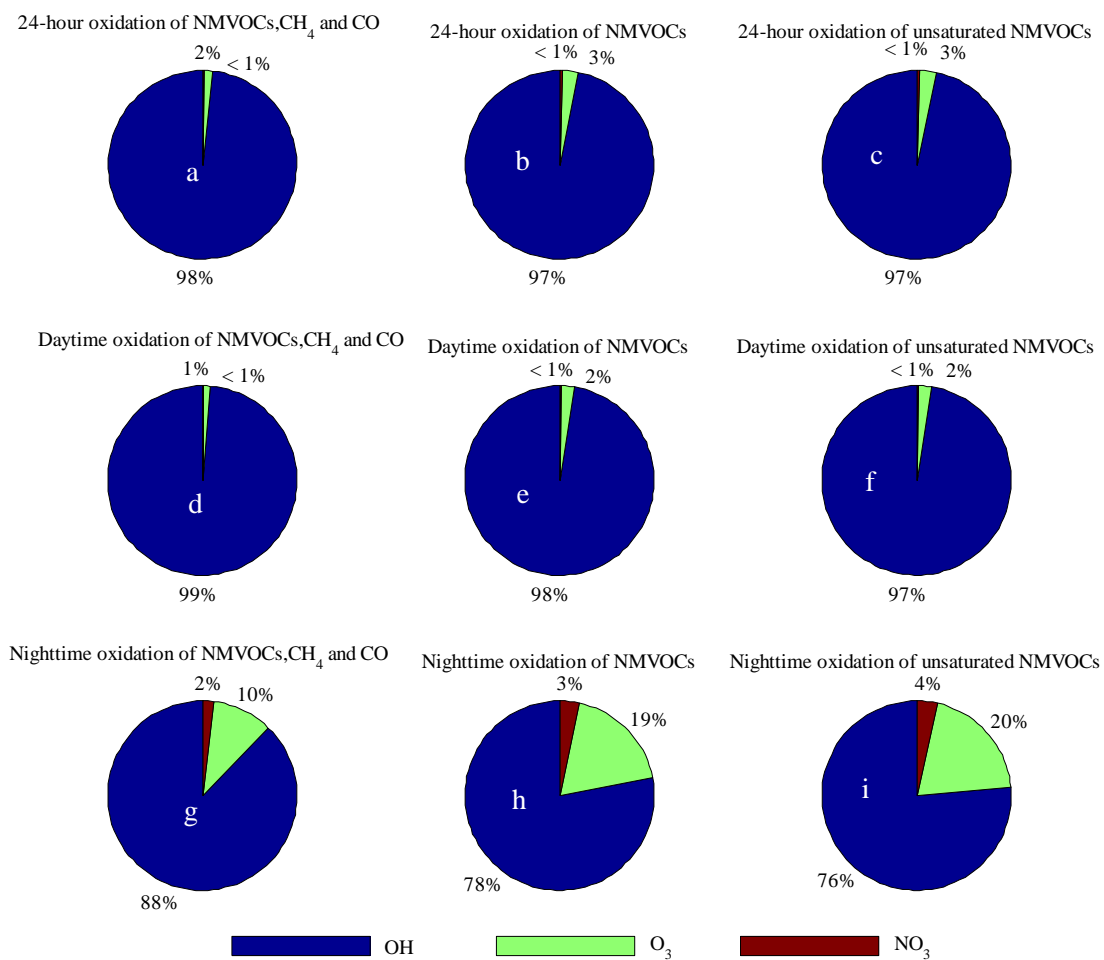
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1001 Figure 8. Comparison of the relative contributions of OH, NO₃ and O₃ to the 24-h, daytime and
1002 nighttime averaged loss rates. Data are calculated for the loss rates of (a, d and g) NMVOCs, CH₄
1003 and CO, (b,e and h) NMVOCs only, and (c,f and i) unsaturated NMVOCs only.

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1014 Table1. Comparison of speciated OH reactivity with former studies in China.

Species	This study	Beijing ^a	Shangdianzi ^a	Heshan ^b	Guangzhou ^c	Chongqing ^c	Beijing ^d	Shanghai ^e
CH ₄	0.346							0.34
Ethane	0.019	0.01	0.01	0.023	0.24	0.59		
Propane	0.100	0.32	0.10	0.081				
iso-Butane	0.058	0.45	0.12	0.075				
n-Butane	0.111	0.09	0.08	0.104				
Cyclopentane	0.001	0.08	0.03	0.011				
iso-Pentane	0.119	1.18	0.25	0.168				
n-Pentane	0.067	0.60	0.16	0.136				
2,2-Dimethylbutane	0.002	0.08	0.08	0.003				
2,3-Dimethylbutane	0.017	0.23	0.11	0.013				
2-Methylpentane	0.016	0.56	0.10	0.077				
3-Methylpentane	0.018	0.44	0.10	0.047				
n-Hexane	0.020	0.60	0.08	0.055				
2,4-Dimethylpentane	0.001			0.069				
Methylcyclopentane	0.019	0.49	0.07	0.024				
2-Methylhexane	0.003	0.22	0.04	0.035				
2,3-Dimethylpentane	0.001		0.00	0.007				
Cyclohexane	0.048	0.26	0.05	0.015				
3-Methylhexane	0.004	0.28	0.05	0.039				
2,2,4-Trimethylpentane	0.002	0.04	0.01	0.036				
n-Heptane	0.006	0.24	0.04	0.033				
Methylcyclohexane	0.003	0.25	0.03	0.015				
2,3,4-Trimethylpentane	0.001	0.03	0.01	0.031				
2-Methylheptane	0.002	-	0.00	0.007				
3-Methylheptane	0.001	0.11	0.03	0.007				
n-Octane	0.004	0.38	0.11	0.014				
Nonane	0.004	0.19	0.03	0.010				
n-Decane	0.003			0.008				
n-Undecane	0.002			0.006				
Ethylene	0.273	0.35	0.18	0.617	0.29	0.73		
Propylene	0.202	4.86	1.00	0.464	0.40	0.52		
trans-2-Butene	0.067	1.98	0.31	0.063				
1-Butene	0.100	1.65	0.73	0.077				
cis-2-Butene	0.145	1.33	0.32	0.084				
1,3-Butadiene	0.034	-	-	-				
1-Pentene	0.023	0.50	0.22	1.136				
trans-2-Pentene	0.006	0.64	0.13	0.066	0.31	0.26		
cis-2-Pentene	0.034	1.20	0.29	0.080				
Isoprene	2.463	5.59	2.81	0.862	0.31	0.92		

1-Hexene	0.007	-	-	0.018		
HCHO	1.797			1.153		
Acrolein	0.027			0.009		
Propanal	0.067			0.139		
Acetone	0.013			0.010		
MTBE	0.009			-		
Methacrolein	0.146			0.072		
n-Butanal	0.024			0.059		
MethylVinylKetone	0.138			0.039		
Methylethylketone	0.014			0.020		
2-Pentanone	0.001			0.001		
Pentanal	0.042			0.028		
3-Pentanone	0.001			0.002		
Hexanal	0.247			0.055		
Benzene	0.017	0.34	0.13	0.030		
Toluene	0.092	2.22	0.39	0.518	0.73	0.15
Ethylbenzene	0.085	0.88	0.18	0.188		
m/p-Xylene	0.749	3.05	0.43	0.754	0.74	0.31
o-Xylene	0.216	0.93	0.12	0.194	0.35	0.10
Styrene	0.193	0.34	0.14	0.900	0.26	0.16
Isopropylbenzene	0.002	0.04	0.01	0.004		
n-Propylbenzene	0.002	0.25	0.16	0.004		
m-Ethyltoluene	0.016			0.026		
p-Ethyltoluene	0.013			0.027		
1,3,5-Trimethylbenzene	0.031	2.90	1.08	0.042		
o-Ethyltoluene	0.006			0.018		
1,2,4-Trimethylbenzene	0.028			0.080	0.16	0.17
1,2,3-Trimethylbenzene	0.008			0.028		
CO	7.196	6.90	5.37			9.13 3.15
NO	2.139					0.58 0.78
NO ₂	9.947					4.08 2.87
SO ₂	0.088					0.33
O ₃	0.076					

1015 ^a (Xu et al., 2011); ^b (Yang et al., 2017); ^c (Tan et al., 2019); ^d (Liu et al., 2009); ^e (Zhu et al., 2020).

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1022 Table 2. The top 10 NMVOCs species in terms of concentration (first column), OH reactivity
 1023 (second column), NO₃ reactivity (third column) and O₃ reactivity (fourth column) and their
 1024 corresponding contributions to concentration, OH, NO₃ and O₃ reactivity towards NMVOCs (%).

First column					Second column				
Species	Concentration	OH reactivity	NO ₃ reactivity	O ₃ reactivity	Species	Concentration	OH reactivity	NO ₃ reactivity	O ₃ reactivity
HCHO	22.3	30.3	1.5	0.2	HCHO	22.3	30.3	1.5	0.2
Propane	11.8	1.9	0.1	0.0	m/p-Xylene	5.1	14.0	0.1	0.0
Acetone	10.2	0.3	0.0	0.1	Ethylene	4.2	5.0	0.1	6.1
Ethane	6.0	0.4	0.0	0.0	Hexanal	1.1	4.6	1.9	0.0
n-Butane	5.1	2.1	0.0	0.1	o-Xylene	2.1	4.0	0.1	0.0
m/p-Xylene	4.3	14.0	0.1	0.1	Propylene	1.0	3.7	1.0	9.0
iso-Pentane	4.2	2.2	0.1	0.1	Styrene	0.4	3.6	70.2	6.6
Ethylene	4.4	5.0	0.1	6.1	Methacrolein	0.7	2.7	0.2	0.7
iso-Butane	3.5	1.1	0.0	0.0	cis-2-Butene	0.3	2.7	11.2	33.0
n-Pentane	2.3	1.3	0.0	0.0	MethylVinylKetone	0.9	2.6	0.1	0.0
Third column					Forth column				
Species	Concentration	OH reactivity	NO ₃ reactivity	O ₃ reactivity	Species	Concentration	OH reactivity	NO ₃ reactivity	O ₃ reactivity
Styrene	0.4	3.6	70.2	6.6	cis-2-Butene	0.3	2.7	11.2	33.0
cis-2-Butene	0.3	2.7	11.2	33.0	trans-2-Butene	0.2	1.3	6.6	26.5
trans-2-Butene	0.2	1.3	6.6	26.5	cis-2-Pentene	0.1	0.8	3.5	10.3
cis-2-Pentene	0.1	0.8	3.5	10.3	Propylene	1.0	3.7	1.0	9.0
Hexanal	1.1	4.6	1.9	0.0	Styrene	0.4	3.6	70.2	6.6
HCHO	22.3	30.3	1.5	0.2	Ethylene	4.2	5.0	0.1	6.1
Propylene	1.0	3.7	1.0	9.0	1-Butene	0.4	1.9	0.6	3.6
1,3-Butadiene	0.1	0.6	0.7	0.4	trans-2-Pentene	0.0	0.1	0.6	2.2
trans-2-Pentene	0.0	0.1	0.6	2.2	1-Pentene	0.1	0.4	0.2	0.9
1-Butene	0.4	1.9	0.6	3.6	Methacrolein	0.7	2.7	0.2	0.7

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