

Measuring and modeling investigation of the Net Photochemical Ozone Production Rate via an improved dual-channel reaction chamber technique

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Abstract. Current process-based research mainly uses box models to evaluate the photochemical ozone production and destruction rates, and it is unclear to what extent the photochemical reaction mechanisms are elucidated. Here, we modified and improved a net photochemical ozone production rate (NPOPR, $P(\text{O}_3)_{\text{net}}$) detection system based on the current dual-channel reaction chamber technique, which makes the instrument applicable to different ambient environments, and its various operating indicators were characterized, i.e., airtightness, light transmittance, wall losses of the reaction and reference chambers, conversion rate of O_3 to NO_2 , air residence time, and performance of the reaction and reference chambers. The limits of detection of the NPOPR detection system were determined to be 0.07, 1.4, and 2.3 ppbv h^{-1} at sampling flow rates of 1.3, 3, and 5 L min^{-1} , respectively. We further applied the NPOPR detection system to field observations at an urban site in the Pearl River Delta (China). During the observation period, the maximum value of $P(\text{O}_3)_{\text{net}}$ was 34.1 ppbv h^{-1} , which was ~ 0 ppbv h^{-1} at night within the system detection error and peaked at approximately noon local time. The daytime (from 6:00–18:00) average value of $P(\text{O}_3)_{\text{net}}$ was 12.8 (± 5.5) ppbv h^{-1} . We investigated the detailed photochemical O_3 formation mechanism in the reaction and reference chambers of the NPOPR detection system using a zero-dimensional box model. We found that the photochemical reactions in the reaction chamber were very close to those in ambient air, but it was not zero chemistry in the reference chamber, the reaction related to the production and destruction of RO_2 ($=\text{HO}_2+\text{RO}_2$) continued in the reference chamber, which

33 led to a small amount of $P(\text{O}_3)_{\text{net}}$. Therefore, the $P(\text{O}_3)_{\text{net}}$ measured here can be regarded as the lower
34 limit of the real $P(\text{O}_3)_{\text{net}}$ in the atmosphere; however, the measured $P(\text{O}_3)_{\text{net}}$ was still ~ 7.5 to 9.3 ppbv h⁻¹
35 higher than the modeled $P(\text{O}_3)_{\text{net}}$ value depending on different modeling methods, which may be due to
36 the inaccurate estimation of HO₂/RO₂ radicals in the modeling study. Short-lived intermediate
37 measurements coupled with direct $P(\text{O}_3)_{\text{net}}$ measurements are needed in the future to better understand
38 O₃ photochemistry. Our results show that the NPOPR detection system can achieve high temporal
39 resolution and continuous field observations, which helps us to better understand photochemical O₃
40 formation and provides a key scientific basis for continuous improvement of air quality in China.

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42

43 **1 Introduction**

44 Surface O₃ pollution has become a major challenge in air quality management in China (Shen et al.,
 45 2021). Elevated surface O₃ mixing ratios exert severe adverse effects on public health, such as respiratory
 46 diseases, and the estimated annual mortality attributable to surface O₃ exposure exceeds 150,000 deaths
 47 in China (Malley et al., 2017). O₃ pollution is also detrimental to key staple crop yields, reducing the
 48 yields of wheat, soybean, and maize by up to 15 %, and is threatening global food security (Avnery et
 49 al., 2011; Mills et al., 2018; Karakatsani et al., 2010; Berman et al., 2012; O'Neill et al., 2003). As a
 50 greenhouse gas, O₃ also contributes significantly to climate change (Bell et al., 2004). With the rapid
 51 economic development and urbanization in the Pearl River Delta (PRD) region in China, O₃ pollution is
 52 pretty severe, especially in summer and autumn (Zou et al., 2015; Zhang et al., 2021).

53 The variation in O₃ in the planetary boundary layer is predominantly influenced by deposition,
 54 advection transport, vertical mixing (i.e., entrainment from the stratosphere), meteorological factors, and
 55 chemical reactions. Therefore, the O₃ budget in the boundary layer can be expressed as Eq. (1):

$$56 \quad \frac{\partial[\text{O}_3]}{\partial t} = \underbrace{P(\text{O}_3)}_{P(\text{O}_3)_{\text{net}}} - \underbrace{D(\text{O}_3)}_{\text{SD}} - \underbrace{\frac{\nu}{H}[\text{O}_3]}_{\text{A}} + u_i \frac{\partial[\text{O}_3]}{\partial x_i} + \text{STE} \quad (1)$$

57

58 where SD, A, and STE represent the surface deposition, advection, and stratosphere-troposphere
 59 exchange (STE), respectively; [O₃], $P(\text{O}_3)$ and $D(\text{O}_3)$ are the ambient O₃ mixing ratios, photochemical
 60 O₃ production and its loss rate, respectively; ν , H , and u_i represent the O₃ deposition velocity, mixing
 61 layer height, and velocity in three directions, respectively; and A consists of u_i times the O₃ gradient in
 62 those three directions.

63 Tropospheric O₃ is a key component of photochemical smog, mainly formed by photochemical
 64 reactions of nitrogen oxides (NO_x=NO+NO₂) and volatile organic compounds (VOCs) (Lee et al., 2010).
 65 The specific process of the photochemical reaction is the photolysis of NO₂ at < 420 nm to generate
 66 O(³P) atoms, thereby promoting the formation of O₃ (Sadanaga et al., 2017). Simultaneously, there is a
 67 RO_x (RO_x =OH + HO₂ +RO₂) radical cycle in the troposphere, which continuously provides HO₂ and
 68 RO₂ to oxidize NO to NO₂ resulting in the accumulation of O₃ (Shen et al., 2021; Sadanaga et al., 2017;
 69 Cazorla et al., 2010).

70 Typical meteorological scenarios for the occurrence of O₃ pollution episodes in polluted urban

71 centers are usually characterized by weak winds, strong solar radiation, and high temperature (T). Under
72 such conditions, local formation of O_3 plays a crucial role in the rapid increase of surface O_3 in daytime.
73 In addition, in Eq. (1), the surface deposition and advection of O_3 are proportional to ambient O_3 mixing
74 ratios, $[O_3]$, which is mainly generated by local photochemistry (Cazorla et al., 2010). If $P(O_3)_{net}$ can be
75 reduced by regulatory measures, overall O_3 levels will decline proportionately over time (Cazorla et al.,
76 2010), thus, the investigation of $P(O_3)_{net}$ formation mechanism is urgently needed.

77 Current studies on $P(O_3)_{net}$ estimation mainly rely on modeling methods, the gas-phase chemical
78 mechanisms were frequently used to identify key drivers of O_3 pollution events and provide guidance for
79 making effective O_3 reduction strategies, such as the Master Chemical Mechanism (MCM), the regional
80 atmospheric chemistry mechanism (RACM), the Carbon Bond mechanisms (CBM) and the Mainz
81 Organic Mechanism (MOM) (Shen et al., 2021; Kanaya et al., 2016; Wang et al., 2014; Tadic et al.,
82 2020; Ren et al., 2013; Lu et al., 2010; Zhou et al., 2014; Mazzuca et al., 2016). However, uncertainties
83 in emission inventories, chemical mechanisms, and meteorology make it difficult to perfectly reproduce
84 real atmospheric processes, which can lead some bias in modeling the $P(O_3)_{net}$. According to the existing
85 field observations, researchers found that the mixing ratios of HO_2 or RO_2 obtained from the model
86 simulation was inconsistent with that obtained from the direct measurement, leading to the deviation of
87 $P(O_3)_{net}$ between observation and model simulation results (Wang et al., 2014; Tadic et al., 2020; Ren et
88 al., 2013; Martinez et al., 2003). Therefore, we urgently need a method that can directly measure the
89 $P(O_3)_{net}$.

90 Recently, researchers have developed sensors that can directly measure $P(O_3)_{net}$ in the atmosphere
91 using the dual-channel chamber technique (Sadanaga et al., 2017; Cazorla et al., 2010; Baier et al., 2015
92 and 2017; Sklaveniti et al., 2018), where ambient air is introduced into two chambers of identical size,
93 one UV transparent chamber (reaction chamber) and one UV protection chamber (reference chamber).
94 In the presence of solar UV light, O_3 is produced by photochemical reactions in the reaction chamber,
95 but not in the reference chamber. The system does not directly measure O_3 mixing ratios, it measures the
96 combined mixing ratios of O_3 and nitrogen dioxide (NO_2). $P(O_3)_{net}$ is determined by the difference of
97 $O_X(O_X=O_3+NO_2)$ mixing ratios between the reaction and reference chambers. These studies have greatly
98 helped us to understand the O_3 photochemical formation mechanism, but defects still exists in current
99 studies, for example, the sensors developed by Cazorla et al. (2010) and Baier et al. (2015) both have an

100 NO₂-to-O₃ converter unit, and uses a modified O₃ monitor (Thermo Scientific, Model 49i, USA) to
101 measure Ox, but the zero point of the O₃ monitor is easy to drift, together with the limitation of the
102 conversion efficiency of NO₂ to O₃ (~ 99.9 %) and the effects of the *T* and relative humidity (RH) to O₃
103 monitor, this method can introduce large measurement uncertainties. Sklaveniti et al. (2018) have shorten
104 the average residence time in the chambers to 4.5 min, which reduced the scattering and increased the
105 time resolution of ΔOx measurement, but large wall loss still exists in their system, which are 5 % and
106 3 % for O₃ and NO₂, respectively. Sadanaga et al. (2017) passed the NO standard gas into the PFA tube
107 to convert O₃ into NO₂ to detect Ox, which is easy to operate, but the LIF-NO₂ detector is less portable
108 and maintainable. Furthermore, all the current sensors have different degrees of wall loss of NO₂ and O₃
109 that can even reach 15 %, which largely affect the accuracy of the evaluation of $P(O_3)_{net}$.

110 In this study, we modified and improved a $P(O_3)_{net}$ sensor based on the dual-channel technique as
111 described above and named it the net photochemical ozone production rate (NPOPR) detection system.
112 Section 2 provides the improvement and characterization of the NPOPR detection system. Furthermore,
113 we applied the NPOPR detection system to an observation campaign conducted at Shenzhen
114 Meteorological Gradient Tower (SZMGT) in the Pearl River Delta (PRD) region in China. A zero-
115 dimensional box model based on the Framework for 0-D Atmospheric Modeling (F0AM) v3.2 coupled
116 with MCM v3.3.1 was used to simulate the photochemical reactions inside both the reaction and
117 reference chambers in the NPOPR system, which allowed us to assess the ability of the current modeling
118 method to model $P(O_3)_{net}$, as described in Sect. 3. The current research could help us study the source
119 and formation mechanism of O₃ and provide effective theoretical support for the prevention and control
120 of O₃ pollution. Because the system can directly obtain real-time $P(O_3)_{net}$ under different environmental
121 conditions, it can meet richer and more specific research needs.

122 **2 Method and materials**

123 **2.1 Development of the NPOPR detection system**

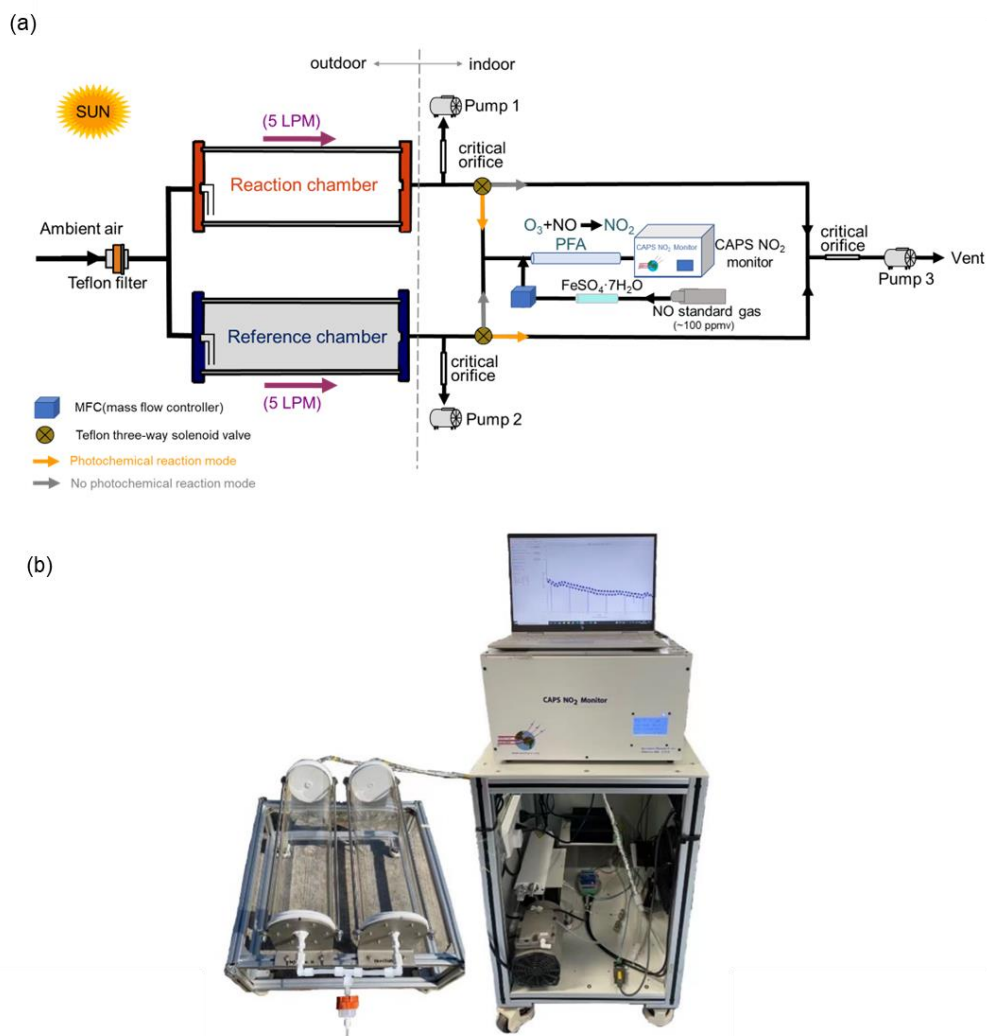
124 A schematic and actual diagram of the NPOPR detection system are shown in Fig. 1. The integral
125 construction is similar to the $P-L(Ox)$ measurement system built by Sadanaga et al. (2017) and Sklaveniti
126 et al. (2018), which mainly consists of reaction and reference chambers with the same geometry and
127 made of quartz (190.5 mm inner diameter and 700 mm length; more details can be found in Fig. S1). To

128 prevent photochemical reactions inside the reference chamber, an ultraviolet (UV) protection Ultem film
129 (SH2CLAR, 3 M, Japan) was used to cover the outer surface to block sunlight with wavelengths < 390
130 nm. During the experiment, both the reaction and reference chambers were located outdoors and exposed
131 to sunlight directly to simulate genuine ambient photochemistry reactions. Ambient air was introduced
132 into the reaction and reference chambers at the same flow rate, and a Teflon filter was mounted before
133 the chamber inlet to remove fine particles. A stream of air from the two chambers was alternately
134 introduced into an NO-reaction chamber every 2 min to convert O₃ in the air to NO₂ in the presence of
135 high mixing ratios of NO (O₃+NO=NO₂), and the Ox mixing ratios from the outlet NO-reaction chamber,
136 i.e., the total NO₂ mixing ratios including the inherent NO₂ in the ambient and that converted from O₃,
137 were measured by a Cavity Attenuated Phase Shift (CAPS) NO₂ Monitor (Aerodyne research, Inc.,
138 Billerica MA, USA) to avoid other nitrogen oxide interferences to the NO₂ measurement (such as alkyl
139 nitrates, peroxyacyl nitrates, peroxyacetic acid, nitrogen pentoxide, etc.). Compared to previous studies
140 that used a dual-channel UV-absorption O₃ monitor (Cazorla et al., 2010) or a laser-induced fluorescence
141 (LIF) LIF-NO₂ monitor (Sadanaga et al., 2017) for Ox measurements, our choice could make the NPOPR
142 detection system have a more stable zero-baseline and be more portable by assembling each part together,
143 i.e., put the CAPS NO₂ monitor, the automatic sampling system, and the automatic data sampling system
144 onto the indoor cabinets with the push-pull base, and put the dual chambers onto the outdoor shelf with
145 the push-pull base. Additionally, we modified the air sampling system to adjust the total air flow rates
146 freely from 1.3 to 5 L min⁻¹ in the reaction and reference chambers, which enabled us to achieve different
147 air residence times from 3.8 to 21 min. This time range covered all the residence times from previous
148 studies using different Ox measurement techniques, which ranged from 4.5 to 20.5 min (Cazorla et al.,
149 2010; Baier et al., 2015; Sadanaga et al., 2017; Sklaveniti et al., 2018). According to the simulation
150 results described in Sect. 3, the reaction rates of O₃ formation and destruction pathways and the radicals
151 that play critical roles in photochemical O₃ formation, such as HO₂, RO₂ and OH, reached quasi-steady
152 states in approximately 3 min, so it was reasonable for us to set the air flow rate highest at 5 L min⁻¹,
153 where the sampled air has already reacted for 3.8 min in the reaction and reference chambers. On the
154 other hand, this also demonstrated that it was reasonable to set the alternate sampling time for the reaction
155 and reference chambers at 2 min, where the sampled air actually has already reacted for at least 3.8 min
156 in the reaction and reference chambers. The switch system was controlled by two Teflon three-way

157 solenoid valves (001-0028-900, Parker, GER) located before the NO-reaction chamber (see Fig. 1). We
158 used homemade circuit control software (Four-Channel-Valves boxed) and a solenoid valve (001-0028-
159 900, Parker, GER) to automatically switch the sampling lines every 2 min. To keep the flow rates in the
160 reaction and reference chambers the same and avoid gas flow accumulation in the chamber, a pump
161 (pump 3) was connected to the Teflon three-way solenoid valves in parallel to the NO-reaction chamber
162 to evacuate the air that was not introduced into the NO-reaction chamber. To reduce NO interference, the
163 system used O_X to infer the amount of O_3 generated by photochemical reactions (Liu et al., 1977; Pan et
164 al., 2015; Lu et al., 2010). The difference between the O_X mixing ratios in the reaction and reference
165 chambers, denoted by ΔO_X , represents the amount of O_3 generated by the photochemical reaction.
166 $P(O_3)_{net}$ was obtained by dividing ΔO_X by the average residence time of air in the reaction chamber $\langle \tau \rangle$:

$$167 \quad P(O_3)_{net} = P(O_X) = \frac{\Delta O_X}{\tau} = \frac{[O_X]_{reaction} - [O_X]_{reference}}{\tau} \quad (2)$$

168 Igor Pro version 6 was used to calculate $P(O_3)_{net}$ as follows: ① separate the data of the reaction
169 and the reference chambers into two sets using the recorded valve number of 1 (reaction chamber) and 0
170 (reference chamber) during the sampling time; ② for each 2 min period of data, delete the first 20 s and
171 the last 20 s when the signal was not stable, then average the rest data, and do the interpolate calculation
172 of the reference chamber dataset; ③ calculate the difference between the O_X mixing ratios in the reaction
173 and reference chambers (i.e., ΔO_X) at the time when the reaction chamber measured O_X ; ④ divide ΔO_X
174 by the average residence time of air in the reaction chamber $\langle \tau \rangle$ and obtain $P(O_3)_{net}$ at a time resolution
175 of 4 min.



176
177 **Figure 1: (a) Schematic and (b) actual diagram of the NPOPR detection system.**

178 The major improvements of the NPOPR detection system described here compared to previous
179 studies to optimize $P(O_3)_{\text{net}}$ measurements are as follows: (1) we improved the design of the reaction and
180 reference chambers to ensure that they have good airtightness, which will increase the measurement
181 accuracy of different species inside the chambers. More details can be found in Sect. 2.2 and Appendix
182 I; (2) two pumps (labeled pump 1 and pump 2 in Fig. 1) were added directly after the reaction and
183 reference chambers to continuously draw ambient air through the two chambers (as the makeup flow) to
184 adjust the total air flow rates freely from 1.3 to 5 L min⁻¹ in the chambers. By doing this, we were able
185 to achieve different limits of detection (LODs) of the NPOPR system (see Sect. 2.4), making the
186 instrument applicable to different ambient environments, i.e., in highly polluted areas, we could use
187 higher air flow rates to reduce the wall loss effects of the chambers, and in less polluted areas, we could
188 use lower flow rates to increase the instrument LOD. (3) We characterized the NPOPR detection system

189 at different air flow rates (including 1.3, 2, 3, 4, and 5 L min⁻¹) and tested the conversion efficiency of O₃
190 by NO to NO₂ in the NO-reaction chamber at different NO mixing ratios and NO-reaction chamber
191 lengths. These efforts enabled us to better understand the running parameters of the NPOPR system and
192 perform data corrections under different air flow rates (see Sect. 2.2); (4) we tested the performance of
193 both the reaction and reference chambers by combining the field measurements and MCM modeling,
194 which indicated that reaction pathways of P(O₃) and D(O₃) and the radicals that play critical roles in
195 photochemical O₃ formation, such as HO₂, RO₂ and OH, reached quasi-steady states in approximately 3
196 min, thus ensuring that the lowest air residence time of 3.8 min (at an air flow rate of 5 L min⁻¹) in the
197 reaction and reference chambers was long enough to obtain accurate P(O₃)_{net} values (see Sect. 3.2). These
198 efforts made the NPOPR system less prone to biases than other systems and increased its applicability.

199 **2.2 Characterization of the NPOPR detection system**

200 We characterized the NPOPR detection system following the same procedures as previous researchers,
201 including the residence time of the air, the wall losses of NO₂ and O₃, the transmittance of light and
202 temperature differences in the reaction and reference chambers, and the quantitative conversion
203 efficiency of O₃ to NO₂ (α) in the NO-reaction chamber. Additionally, we investigated the residence time
204 of the air and the wall losses of NO₂ and O₃ in the reaction and reference chambers at different flow rates
205 (including 1.3, 2, 3, 4, and 5 L min⁻¹) and the conversion efficiency of O₃ by NO to NO₂ in the NO-
206 reaction chamber at different NO mixing ratios and NO-reaction chamber lengths. The detailed
207 experimental performances and data analysis are shown in Appendix I, and the corresponding results are
208 described as follows.

209 ***The residence time.*** We tested the residence time of air in both chambers under different air flow
210 rates, including 1.3, 2, 3, 4, and 5 L min⁻¹, the obtained related residence time in the reaction chamber
211 were 0.35, 0.16, 0.11, 0.07, and 0.06 h, respectively. By setting different air flow rates, we were able to
212 obtain different residence time thus different limit of detection of NPOPR system, which make it
213 applicable to different ambient environment. To make sure that the mean residence time of air is the same
214 in the reaction and reference chambers, we also tested the residence time of air in the reference chamber
215 in parallel, which were not much difference with that in the reaction chamber, as shown in Table S1. The
216 experimental schematic diagram is shown in Fig. S2, the related results of different air flow rates are

217 shown in Fig. S3 and Table S1.

218 **Wall losses of NO₂ and O₃.** At air flow rates of 1.3, 2, 3, 4, and 5 L min⁻¹, the wall losses of O₃ in
219 the reaction chamber were found to be approximately 2 %, 0 %, 0 %, 0 %, and 0 %, respectively, and the
220 wall losses of O₃ in the reference chamber were found to be approximately 2 %, 1 %, 1 %, 0 %, and
221 0.7 %, respectively. While the wall losses of NO₂ in the reaction chamber at air flow rates of 1.3, 2, 3, 4,
222 and 5 L min⁻¹ were found to be approximately 4 %, 4 %, 2 %, 0 %, and 0.3 %, respectively, the wall
223 losses of NO₂ in the reference chamber were found to be approximately 2 %, 1 %, 0 %, 0 %, and 0.6 %, respectively.
224 The experimental schematic diagram is shown in Fig. S4, and the related results of different
225 air flow rates are shown in Figs. S5-S6 and Tables S2-S5. We further compared the wall losses of O₃ and
226 NO₂ in the reaction and reference chambers at 5 L min⁻¹ with previous studies (as shown in Table S6)
227 and found that they were significantly smaller, but even with a flow rate of 1.3 L min⁻¹, the wall losses
228 were still smaller than 4 % and 2 % in the reaction chamber and the reference chambers, respectively.
229 We also tested the wall losses of NO₂ and O₃ in the chamber at a 5 L min⁻¹ flow rate at different humidities
230 of 35-75 %, the detailed results are shown in Fig. S7 and S8, which shows that the variation in humidity
231 effected the wall loss of NO₂ and O₃ by 0.03-0.12 % and 1.06-1.19 %, respectively, which is much
232 smaller than the instrument detection error (which is 2 % at ambient NO₂ mixing ratios of 0-100 ppb),
233 which indicates the small effects of Ox loss on $P(O_3)_{net}$ measurements in our NPOPR detection system.

234 **The light transmittance and temperature differences in the reaction and reference chambers.** It
235 is worth noting that there was still low transmittance of light ranging from 390 nm to 790 nm through
236 the UV protection film, and the reference chamber could not be regarded as completely dark; thus, we
237 tested the solar UV transmittance through the reaction and reference chambers of the NPOPR detection
238 system in the laboratory using a sunlight simulation lamp (SERIC XG-500B, Japan) to provide different
239 intensities of illumination. The photolysis frequencies of NO₂, O₃, HONO, H₂O₂, NO₃_M (photolysis of
240 NO₃ generates NO+O₂), NO₃_R (photolysis of NO₃ generates NO₂+O), HCHO_M (photolysis of HCHO
241 generates H₂+CO), and HCHO_R (photolysis of HCHO generates H+HCO) inside and outside the
242 reaction and reference chambers were measured using an actinic flux spectrometer (PFS-100; Focused
243 Photonics Inc., China). Table 1 presents the $J(NO_2)$, $J(O^1D)$, and $J(HONO)$ results for the outside and
244 inside chambers from this study and from the literature. $J(H_2O_2)$, $J(NO_3_M)$, $J(NO_3_R)$, $J(HCHO_M)$,
245 and $J(HCHO_R)$ are shown in Table S7.

246 The photolysis frequencies of all species inside the reaction chamber were in agreement with those
247 measured outside the reaction chamber within 4 %. Table S7 shows that the transmittivities of $J(\text{H}_2\text{O}_2)$,
248 $J(\text{NO}_3\text{-M})$, $J(\text{NO}_3\text{-R})$, $J(\text{HCHO-M})$, and $J(\text{HCHO-R})$ in the reaction chamber were more than 90 %.
249 However, we have observed that the transmittivities of $J(\text{O}^1\text{D})$ were even higher than those of $J(\text{HONO})$
250 (as shown in Table 1) in the reference chamber (which blocks sunlight at wavelengths < 390 nm),
251 theoretically, this is not possible according to JPL Publication 19-5 (Burkholder et al., 2020), where the
252 absorption cross section of HONO at wavelengths of 390-395 ranged from approximately $4.0\text{-}17.1 \times 10^{-21}$
253 cm^2 , which is about two or three orders of magnitude higher than that of ozone (which ranged from
254 approximately $0.8\text{-}2.6 \times 10^{-23} \text{ cm}^2$ at wavelengths of 390-410 nm), and the photolysis quantum yield of
255 HONO at wavelengths of 390-395 is unity, which is about ten times higher than that of ozone (~ 0.08).
256 This will surely make the J values of HONO inside the reference chamber (which only has sunlight with
257 wavelengths > 390 nm) higher than that of ozone, according to the Eq. (S9). We also found that the
258 transmittivity of HONO and O_3 in the reference chamber obtained from the TUV simulation (as described
259 in Sect. 3.2) were 0.01 and 0, respectively, as shown in Table S13. Therefore, we believe the non-zero
260 measurement results of the transmittivity of O_3 shown in Table 1 and Table S7 are mostly probably due
261 to the instrument measurement error, this error is relatively large due to a limit number of measurement
262 points (3 points for each species). We further evaluated the measurement error of J values based on the
263 instrument measurement error of the actinic flux spectrometer, which can reach ± 5 % according to Bohn
264 et al. (2017), and re-evaluated the transmittivity error listed in Table 1 and Table S7 following the
265 procedures described in supplementary materials (Sect. 1.5). The calculation result from Eq. (S5) show
266 that the transmittivities errors are 0.07 for all species, within this error range, $J(\text{O}^1\text{D})$, $J(\text{HONO})$, $J(\text{H}_2\text{O}_2)$,
267 $J(\text{HCHO-M})$, and $J(\text{HCHO-R})$ can be considered statistically indistinguishable from 0 in reference
268 chamber. However, $J(\text{NO}_2)$, $J(\text{NO}_3\text{-M})$, and $J(\text{NO}_3\text{-R})$ still distinctly positive values. Specifically, the
269 transmittivities of $J(\text{NO}_3\text{-M})$ and $J(\text{NO}_3\text{-R})$ of the reference chamber were more than 90 % (Table S7).
270 The influence of the measurement error of J values of all species on $P(\text{O}_3)_{\text{net}}$ will be discussed in Sect. 3.

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278 **Table 1. Transmittivities of photolysis frequency J (s^{-1}) values of different species in the reaction and reference**
 279 **chambers. The shaded and clear regions correspond to the transmittivities of J values in the reference (Ultem**
 280 **coated) and reaction (clear) chambers, respectively. The “transmittivities” column shows the transmittivities**
 281 **of the tested species from the measurements conducted with the set photolysis frequencies using SERIC XG-**
 282 **500B sunlight (this study) and ambient (literature). It should be noted that the errors listed here are relatively**
 283 **large and may not reliable due to a limit number of measurement points (3 points for each species). The**
 284 **calculated transmittivity errors are 0.07 for all species based on the ± 5 % measurement error of the**
 285 **instrument.**

	Transmittivities			
	Averaged (this study)	Cazorla <i>et al.</i> , 2010	Baier <i>et al.</i> , 2015	Sadanaga <i>et al.</i> , 2017
$J(\text{NO}_2)$	0.985 ± 0.037 0.094 ± 0.014	0.974 0.021	0.990 0.01	0.986 0.121
$J(\text{O}^1\text{D})$	1.020 ± 0.04 0.019 ± 0.011	0.991 0.0058	0.978 0.001	1.030 ~0
$J(\text{HONO})$	0.983 ± 0.037 0.002 ± 0.0002	0.976 0.0067	0.982 ~0	0.988 0.017

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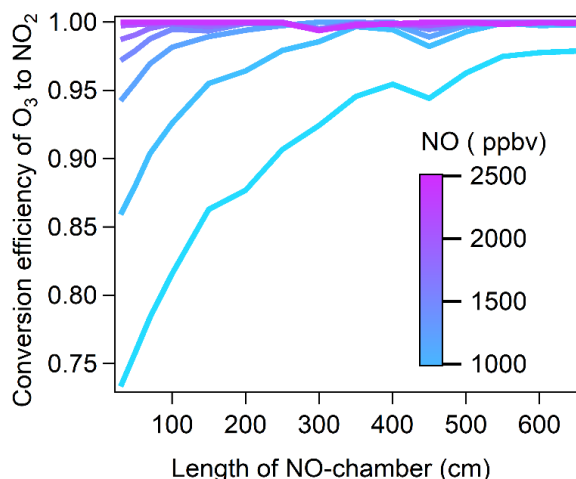
287 We further detected the temperature in both the reaction and reference chambers when running the
 288 NPOPR system in an ambient observation campaign during November 2022 on the Panyu campus of
 289 Jinan University in Guangzhou, China (113° 36' E, 23° 02' N). We found that the UV protection
 290 Ultem film on the reference chamber did not block the heat outside the chamber, and the temperature
 291 remained the same in the reaction and reference chambers during the measurement test, as shown in Fig.
 292 S10.

293 ***The quantitative conversion efficiency of O_3 to NO_2 (α)*** in the NO-reaction chamber is crucial for
 294 accurate measurement of $P(\text{O}_3)_{\text{net}}$. Here, we used a perfluoroalkoxy (PFA) tube (outer diameter of 12.7
 295 mm; inner diameter of 9.5 mm) as the NO-reaction chamber. The experimental schematic diagram is
 296 shown in Fig. S12. Known mixing ratios of O_3 and NO standard gas were introduced into the NO-reaction
 297 chamber, and NO reacted with O_3 to produce NO_2 . To avoid the influence of small amounts of NO_2
 298 impurity in the NO standard gas used for conversion, we added a cylinder filled with partialized crystals
 299 of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ to reduce NO_2 in the NO/N_2 gas cylinder to NO. We injected ~1800 ppbv NO into the
 300 NO-reaction chamber and tested the NO_2 mixing ratios from its outlet using a CAPS NO_2 monitor, as
 301 shown in Fig. S13. We found that the standard deviation of the NO_2 mixing ratios was lower than 0.027

302 ppbv, which is smaller than the baseline drifts of the CAPS (which were 0.043 and 0.030 ppbv (1σ) at
303 integration times of 35 and 100 s, respectively, as mentioned in Sect. 2.3), so we believe the particulate
304 crystals of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ performed well and the potential bias introduced by the impurity in NO mixing
305 ratio for $P(\text{O}_3)_{\text{net}}$ was negligible. Finally, the total NO_2 mixing ratios, including that from the ambient air,
306 were measured using a CAPS NO_2 monitor ($[\text{NO}_2]_{\text{CAPS}}$). The O_3 mixing ratios were controlled at
307 approximately 310 ppbv according to the maximum mixing ratio range in the normal ambient atmosphere
308 (to ensure that all ambient and newly generated O_3 can react with NO and produce equivalent amounts
309 of NO_2). An O_3 generator equipped with a low-pressure mercury lamp was employed to generate O_3 , and
310 the generated O_3 mixing ratios ($[\text{O}_3]_{\text{g}}$) were measured by a 2B O_3 monitor as mentioned above. Here, we
311 note that the O_3 mixing ratios were diluted by the added NO/N_2 gas (with a flow rate of 20 mL min^{-1}) in
312 the NO-reaction chamber (with a total flow rate of 1.11 L min^{-1}), taking 1800 ppbv NO/N_2 gas as an
313 example, the relationship between $[\text{NO}_2]_{\text{CAPS}}$ and $[\text{O}_3]_{\text{g}}$ can be described by Eq. (3):

$$314 \quad [\text{NO}_2]_{\text{CAPS}} = \frac{1.09}{1.11} [\text{O}_3]_{\text{g}} \alpha \quad (3)$$

315 To determine the optimal length of the NO-reaction chamber and NO mixing ratios, we performed
316 a cross test of α under the following scenarios: the NO-reaction chamber lengths were increased from 30
317 to 650 cm in 50 cm steps, and the NO standard gas (102.1 ppmv) was diluted to 600, 900, 1200, 1500,
318 1800, 2100, and 2400 ppbv in the NO reaction chamber. The results are shown in Fig. 2. We found that
319 at $[\text{O}_3]_{\text{g}}$ of approximately 310 ppbv, with NO mixing ratios ≥ 1800 ppbv in the NO reaction chamber, α
320 reached 99 %, 99.6 %, and 99.9 % with NO-reaction chamber lengths of 50, 70, and 100 cm, respectively,
321 where the corresponding O_3 residence times in the NO reaction chamber were 1.95, 2.74, and 3.91 s,
322 respectively. Considering both the optimal reaction time in the NO reaction chamber and α , we selected
323 the NO reaction chamber length as 100 cm with an NO mixing ratio of 1800 ppbv for the NPOPR
324 detection system.



325

326 **Figure 2: The conversion efficiency of O₃ by NO to NO₂ in the NO reaction chamber as a function of the NO**
 327 **chamber length, color coded by the NO mixing ratios.**

328 *The airtightness of the reaction and reference chambers* We also checked the airtightness of the

329 reaction and reference chambers by passing through gases with different flow rates based on the

330 schematic diagram shown in Fig. S14 and compared the values of [air flow rate × pressure] between the

331 inlet and outlet of the chambers (as indicated in Fig. 3). We found that the deviations in [air flow rate ×

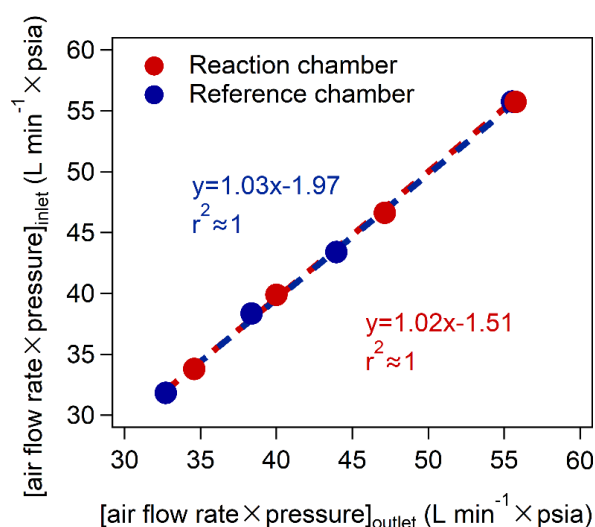
332 pressure] at the inlet and outlet of the reaction and reference chambers at different flow rates were <3 %

333 (as shown in Table S8), indicating the good airtightness of the reaction and reference chambers. This

334 ensured that the photochemical reactions in the reaction and reference chambers would not be affected

335 by the ambient air outside the chambers.

336



337

338 **Figure 3: The relationship of the values of [air flow rate × pressure] between the inlet and outlet of the**
 339 **chambers (psia: Pounds Per Square Inch Absolute).**

340

341 ***The flow states in the reaction and reference chambers*** We calculated the Reynolds number to
342 check the gas flow state in the reaction and reference chambers. The Reynolds number (expressed as Eq.
343 (4)) is a dimensionless number that can be used as the basis for judging the flow characteristics of a fluid:

$$344 \text{Re} = \rho v d / \mu \quad (4)$$

345 where v , ρ and μ are the flow velocity, density and viscosity coefficient of the fluid, respectively. In this
346 study, the fluid is air, and d is the equivalent diameter of the reaction and reference chambers. The
347 calculated Reynolds numbers in the two chambers under flow rates of 1.3, 2, 3, 4, and 5 L min⁻¹ were
348 9.39, 14.58, 21.75, 29.05, and 36.34, respectively, indicating laminar flows in both chambers at different
349 flow rates.

350 ***The HONO production in the reaction and reference chambers*** We tested the HONO production
351 in the reaction and reference chambers under weather conditions similar to those during the SZMGT
352 observations (humidity of 60-90% at a temperature of ~ 20 °C and $J(\text{NO}_2)$ of ~ $0.8 \times 10^{-3} \text{ s}^{-1}$) at a 5 L
353 min⁻¹ sampling flow rate. We found that the HONO mixing ratios in the reaction and reference chambers
354 were almost the same and not statistically different from that in the ambient air within the standard
355 deviation, as shown in Fig. S9; therefore, we assumed that the HONO production in the reaction and
356 reference chambers would not cause a significant difference in $P(\text{O}_3)_{\text{net}}$ in the two chambers.
357 Unfortunately, we did not test HONO during the field observation period, but we have added the modeled
358 HONO produced from the precursors before the ambient air was injected into the NPOPR system, as
359 described in Sect. 3.2.

360 **2.3 Calibration and measurement error of the CAPS NO₂ monitor**

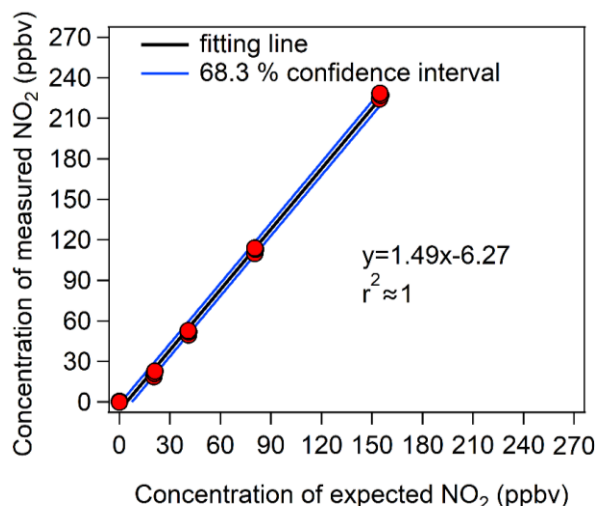
361 The Ox in the NPOPR detection system was measured by the CAPS NO₂ monitor. Detailed descriptions
362 of this technique can be found elsewhere (Kebabian et al., 2008, 2005). We calibrated the CAPS NO₂
363 monitor using a NO₂ standard gas (with an original mixing ratio of 2.08 ppmv), which was first calibrated
364 using the gas-phase titration method using NO standard gas and excessive O₃. The related experimental
365 results are shown in Fig. S15. The detailed calibration procedure is as follows: a. injected ~ 10–100 ppbv
366 of NO₂ standard gas for 30 min to passivate the surfaces of the monitor and then injected dry pure air for
367 ~ 10 min to minimize the zero point drift, which were 0.043 and 0.047 ppbv at integration times of 35
368 and 100 s, respectively, and resulted in LODs of CAPS of 0.13 and 0.14 ppbv (3 σ), respectively; b.

369 injected a wide range of NO₂ mixing ratios (from 0–160 ppbv) prepared by mixing the NO₂ standard gas
370 with ultrapure air into the CAPS NO₂ monitor and repeated the experiments three times at each NO₂
371 mixing ratio. The final results are shown in Fig. 4. To check the baseline drift of the CAPS at different
372 humidities, we added another two sets of tests (as shown in Fig. S11) using ambient air and wet pure air
373 and found that (a) when injecting ambient air into the CAPS (RH ranged from ~30-35%), the baseline
374 drifts were 0.035 and 0.032 ppbv (1 σ) at integration times of 35 and 100 s, respectively; and (b) when
375 injecting wet pure air into the CAPS (RH ranged from 35-70%), the baseline drifts were 0.043 and 0.030
376 ppbv (1 σ) at integration times of 35 and 100 s, respectively. These baseline drifts were smaller than those
377 when injecting dry pure air to estimate the LOD of the CAPS. We chose the largest baseline drift when
378 injecting dry pure air to estimate the $P(O_3)_{\text{net}}$ error in the following analysis; by doing this, we were able
379 to include all the short-duration baseline drifting in the CAPS NO₂ monitor under different humidities.

380 To obtain an accurate measurement error of the CAPS NO₂ monitor ($(O_{X_{\text{CAPS}}})_{\text{error}}$), we fitted the
381 calibration results with a 68.3 % confidence level, and the blue line in Fig. 4 represents the maximum
382 fluctuation range under this confidence level. $(O_{X_{\text{CAPS}}})_{\text{error}}$ was then calculated from the fluctuation
383 range of the 68.3 % confidence interval of the calibration curve. The relationship between $(O_{X_{\text{CAPS}}})_{\text{error}}$
384 and the measured Ox value ($[Ox]_{\text{measured}}$) can be expressed as a power function curve, as shown in Eq.
385 (5):

$$386 \quad (O_{X_{\text{CAPS}}})_{\text{error}} = 9.72 \times [Ox]_{\text{measured}}^{-1.0024} \quad (5)$$

387 Subsequent $P(O_3)_{\text{net}}$ error estimation according to the instrument measurement error of the CAPS
388 NO₂ monitor and the O₃ light-enhanced loss in the reaction and reference chambers are described in
389 Appendix II.



390

391 **Figure 4: Calibration results of the CAPS NO₂ monitor with different NO₂ mixing ratios. The y-axis represents**
 392 **the NO₂ mixing ratios measured by the CAPS NO₂ monitor, and the x-axis represents the prepared NO₂**
 393 **mixing ratios from the diluted NO₂ standard gas.**

394 2.4 The measurement error of $P(O_3)_{net}$ and the LOD of the NPOPR detection system

395 To assess the measurement error of $P(O_3)_{net}$ and the LOD of the NPOPR detection system, dry pure air
 396 was introduced into the NPOPR detection system in sequence to adjust the system for ~ 2 h, followed by
 397 dry pure air or ambient air when the time resolution of the CAPS NO₂ monitor was 1 s and the integration
 398 time period was 100 s (the measurement durations for the reaction and reference chambers were both 2
 399 min). The LOD of the NPOPR detection system was obtained as three times the measurement error of
 400 $P(O_3)_{net}$, which was determined at a time resolution of 4 min by propagating the errors of the Ox measured
 401 by the CAPS NO₂ monitor when ultrapure air or ambient air was introduced into the NPOPR detection
 402 system, combined with the related $\langle \tau \rangle$ under different flow rates, i.e., $\langle \tau \rangle$ was 0.063 h at a flow rate of 5
 403 L min⁻¹. The detailed calculation method is shown in Eq. (6):

$$404 \text{ LOD} = \frac{3 \times \sqrt{([O_X]_{\text{rea_std}})^2 + ([O_X]_{\text{ref_std}})^2}}{\tau} \quad (6)$$

405 where $[O_X]_{\text{rea_std}}$ and $[O_X]_{\text{ref_std}}$ represent the standard deviation of O_X in the reaction and reference
 406 chambers measured by the CAPS NO₂ monitor with an integration time period of 100 s, respectively.

407 However, considering that the background Ox mixing ratios (measured by the CAPS NO₂ monitor
 408 of the air in the reference chamber) changed when measuring the ambient air, the measured O_X errors in
 409 the reaction and reference chambers changed with the Ox mixing ratios (as shown in Sect. 2.3), and the
 410 LOD must also be a function of the intrinsic ambient and photochemically formed O₃ and NO₂ mixing

411 ratios (i.e., the O_x mixing ratios measured by the CAPS NO₂ monitor). It is worth noting that the
 412 measured O_x errors may also be influenced by the light-enhanced loss of O₃ in the reaction and reference
 413 chambers under ambient conditions when the light intensity (especially $J(O^1D)$) and O₃ mixing ratios are
 414 high, as tested and shown in Appendix II, but this effect is included in the measured O_x errors. Therefore,
 415 when injecting ambient air into the NPOPR system, the error and LOD of $P(O_3)_{net}$ with a residence time
 416 of τ can be calculated using Eq. (7) and Eq. (8), respectively:

$$417 \quad P(O_3)_{net_error} = \frac{\sqrt{\left((O_{X\gamma})_{rea_error} \right)^2 + \left((9.72 \times [O_X]_{rea_measured})^{-1.0024} \right)_{rea_std}^2 + \left((O_{X\gamma})_{ref_error} \right)^2 + \left((9.72 \times [O_X]_{ref_measured})^{-1.0024} \right)_{ref_std}^2}}{\tau} \quad (7)$$

$$418 \quad LOD = 3 \times P(O_3)_{net_error} \quad (8)$$

419 where $(O_{X\gamma})_{rea_error}$ and $(O_{X\gamma})_{ref_error}$ represent the measurement error caused by the light-enhanced loss
 420 of O₃ in the reaction and reference chambers, respectively, and $(9.72 \times [O_X]_{measured})^{-1.0024}$ _{rea_std} and
 421 $(9.72 \times [O_X]_{measured})^{-1.0024}$ _{ref_std} represent the standard deviation of O_x in the reaction and reference
 422 chambers caused by the CAPS NO₂ monitor with an integration time period of 100 s, respectively. More
 423 details about the $(O_{X\gamma})_{rea_error}$ and $(O_{X\gamma})_{ref_error}$ estimation method can be found in Appendix II.

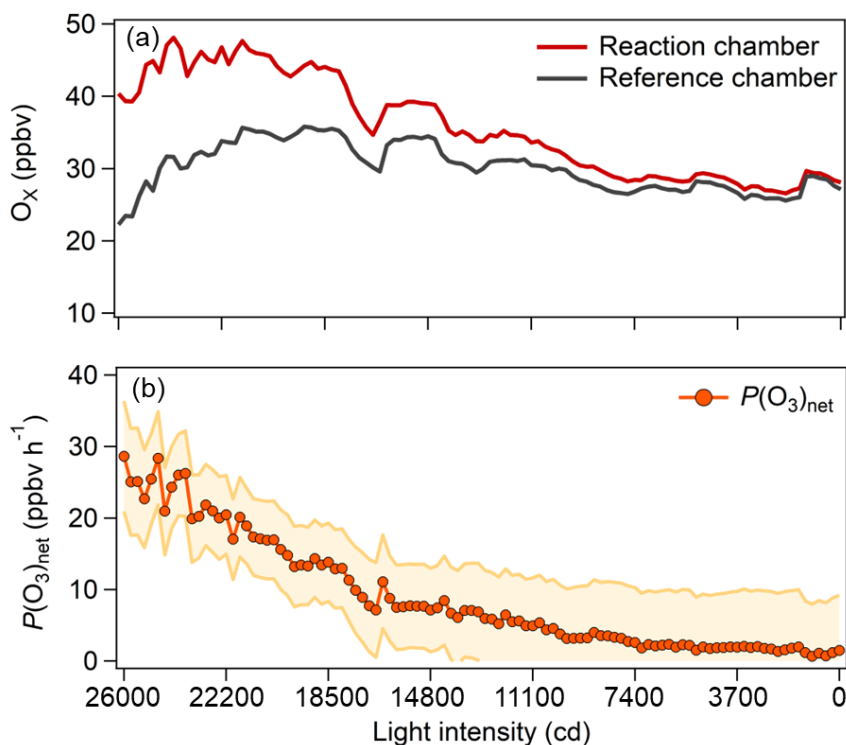
424 In conclusion, the LOD of the NPOPR detection system is determined to be three times $P(O_3)_{net_error}$,
 425 where $P(O_3)_{net_error}$ is mainly determined by the measurement error of O_x (including the O_x measurement
 426 error of the CAPS NO₂ monitor, the light-enhanced loss of O₃, and the chamber O_x losses). Because the
 427 measurement error of the CAPS NO₂ monitor decreases with increasing O_x mixing ratios (as shown in
 428 Sect. 2.3), higher LODs could be obtained when injecting dry pure air into the NPOPR detection system,
 429 which were approximately 0.07, 1.4, and 2.3 ppbv h⁻¹ at air flow rates of 1.3, 3, and 5 L min⁻¹, respectively.
 430 The results are summarized in Table S9.

431 During the field observations, the LOD values were highly dependent on the ambient conditions,
 432 especially the light intensity and the O_x mixing ratios, and higher O₃ mixing ratios and lower light
 433 intensity will likely result in lower LOD values.

434 2.5 Laboratory tests of the NPOPR detection system

435 We conducted an experiment in the laboratory to test the performance of the NPOPR detection system at
 436 Jinan University Panyu Campus (23.0° N, 113.4° E) on 26 March 2021. Ambient air (5 L min⁻¹) was

437 simultaneously injected into the reaction and reference chambers of the NPOPR detection system in
 438 parallel, and the sunlight simulation lamp mentioned above was used to simulate sunlight radiation. The
 439 light intensities of the sunlight simulation lamp were decreased from 26000 cd to 0 cd in steps of 3700
 440 cd, where cd indicates the light intensity SI unit candela. $P(\text{O}_3)_{\text{net}}$ was 28.6 ppbv h⁻¹ at a light intensity of
 441 26000 cd and gradually approached 0 ppbv h⁻¹ at 0 cd (as shown in Fig. 5), indicating that the $P(\text{O}_3)_{\text{net}}$
 442 change due to the different sunlight radiation could be well captured by the NPOPR detection system.



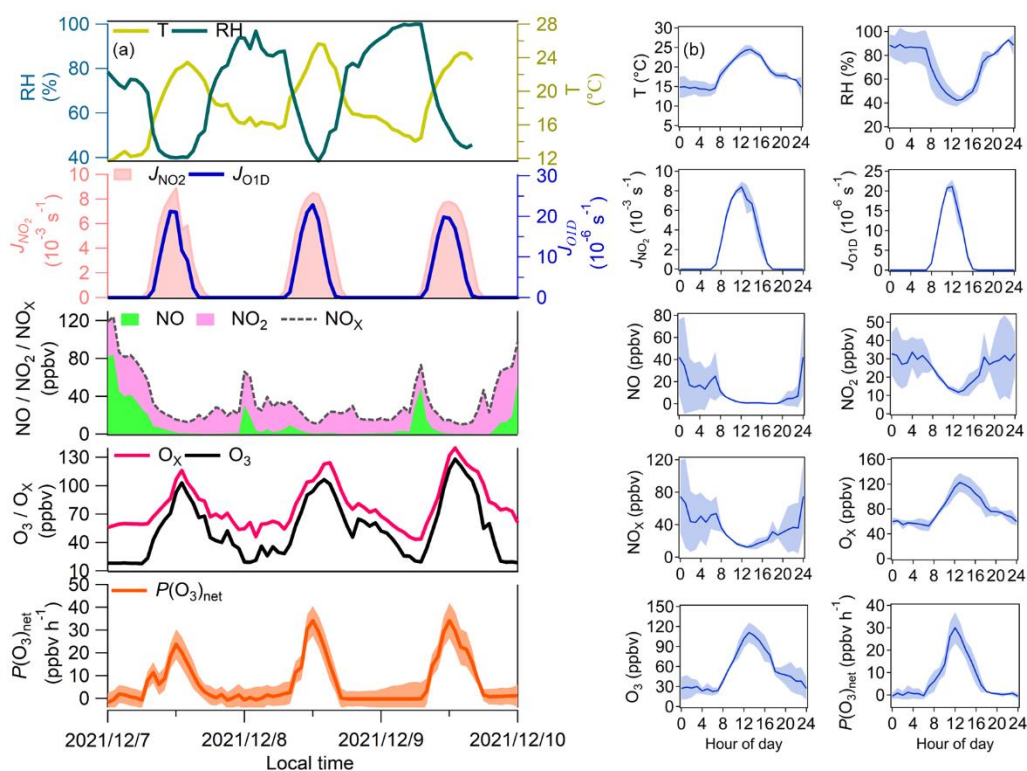
443
 444 **Figure 5: (a) Measured O_x mixing ratios in the reaction and reference chambers and (b) the related $P(\text{O}_3)_{\text{net}}$**
 445 **as a function of the light intensity during the experiment.**

446 3 Atmospheric study and discussion

447 3.1 Field observations

448 The self-built NPOPR detection system was employed in the field campaign conducted at SZMGT, which
 449 is located in Shenzhen, China (as shown in Fig. S17), from 7 to 9 December 2021. During the campaign,
 450 to achieve the lowest O₃ and NO₂ wall loss, we used a 5 L min⁻¹ air flow rate in the reaction and reference
 451 chambers (with a residence time of ~ 4 min). The photolysis frequencies of different species were
 452 measured using the actinic flux spectrometer as mentioned above. O₃ and NO_x (NO+NO₂) mixing ratios
 453 were measured using a 2B O₃ monitor and a chemiluminescence NO_x monitor (Model 42i, Thermo

454 Fisher Scientific, USA), respectively. T and RH were measured by a portable weather station (Met Pak,
 455 Gill Instruments Ltd, UK). Volatile organic compounds (VOCs) were measured by high-resolution
 456 proton transfer reaction time-of-flight mass spectrometry (PTR-ToF-MS, Ionicon Analytik, Austria)
 457 (Wang et al., 2020a; Wu et al., 2020) and an off-line gas chromatography mass spectrometry flame
 458 ionization detector (GC–MS-FID) technique (Wuhan Tianhong, Co. Ltd, China) (Yuan et al., 2012)
 459 (Table S11). Additionally, a self-built formaldehyde analyzer was used to detect formaldehyde (HCHO)
 460 (Zhu et al., 2020). Figure 6 presents the temporal and diurnal variations in the $P(\text{O}_3)_{\text{net}}$, O_x , O_3 , NO ,
 461 NO_2 , NO_x , T , RH, $J(\text{O}^1\text{D})$, and $J(\text{NO}_2)$ mixing ratios at SZMGT during the campaign.



462
 463 **Figure 6: (a) Time series and (b) average diurnal variations of $P(\text{O}_3)_{\text{net}}$, $J(\text{NO}_2)$, $J(\text{O}^1\text{D})$, T , RH , O_x , NO_2 and**
 464 **NO measured at SZMGT from 7 to 9 December 2021. The shaded areas represent the error of each measured**
 465 **species, where the error of $P(\text{O}_3)_{\text{net}}$ was calculated according to the method described in Appendix II (the**
 466 **estimation of the $P(\text{O}_3)_{\text{net}}$ error).**

467
 468 During the measurement period, $P(\text{O}_3)_{\text{net}}$ ranged from ~ 0 to 34.1 ± 7.8 ppbv h^{-1} , with an average
 469 daytime (from 6:00–18:00) value of $12.8 (\pm 5.5)$ ppbv h^{-1} . The maximum $P(\text{O}_3)_{\text{net}}$ at SZMGT was lower
 470 than that measured in the urban area of Houston in the US ($40\text{--}50$ ppbv h^{-1} and 100 ppbv h^{-1} in autumn
 471 and spring, respectively) (Baier et al., 2015; Ren et al., 2013), close to that measured in Indiana in the
 472 US (~ 30 ppbv h^{-1} in spring) (Sklaveniti et al., 2018), and much higher than that measured at the

473 Wakayama Forest Research Station, a remote area of Japan (10.5 ppbv h⁻¹ in summer) (Sadanaga et al.,
474 2017) and an urban area of Pennsylvania in the US (~ 8 ppbv h⁻¹ in summer) (Cazorla et al., 2010). The
475 result indicates the rationality of the measured $P(O_3)_{net}$ in this study. From previous studies, the O₃
476 pollution in the PRD area is more severe in summer and autumn than in winter and spring (Zhang et al.,
477 2021). In this study, $P(O_3)_{net}$ was measured in wintertime, which was already high, so we believe that the
478 O₃ pollution of the PRD is severe and urgently needs to be controlled. More measurements of $P(O_3)_{net}$
479 worldwide are listed in Table S10, and we found that $P(O_3)_{net}$ was much higher in urban areas than in
480 remote areas using both modeling and direct measurement methods.

481 According to the diurnal variation in all the measured pollutant indicators, $P(O_3)_{net}$ started to
482 increase at approximately 7:00 local time, which may be due to two reasons: (1) the rise in O₃ precursors
483 (i.e., VOCs) due to the high-altitude atmospheric residual layer transported downward near the surface
484 at this time and (2) the increase in solar radiation intensity after 7:00, which increased the oxidation
485 capacity of the pollutants. These two factors jointly enhanced the photochemical oxidation reaction of
486 VOCs and gradually increased $P(O_3)_{net}$. $P(O_3)_{net}$ then peaked at approximately 12:00, which was
487 consistent with $J(NO_2)$, but this peak time occurred earlier than that of O₃, which peaked at approximately
488 14:00, which may be due to the photochemical reactions dominating O₃ mixing ratio changes between
489 12:00 and 14:00. After 14:00, the O₃ mixing ratios started to decrease, which may be due to other
490 processes dominating the O₃ mixing ratio changes at this time, such as O₃ reacting with other pollutants
491 or surface deposition and the outflow of O₃ by physical transport. In conclusion, the changes in O₃ mixing
492 ratios were influenced by both photochemical production and physical transport. Because HO₂ and RO₂
493 were not well captured in the model, the simulations could lead to an underestimation of $P(O_3)_{net}$.

494 **3.2 Model simulation of $P(O_3)_{net}$ in the reaction and reference chambers**

495 **3.2.1 Modeling method**

496 To obtain a comprehensive understanding of the ozone production rate $P(O_3)$ and ozone destruction rate
497 $D(O_3)$ during a 4-min photochemical reaction in the reaction and reference chambers, we modeled $P(O_3)$
498 and $D(O_3)$ at 12:00 on 7 December 2021 based on field observation data using a zero-dimensional box
499 model based on the F0AM v3.2 coupled with MCM v3.3.1, which contains a total of 143 VOCs, more
500 than 6700 species, involving more than 17000 reactions (Jenkin et al., 2015). $P(O_3)_{net}$ can be expressed
501 by the difference between $P(O_3)$ and $D(O_3)$, and $P(O_3)$ and $D(O_3)$ can be expressed as Eqs. (9) and (10),

502 respectively.

$$503 \quad P(\text{O}_3) = k_{\text{HO}_2+\text{NO}}[\text{HO}_2][\text{NO}] + \sum_i k_{\text{RO}_{2,i}+\text{NO}}[\text{RO}_{2,i}][\text{NO}]\varphi_i \quad (9)$$

$$504 \quad D(\text{O}_3) = k_{\text{O}(\text{D})+\text{H}_2\text{O}}[\text{O}(\text{D})][\text{H}_2\text{O}] + k_{\text{OH}+\text{O}_3}[\text{OH}][\text{O}_3] + k_{\text{HO}_2+\text{O}_3}[\text{HO}_2][\text{O}_3]$$

$$505 \quad + \sum_i (k_{\text{O}_3+\text{Alkene}_i}[\text{O}_3][\text{Alkene}_i] + k_{\text{OH}+\text{NO}_2}[\text{OH}][\text{NO}_2] + k_{\text{RO}_{2,i}+\text{NO}_2}[\text{RO}_{2,i}][\text{NO}_2]) \quad (10)$$

506 where $k_{\text{M+N}}$ represents the bimolecular reaction rate constant of M and N, and φ_i is the yield of NO_2 from

507 the $\text{RO}_{2,i} + \text{NO}$ reaction. The relevant reaction rates of $P(\text{O}_3)$ and $D(\text{O}_3)$ and the VOCs mixing ratios from

508 7–9 December 2021 at the SZMGT used in the model are listed in Tables 2 and S11.

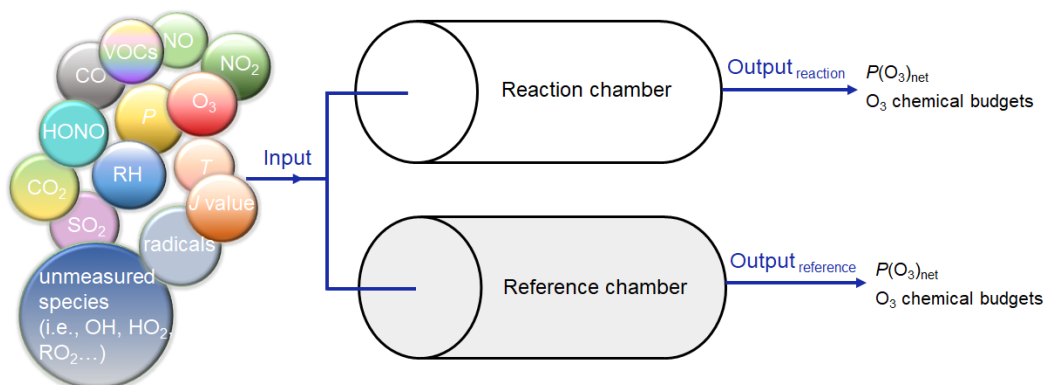
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510 **Table 2. O_3 production and destruction reactions and the relevant reaction rates used in the model.**

Reactions	Rate coefficient/unit	Number
O ₃ production pathways - $P(\text{O}_3)$		
$\text{RO}_2 + \text{NO} \rightarrow \text{RO} + \text{NO}_2$	$2.7 \times 10^{-12} \times \exp(360/T) / \text{molecules}^{-1} \text{ cm}^3 \text{ s}^{-1}$	(R1)
$\text{HO}_2 + \text{NO} \rightarrow \text{OH} + \text{NO}_2$	$3.45 \times 10^{-12} \times \exp(270/T) / \text{molecules}^{-1} \text{ cm}^3 \text{ s}^{-1}$	(R2)
O ₃ loss pathways - $D(\text{O}_3)$		
$\text{O}_3 + \text{h}\nu \rightarrow \text{O}^1\text{D} + \text{O}_2$	Measured $\text{JO}^1\text{D}/\text{s}^{-1}$	(R3)
$\text{O}_3 + \text{C}_2\text{H}_4 \rightarrow \text{HCHO} + \text{CH}_2\text{OOA}$	$9.1 \times 10^{-15} \times \exp(-2580/T) / \text{molecules}^{-1} \text{ cm}^3 \text{ s}^{-1}$	(R4)
$\text{O}_3 + \text{C}_3\text{H}_6 \rightarrow \text{CH}_2\text{OOB} + \text{CH}_3\text{CHO}$	$2.75 \times 10^{-15} \times \exp(-1880/T) / \text{molecules}^{-1} \text{ cm}^3 \text{ s}^{-1}$	(R5)
$\text{O}_3 + \text{C}_3\text{H}_6 \rightarrow \text{CH}_3\text{CHOOA} + \text{HCHO}$	$2.75 \times 10^{-15} \times \exp(-1880/T) / \text{molecules}^{-1} \text{ cm}^3 \text{ s}^{-1}$	(R6)
$\text{O}_3 + \text{C}_3\text{H}_8 \rightarrow \text{CH}_2\text{OOE} + \text{MACR}$	$3.09 \times 10^{-15} \times \exp(-1995/T) / \text{molecules}^{-1} \text{ cm}^3 \text{ s}^{-1}$	(R7)
$\text{O}_3 + \text{C}_3\text{H}_8 \rightarrow \text{CH}_2\text{OOE} + \text{MVK}$	$2.06 \times 10^{-15} \times \exp(-1995/T) / \text{molecules}^{-1} \text{ cm}^3 \text{ s}^{-1}$	(R8)
$\text{O}_3 + \text{C}_3\text{H}_8 \rightarrow \text{HCHO} + \text{MACROOA}$	$3.09 \times 10^{-15} \times \exp(-1995/T) / \text{molecules}^{-1} \text{ cm}^3 \text{ s}^{-1}$	(R9)
$\text{O}_3 + \text{C}_5\text{H}_8 \rightarrow \text{HCHO} + \text{MVKOOA}$	$2.06 \times 10^{-15} \times \exp(-1995/T) / \text{molecules}^{-1} \text{ cm}^3 \text{ s}^{-1}$	(R10)
$\text{O}_3 + \text{HO}_2 \rightarrow \text{OH}$	$2.03 \times 10^{-16} \times (T/300)^{4.57} \times \exp(693/T) / \text{molecules}^{-1} \text{ cm}^3 \text{ s}^{-1}$	(R11)
$\text{RO}_2 + \text{NO}_2 \rightarrow \text{peroxy nitrates}$	$(3.28 \times 10^{-28} \times 7.24 \times 10^{18} \times P/T \times (T/300)^{-6.87} \times 1.125 \times 10^{-11} \times (T/300)^{-1.105}) \times 10^{(\log_{10}(0.30))} / (1 + (\log_{10}(2.93 \times 10^{-17} \times 7.24 \times 10^{18} \times P/T \times (T/300)^{-5.765}) / 0.75 - 1.27 \times \log_{10}(0.30))^2) / (2.926 \times 10^{-17} \times 7.24 \times 10^{18} \times P/T \times (T/300)^{-5.765}) / \text{molecules}^{-1} \text{ cm}^3 \text{ s}^{-1}$	(R12)
$\text{NO}_2 + \text{OH} \rightarrow \text{HNO}_3$	$3.2 \times 10^{-30} \times 7.24 \times 10^{18} \times P/T \times (T/300)^{-4.5} \times 3 \times 10^{-11} \times 10^{\log_{10}(0.41)} / (1 + (\log_{10}(3.2 \times 10^{-30} \times 7.24 \times 10^{18} \times P/T \times (T/300)^{-4.5} / 3 \times 10^{-11})) / (0.75 - 1.27 \times (\log_{10}(0.41))^2) / (3.2 \times 10^{-30} \times 7.24 \times 10^{18} \times P/T \times (T/300)^{-4.5} + 3 \times 10^{-11})) / \text{molecules}^{-1} \text{ cm}^3 \text{ s}^{-1}$	(R13)
$\text{O}_3 + \text{OH} \rightarrow \text{HO}_2$	$1.70 \times 10^{-12} \times \exp(-940/T) / \text{molecules}^{-1} \text{ cm}^3 \text{ s}^{-1}$	(R14)

511 *The rate coefficient obtained from the MCM v3.3.1 model.

512 In total, three-stage simulations were carried out to obtain the 4-min photochemical reactions in
 513 the reaction and reference chambers, and all three-stage models were operated in a time-dependent mode
 514 with a 1 s resolution. In the 1st-stage, to establish a real atmospheric environment system, all observations
 515 on 7 December 2021, from 6:00-11:30, were used to constrain the model to obtain the mixing ratios of
 516 the unmeasured species in the ambient atmosphere, including oxygenated VOCs (OVOCs, in total 16
 517 species), and nonmethane hydrocarbons (in total 47 species), O₃, NO, NO₂, *J* values, T, RH, and pressure
 518 (*P*). Because O₃-NO-NO₂ was not in a steady state when all species were constrained, we conducted a
 519 2nd-stage simulation from 11:30–12:00. In this stage, we used the output mixing ratios of the unmeasured
 520 species from the simulation in the last 1 s of the 1st-stage simulation as the input, which were not
 521 constrained after providing initial values. For the measured species, O₃, NO, and NO₂ were no longer
 522 constrained after providing initial values, while all other variables (including NO_x, VOCs, *J* values, RH,
 523 *T*, *P*, etc.) were still constrained in a time-dependent mode with a 1 s resolution after providing initial
 524 values. In the 3rd-stage, we modeled the 4-min photochemical reactions in the reaction and reference
 525 chambers. We used the output mixing ratios of the unmeasured species (i.e., OH, HO₂, RO₂, SO₂, HONO,
 526 etc.) from the simulation in the last 1 s of the 2nd-stage simulation and all measured values (i.e., O₃, NO,
 527 NO₂, VOCs, *J* values, RH, *T*, *P*, etc.) as the model input, which were not constrained after providing
 528 initial values. In addition, while maintaining the setup conditions for the 2nd-stage of the simulation, we
 529 extended the simulation of the environment to 12:04 to obtain the modeled $P(O_3)_{net}$ in the environment
 530 in the 3rd-stage simulation. The result is shown in orange marker in Fig. 10d. Figure 7 shows an explicit
 531 explanation of the 3rd-stage simulation in the reaction and reference chambers.



532
 533 **Figure 7: Explicit explanation of the 3rd-stage model simulation (input meteorological conditions: *P*: 1015.3**
 534 **hPa, *T*: 295.6 K, RH: 39.7 %).**

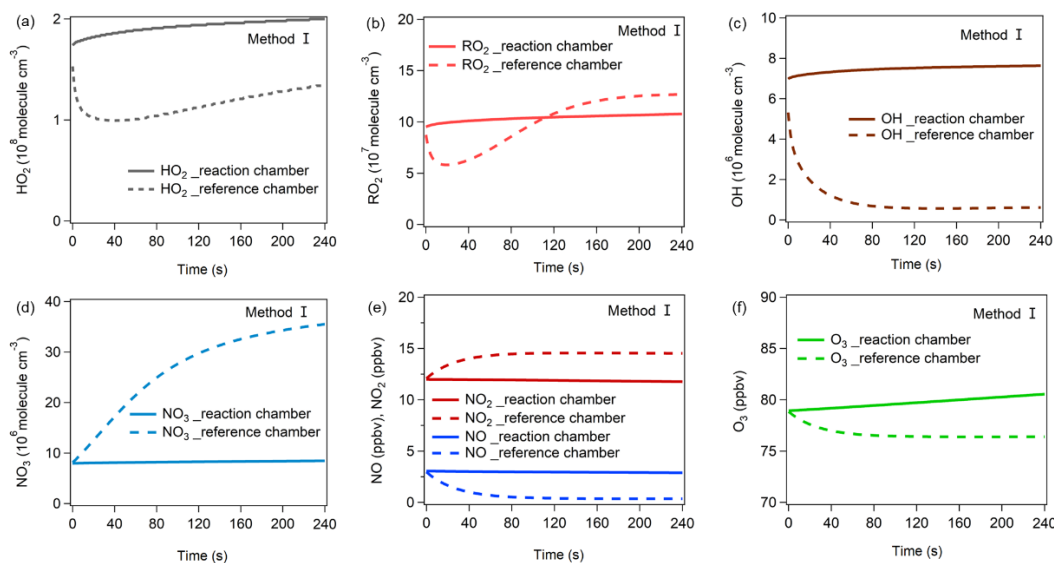
535 Specifically, because the photolysis frequencies play critical roles in the simulation of $P(O_3)_{net}$, the

536 *J* values obtained from two methods (labeled methods I and II) were used in the 3rd-stage 4-min
537 simulation. The *J* values used in method I were obtained from the measured values (including *J*(NO₂),
538 *J*(O¹D), *J*(HONO), *J*(H₂O₂), *J*(NO₃_M), *J*(NO₃_R), *J*(HCHO_M), and *J*(HCHO_R)) and the simulated values
539 using the Tropospheric Ultraviolet and Visible (TUV) radiation model (version 5.3) (including *J*(HNO₃),
540 *J*(CH₃CHO), *J*(MACR), *J*(MEK), *J*(HOCH₂CHO), *J*(C₂H₅CHO), *J*(C₃H₇CHO), and *J*(C₄H₉CHO).), while the *J*
541 values in method II were all obtained from the simulated values using the TUV model, detailed
542 information on these two methods is introduced in Appendix IV (Tables S12 and S13, respectively).

543 **3.2.2 Radical chemistry in the reaction and reference chambers**

544 The variations in the radical mixing ratios (i.e., HO₂, OH, RO₂) and NO₃, NO, NO₂, and O₃ mixing
545 ratios obtained from method I and method II during the 3rd-stage 4-min model simulation are shown in
546 Fig. 8 and Fig. S18, respectively. The production and destruction reactions of HO₂, OH, RO₂, and NO₃
547 in the reaction and reference chambers obtained from methods I and II are shown in Fig. 9 and Fig. S19,
548 respectively, the production and destruction reactions of RO_x in the reaction and reference chambers
549 obtained from methods I and II are shown in Fig. S20, the detailed RO_x production pathways of
550 NO₃+VOCs are shown in Fig. S21, and the final modeling results are shown in Fig. 10 and Fig. S22.

551 From Fig. 8, in the reaction chamber, the HO₂, OH, RO₂, and NO₃ concentrations first slightly
552 increased and then became stable, and their final concentrations were 2.00×10^8 , 7.64×10^6 , 1.08×10^8 , and
553 8.47×10^6 molecules cm⁻³, respectively. In the reference chamber, the HO₂ and RO₂ concentrations
554 dropped during the 1st half minute and rose afterward. The final HO₂ concentration (1.35×10^8 molecules
555 cm⁻³) was lower than that in the reaction chamber, while the RO₂ concentration exceeded that in the
556 reaction chamber at the end of the 2nd minute and gradually became stable at 1.27×10^8 molecules cm⁻³.
557 The OH concentration dropped significantly at the 1st minute and then became stable at approximately
558 6.16×10^5 molecules cm⁻³. The NO₃ concentration rose significantly during the 4-min simulation and
559 reached 3.55×10^7 molecules cm⁻³ at the end, which was much higher than that in the reaction chamber.

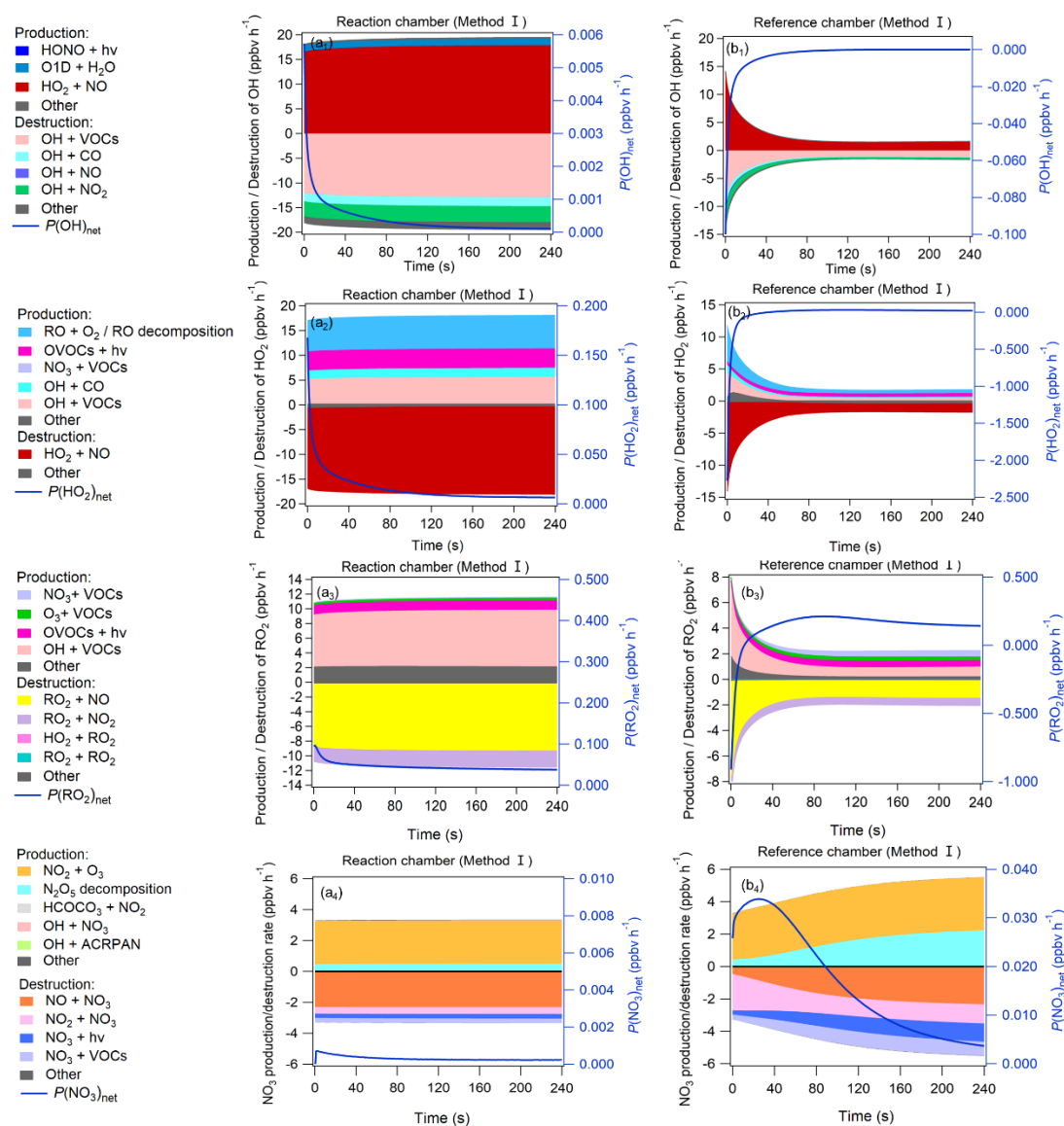


560

561 **Figure 8: The variations of (a)HO₂, (b) RO₂, (c) OH, (d)NO₃, (e) NO, NO₂, and (f) O₃ mixing ratios during the**
 562 **3rd-stage 4-min model simulation using method I. The mixing ratios changes of these items for method II is**
 563 **shown in Fig. S18.**

564 The OH, HO₂, RO₂, and NO₃ concentrations greatly impact the O₃ production and destruction rate.
 565 To better understand the factors that drive the OH, HO₂, RO₂, and NO₃ concentration changes, we have
 566 added their production and destruction pathways in Fig. 9. We found that the decrease in HO₂ and RO₂
 567 concentrations in the reference chamber in the 1st half minute was mainly due to NO titration effects, as
 568 high NO mixing ratios existed during the 1st half minute. The increase in HO₂ concentrations afterward
 569 was largely attributable to RO+O₂ reaction/RO decomposition, OH+CO/VOCs reaction, OVOCs
 570 photolysis (i.e., C₃H₄O₂, C₂H₂O₂, C₄H₆O₂), and NO₃+VOCs reaction, and the increase in RO₂
 571 concentrations afterward were largely attributable to OH+VOCs oxidation, OVOCs photolysis and
 572 O₃+VOCs reaction. The main OH sources in the reference chamber were both HO₂+NO in method I and
 573 method II. Due to sufficiently high $J(\text{NO}_3)$ (~ 90% of that in the reaction chamber) and NO₂
 574 concentrations in the reference chamber, the NO₃ photolysis and NO₂+NO₃ reaction consumed NO₃ in
 575 the reference chamber, but the NO₃ concentrations were still sufficiently high due to high production
 576 rates of NO₃ at the same time. The main NO₃ source in the reference chamber was the NO₂+O₃ reaction,
 577 followed by N₂O₅ decomposition. The NO₂ concentrations were relatively high in the 1st minute and
 578 consumed NO₃ very quickly, but due to continuous NO₃ sources, the net NO₃ production rates ($P(\text{NO}_3)_{\text{net}}$)
 579 were positive (as shown in Fig. 9), which caused the NO₃ concentration to continue to increase (as shown
 580 in Fig. 8d). The main difference in NO₃ production in the reference chamber compared to that in the

581 reaction chamber was the much higher N_2O_5 decomposition, which was mainly due to the high NO_2
 582 concentrations in the reference chamber. On the other hand, although the $\text{NO}+\text{NO}_3$ reaction was also one
 583 of the dominant NO_3 destruction pathways, NO_3 consumed by the $\text{NO}+\text{NO}_3$ reaction was significantly
 584 smaller than NO_3 produced by the NO_2+O_3 reaction. Furthermore, in order to check if the NO_3+VOCs
 585 reactions exists, we extracted all the $P(\text{ROx})$ pathways related to NO_3+VOCs reactions during the 3rd-
 586 stage 4-min model simulation in the reaction and reference chambers in method I, as shown in Fig. S20.
 587 We found that the NO_3+VOCs reactions are mostly related to the OVOCs (i.e. 6-Ethyl-m-cresol and 3-
 588 Ethyl-6-methylbenzene-1,2-diol) in Fig. S21. The production and destruction rates of ROx are shown in
 589 Fig. S20.
 590

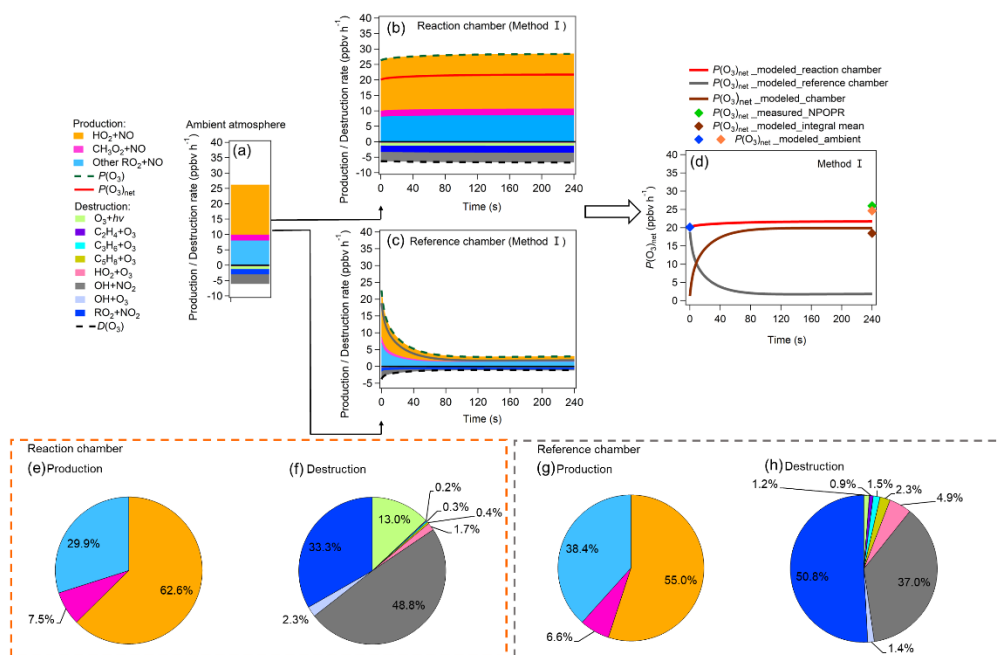


591
 592 **Figure 9: Production and destruction pathways of OH (a1-b1), HO₂ (a2-b2), RO₂ (a3-b3), and NO₃ (a4-b4) during**

593 the 3rd-stage 4-min model simulation in the reaction and reference chambers in method I. The related contents
 594 for method II (c)-(d) are shown in Fig. S19 in the supplementary materials.

595 3.2.3 $P(O_3)_{net}$ formation and destruction pathways in the reaction and reference chambers

596 Figures 10a–d show the modeled $P(O_3)_{net}$ and the sources and sinks of various species during the
 597 3rd-stage 4-min simulation. Figure 10a shows the steady state of $P(O_3)_{net}$ and the various species in the
 598 ambient atmosphere achieved in the last 1 s of the 2nd-stage simulation; Figures 10b and c show the
 599 modeled $P(O_3)_{net}$ and the O_3 chemical budgets in the reaction and reference chambers during the model
 600 simulation period; Figure 10d summarizes the modeled $P(O_3)_{net}$ in the ambient air (represented as blue
 601 and orange markers at the time when the ambient air was going in and out of the NPOPR system,
 602 respectively) and the modeled $P(O_3)_{net}$ in the reaction and reference chambers. To compare the modeled
 603 results with our measured results, we calculated the integral mean of the modeled $P(O_3)_{net}$ in the reaction
 604 and reference chambers and appended the related measured $P(O_3)_{net}$ value during the 4-min simulation
 605 time onto Fig. 10d (green maker). Furthermore, the reaction weights of different production and
 606 destruction reaction processes of O_3 are shown in Figs. 10e–h.



607
 608 **Figure 10: (a)–(c) Modeled $P(O_3)_{net}$ values and O_3 chemical budgets in (a) ambient air when injected into the**
 609 **reaction and reference chambers and (b–c) the reaction and reference chambers during the 4-min model**
 610 **simulation; (d) $P(O_3)_{net}$, where $P(O_3)_{net_modeled_ambient}$ represent the modeled $P(O_3)_{net}$ in the ambient air**
 611 **at the time before (blue marker) and after (orange marker) the sampled ambient air was injected into the**
 612 **dual-channel reaction chamber. $P(O_3)_{net_modeled_reaction\ chamber}$ and $P(O_3)_{net_modeled_reference$**
 613 **chamber represent the $P(O_3)_{net}$ change trends during the 4-min photochemical reactions in the reaction and**
 614 **reference chambers, respectively. $P(O_3)_{net_modeled_chamber} = P(O_3)_{net_modeled_reaction\ chamber}$ –**

615 $P(O_3)_{\text{net_modeled_reference chamber}}$, and $P(O_3)_{\text{net_modeled_integral}}$ mean represents the integral mean of
616 the $P(O_3)_{\text{net_modeled_chamber}}$. Moreover, $P(O_3)_{\text{net_measured_NPOPR}}$ is the $P(O_3)_{\text{net}}$ measured by NPOPR
617 detection system. (e)–(h) Reaction weights of each production and destruction reaction process of O_3 in the
618 reaction and reference chambers in method I.

619 Figure 10a-h show the contributions of different reaction pathways to $P(O_3)$ and $D(O_3)$. $P(O_3)$ and
620 $D(O_3)$ were almost the same within the 4-min reaction in the reaction chamber (all species reached a
621 steady-state condition), while $P(O_3)$ and $D(O_3)$ in the reference chamber significantly decreased within
622 the 1st min and remained stable in the following minutes. In the reaction chamber, the HO_2+NO reaction
623 contributed the most to $P(O_3)$, accounting for 62.6 % of the total $P(O_3)$, with an integral mean value of
624 17.5 ppbv h⁻¹ in the reaction chamber. The second important pathway of $P(O_3)$ was RO_2+NO (accounting
625 for 37.4 % of the total $P(O_3)$). The RO_2+NO core reaction accounts for more than approximately 1200
626 types of RO_2 radicals, and the pathway of CH_3O_2+NO contributed 7.5 % to the total $P(O_3)$. The most
627 important contributor of $D(O_3)$ was $OH+NO_2$ (48.8 %), followed by RO_2+NO_2 (33.3 %), O_3 photolysis
628 (13.0 %), O_3+OH (2.3 %), O_3+HO_2 (1.7 %), $C_5H_8+O_3$ (0.4 %), $C_3H_6+O_3$ (0.3 %), and $C_2H_4+O_3$ (0.2 %).
629 In the reference chamber, the integral mean value of the HO_2+NO reaction was 2.3 ppbv h⁻¹, which had
630 the largest contribution to $P(O_3)$ (accounting for 55.0 %). The second largest contributor to $P(O_3)$ was
631 RO_2+NO (accounting for 45.0 % of the total $P(O_3)$), in which the pathway of CH_3O_2+NO contributed
632 6.6 % to the total $P(O_3)$. The most important contributor of $D(O_3)$ was RO_2+NO_2 (50.8 %), followed by
633 $OH+NO_2$ (37.0 %), O_3+HO_2 (4.9 %), $C_5H_8+O_3$ (2.3 %), $C_3H_6+O_3$ (1.5 %), O_3+OH (1.4 %), O_3 photolysis
634 (1.2 %), and $C_2H_4+O_3$ (0.9 %). For all $P(O_3)$ reactions, the weight of the RO_2+NO reaction in the
635 reference chamber was 7.5 % higher than that in the reaction chamber; however, for all $D(O_3)$ reactions,
636 the weight of the RO_2+NO_2 reaction in the reference chamber was 17.5 % higher than that in the reaction
637 chamber, which mitigated the high $P(O_3)$ value caused by RO_2+NO in the reference chamber.
638 Furthermore, the weight of the $OH+NO_2$ reaction in the reference chamber was 11.9 % lower than that
639 in the reaction chamber, which may be the main reason that led to NO_2 mixing ratios in the reference
640 chamber being much higher than those in the reaction chamber. It is worth noting that the different
641 reaction pathways of $P(O_3)$ and $D(O_3)$ stabilized at approximately 1.5 min for both methods I and II (as
642 shown in Figs. 10 and S22, respectively), and the radicals that play critical roles in photochemical O_3
643 formation, such as HO_2 , RO_2 and OH , reached quasi-steady states in approximately 3 min (as shown in
644 Figs. 8 and S18). As the lowest experimental residence time in the reaction and reference chambers was
645 3.8 min at an air flow rate of 5 L min⁻¹, the photochemical reaction time at different air flow rates in the

646 NPOPR system was sufficient for $P(\text{O}_3)_{\text{net}}$ investigation, and it is reasonable for us to set the alternate
647 ambient air sampling time for the reaction and reference chambers to 2 min, where the ambient air
648 actually had already reacted for at least 3.8 min in the chambers.

649 The $P(\text{O}_3)_{\text{net}}$ value measured by the NPOPR detection system at 12:04 was 26.0 ppbv h⁻¹, which is
650 1.4 ppbv h⁻¹ higher than the modeled $P(\text{O}_3)_{\text{net}}$ value in the ambient air (orange marker in Fig. 10d; 24.6
651 ppbv h⁻¹) and 7.5 ppbv h⁻¹ higher than the modeled $P(\text{O}_3)_{\text{net}}$ value of the NPOPR system (brown marker
652 in Fig. 10d; 18.5 ppbv h⁻¹, as calculated from the integral mean of $P(\text{O}_3)_{\text{net}}$ in the 3rd-stage 4-min
653 simulation in the reaction and reference chambers). Here, we note that for a better comparison between
654 the measured and modeled $P(\text{O}_3)_{\text{net}}$ values, the measured $P(\text{O}_3)_{\text{net}}$ used here was obtained from a 4-min
655 time resolution, which is 1.4 ppbv h⁻¹ higher than the measured $P(\text{O}_3)_{\text{net}}$ value used in Fig. 6 (1-h time
656 resolution). The ratio of the measured and modeled $P(\text{O}_3)_{\text{net}}$ values was 1.4, which is consistent with the
657 measured-to-modeled ratio of the cumulative $P(\text{O}_3)_{\text{net}}$ (1.3 and 1.4) obtained from previous studies
658 (Cazorla et al., 2012; Ren et al., 2013), where $P(\text{O}_3)_{\text{net}}$ values were also directly measured in the
659 atmosphere and were independent of the OH and HO₂ measurements. The reason for the difference
660 between the measured and modeled $P(\text{O}_3)_{\text{net}}$ here may be due to the inaccurate estimation of HO₂/RO₂
661 radicals; for example, Ren et al. (2013) found that $P(\text{O}_3)$ calculated from the modeled HO₂ was lower
662 than that calculated from the measured HO₂. The unknown HO₂ source should be identified for a more
663 accurate estimation of $P(\text{O}_3)_{\text{net}}$ in future studies.

664 Additionally, the modeled $P(\text{O}_3)_{\text{net}}$ using the J values obtained from method II was 9.3 ppbv h⁻¹
665 lower than the measured $P(\text{O}_3)_{\text{net}}$, and this discrepancy was slightly larger than that using method I, as
666 shown in Appendix IV (Fig. S22). The differences in the measured and modeled $P(\text{O}_3)_{\text{net}}$ by methods I
667 and II were 28.8 % and 35.8 %, respectively. This difference was mainly due to the transmittance of
668 $J(\text{NO}_2)$ in method II (30 %) being much higher than that in method I (9 %), and NO₂ photolysis products
669 were involved in the main reaction of O₃ production through HO₂+NO and RO₂+NO, so the modeled
670 $P(\text{O}_3)_{\text{net}}$ in the reference chamber was slightly overestimated in method II, thus leading to an
671 underestimation of the final $P(\text{O}_3)_{\text{net}}$.

672 Furthermore, because the NO₂ data used here were measured by a commercially available
673 chemiluminescence NO_x monitor, the NO₂ and NO_x mixing ratios could be overestimated due to NO_z
674 interference (i.e., HNO₃, peroxyacetyl nitrate (PANs), HONO, etc.) (Dunlea et al., 2007). According to

675 our results, the chemiluminescence technique could bias NO_2 by 5 % compared to the CAPS technique,
676 which is regarded as a trustworthy NO_2 measurement technique without chemical interference. Therefore,
677 we simulated the interference of NO_2 measured by a chemiluminescence NO_x monitor in method I as
678 follows: reducing and increasing the ambient NO_2 mixing ratios in the reaction and reference chambers
679 by 5 % in the 3rd-stage 4-min simulation. The results showed that increasing and decreasing NO_2 by 5 %
680 resulted in a decrease in $P(\text{O}_3)_{\text{net}}$ by 1.64 % and 3.68 %, respectively (as shown in Fig. S23), which is
681 much smaller than the bias caused by $P(\text{O}_3)_{\text{net}}$ in the reference chamber (which were 13.9 % and 22.3 %
682 for methods I and II, respectively). To evaluate $P(\text{O}_3)_{\text{net}}$ error caused by the measurement error of J values,
683 we introduced a ± 5 % error to the measured J values during the 3rd stage of the 4-min simulation in
684 method I. The modeled $P(\text{O}_3)_{\text{net}}$ results are presented in Fig. S24 in the supplementary materials. We
685 observed that the inclusion of a -5 % measurement error in J values led to a decrease in $P(\text{O}_3)_{\text{net}}$ by
686 7.27 %, while adding a +5 % measurement error in J values caused an increase in $P(\text{O}_3)_{\text{net}}$ by 3.08 %.
687 This implies that the maximum bias of $P(\text{O}_3)_{\text{net}}$ caused by the measurement error of J values falls within
688 the error range of the currently assessed $P(\text{O}_3)_{\text{net}}$ error, which was 13.9 % for method I. Therefore, we
689 conclude that this type of error will not influence our final modeling results and conclusions.

690 In conclusion, modeling tests demonstrated that the radicals and gas species in the reaction
691 chamber of the NPOPR detection system were similar to those in genuine ambient air, while these
692 radicals also unexpectedly existed in the reference chamber. This was mainly because the UV protection
693 film used by the reference chamber did not completely filter out sunlight, which led to the low
694 transmittance of light ranging from 390 nm to 790 nm. The $P(\text{O}_3)_{\text{net}}$ biases caused by this interference
695 modeled in methods I and II were 13.9 % and 22.3 %, respectively, which ensured that the measured
696 $P(\text{O}_3)_{\text{net}}$ by the NPOPR detection system should be regarded as the lower limit values of real $P(\text{O}_3)_{\text{net}}$ in
697 the atmosphere. We recommend that the J values obtained from method I should be used in the model
698 simulation, which can better explain the photochemical formation of O_3 in the actual atmosphere, but if
699 direct J value measurements cannot be achieved during field observations, the J values obtained from
700 method II would also be acceptable in modeling studies.

701 **4 Conclusions**

702 We modified and improved a net photochemical ozone production rate (NPOPR) detection system based

703 on a dual-channel reaction chamber technique, which provides more accurate results and has broader
704 application potential compared to previous studies. The main improvements of NPOPR detection system
705 compared to previous studies were as follows: (1) improved the design of the reaction and reference
706 chambers to make sure they have good airtightness; (2) changed the air sampling structure to enable the
707 total air flow rates change freely from 1.3 to 5 L min⁻¹ in the reaction and reference chambers, which can
708 make the NPOPR system achieve different limits of detection (LODs) and applicable to different ambient
709 environment; (3) characterized the NPOPR detection system at different air flow rates to optimize the
710 $P(\text{O}_3)_{\text{net}}$ measurements, the LODs of the NPOPR detection system are 0.07, 1.4, and 2.3 ppbv h⁻¹ at air
711 flow rates of 1.3, 3, and 5 L min⁻¹, respectively; (4) tested the performance of both reaction and reference
712 chambers by combining the field measurement and the MCM modeling method.

713 The NPOPR detection system was employed in the field observation at the Shenzhen
714 Meteorological Gradient Tower (SZMGT), which is located in PRD, China. During the measurement
715 period, the $P(\text{O}_3)_{\text{net}}$ was around zero during nighttime and ranged from ~ 0 to 34.1±7.8 ppbv h⁻¹ during
716 daytime (from 6:00–18:00), with the average value of 12.8 (±5.5) ppbv h⁻¹. Besides, $P(\text{O}_3)_{\text{net}}$ start to
717 increase at around 7:00 at local time, this may be due to the rise of the O₃ precursors (i.e., VOCs)
718 transported down from the high-altitude atmospheric residual layer to the near-surface and the increase
719 of solar radiation intensity increased the atmospheric oxidation capacity. $P(\text{O}_3)_{\text{net}}$ was then reaches a peak
720 at around 12:00 at noon time, by coupling with diurnal O₃ mixing ratios trends, we confirmed that the
721 ground-level O₃ mixing ratios were influenced by both photochemical production and physical transport.

722 In order to clarify the detailed photochemical reaction processes in the reaction and reference
723 chambers of NPOPR system, we modeled the $P(\text{O}_3)_{\text{net}}$ on 7 December 2021, 12:00-12:04 in the reaction
724 and reference chambers using MCM v3.3.1. As the photolysis frequencies of different species (J values)
725 play critical roles in the formation of $P(\text{O}_3)_{\text{net}}$, the J values obtained from two methods were used in the
726 4-min chamber photochemical reaction (labeled as method I and method II), in method I, eight main J
727 values (e.g., $J(\text{NO}_2)$, $J(\text{O}^1\text{D})$, $J(\text{HONO})$, etc.) were measured directly, and other J values were obtained
728 from the simulated values using the Tropospheric Ultraviolet and Visible (TUV) radiation model, while
729 in method II, J values were all obtained from the simulated values using TUV model (as described in
730 Sect. 3.2). Modeling tests demonstrated that the mixing ratios of different radicals and gas species (i.e.,
731 OH, HO₂, RO₂, NO₃, NO, NO₂, and O₃) in the reaction chamber were similar with those in the real

732 ambient environment, while due to the UV protection film used by the reference chamber does not
733 completely filter out the sunlight, there was low transmittance of the light ranged from 390 nm to 790
734 nm. In the reaction chamber, the contribution of different reactions to $P(O_3)$ and $D(O_3)$ modeled by
735 method I and II were quite similar, where the HO_2+NO reaction contributed most to $P(O_3)$ (~ 62.6 %),
736 followed by the RO_2+NO reaction (~ 37.4 %). The $OH+NO_2$ reaction contributed most to $D(O_3)$, which
737 accounted for ~ 48.9 %, followed by the RO_2+NO_2 reaction O_3 photolysis, which accounted for ~ 33.3 %
738 and 13.0 %, respectively. In the reference chamber, the contribution of different reactions to $P(O_3)$ and
739 $D(O_3)$ modeled by method I and II were different, where the HO_2+NO reaction contributed ~ 55.0 % and
740 ~ 58.2 % to the total $P(O_3)$, respectively, and RO_2+NO contributed ~ 44.9 % and 41.8 % to the total
741 $P(O_3)$, respectively. The most important contributor of $D(O_3)$ modeled by method I was RO_2+NO_2
742 (50.8 %), followed by $OH+NO_2$ (37.0 %), while the most important contributor of $D(O_3)$ modeled by
743 method II was $OH+NO_2$ (46.8 %), followed by RO_2+NO_2 (44.1 %). For all $P(O_3)$ reactions, the weight
744 of RO_2+NO reaction in the reference chamber was 7.5 % and 4.3 % higher than that in the reaction
745 chamber in method I and II, respectively, however, for all $D(O_3)$ reactions, the weight of RO_2+NO_2
746 reaction in the reference chamber was 17.5 % and 10.9 % higher than that in the reaction chamber in
747 method I and II, respectively, which will somehow mitigate the high $P(O_3)$ caused by RO_2+NO in the
748 reference chamber. The different reaction pathways of $P(O_3)$ and $D(O_3)$ had stabilized at around 1.5 min,
749 and the radicals that play critical roles in photochemical O_3 formation, such as HO_2 , RO_2 and OH , reached
750 quasi-steady states in about 3 min, the long enough ambient air residence time in the reaction and
751 reference chambers (≥ 3.8 min) make the photochemical reaction time at different air flow rates in the
752 NPOPR system sufficient enough for investigating the $P(O_3)_{net}$, and it is reasonable for us to set the
753 alternate ambient air sampling time for the reaction and reference chambers at 2 min, where the ambient
754 air actually has already reacted for at least 3.8 min in the chambers.

755 The biases of the modeled $P(O_3)_{net}$ caused by the interference of the reactions in the reference
756 chamber in methods I and II were 13.9 % and 22.3 %, respectively; thus, the measured $P(O_3)_{net}$ by the
757 NPOPR detection system should be regarded as the lower limit values of the real $P(O_3)_{net}$ in the
758 atmosphere. Nevertheless, the measured $P(O_3)_{net}$ values were 7.5 and 9.3 ppbv h^{-1} higher than the
759 modeled $P(O_3)_{net}$ values obtained from methods I and II, respectively, which may be due to the inaccurate
760 modeling of HO_2/RO_2 radicals. Short-lived intermediate measurements coupled with direct $P(O_3)_{net}$

761 measurements are needed in future study in order to studies to better understand the photochemical
762 production and destruction mechanisms of O₃. We recommend that the *J* values obtained from method I
763 should be used in the model simulation, which can better explain the photochemical formation of O₃ in
764 the actual atmosphere, but if direct *J* value measurements cannot be achieved during field observations,
765 the *J* values obtained from method II would also be acceptable in modeling studies.

766 The self-built NPOPR detection system in this study filled the gap in the observation method in
767 China. The research results not only help us to better understand the tropospheric O₃ budget but also
768 provide an important data basis for formulating correct O₃ pollution prevention measures and control
769 strategies.

770

771 *Data availability.* The observational data used in this study are available from corresponding authors
772 upon request (junzhou@jnu.edu.cn).

773 *Author contributions.* JZ, BY, and MS designed the experiment, JZ and YXH developed and assembled
774 the NPOPR detection system, YXH, JZ, JPZ, BY, YW, YFW, SCY, YWP, JPQ, XJH, XS and YBC
775 collected and analyzed the data, YXH and JZ wrote the manuscript, all authors revised the manuscript.

776 *Competing interests.* The authors declare that they have no known competing interests.

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