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1 **A Large-Scale Outdoor Atmospheric Simulation Smog Chamber for Studying**
2 **Atmospheric Photochemical Processes: Characterization and Preliminary**
3 **Application**

4

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28

29 **Abstract:** Understanding the formation mechanisms of secondary air pollution is very
30 important for the formulation of air pollution control countermeasures in China. Thus,

31 a large-scale outdoor atmospheric simulation smog chamber was constructed at Chinese
32 Research Academy of Environmental Sciences (the CRAES Chamber), which was
33 designed for simulating the atmospheric photochemical processes under the conditions
34 close to the real atmospheric environment. The chamber consisted of a 56 m³
35 fluorinated ethylene propylene (FEP) Teflon film reactor, an electrically-driven stainless
36 steel alloy shield, an auxiliary system, and multiple detection instrumentations. By
37 performing a series of characterization experiments, we obtained basic parameters of
38 the CRAES chamber, such as the mixing ability, the background reactivity, and the wall
39 loss rates of gaseous compounds (propene, NO, NO₂, ozone) and aerosols (ammonium
40 sulfate). Oxidation experiments were also performed to study the formation of ozone
41 and secondary organic aerosol (SOA), including α -pinene ozonolysis, propene and
42 1,3,5-trimethylbenzene photooxidation. Temperature and seed effects on the vapor wall
43 loss and SOA yields were obtained in this work: higher temperature and the presence
44 of seed could reduce the vapor wall loss; SOA yield was found to depend inversely on
45 temperature, and the presence of seed could increase SOA yield. The seed was
46 suggested to be used in the chamber to reduce the interaction between the gas phase
47 and chamber walls. The results above showed that the CRAES chamber was reliable
48 and could meet the demands for investigating tropospheric chemistry.

49 **Keywords:**

50 Outdoor smog chamber

51 Characterization experiments

52 Photooxidation reactions

53 Secondary organic aerosol

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57 **Introduction**

58 Air pollution has been one of the most important global environmental issues in the past
59 few decades, which is related to human health, ecological environment, and climate

60 change (Guo et al., 2014; Huang et al., 2014; Menon et al., 2002; Zhang et al., 2016).
61 To study the chemical processes of atmospheric pollution, many smog chambers had
62 been developed worldwide. Smog chambers were initially constructed for developing
63 and evaluating atmospheric gas-phase chemical mechanisms, generating and validating
64 computer models of the chemistry occurring in polluted atmosphere (Akimoto et al.,
65 1979a; CARTER et al., 1982a). Now the smog chambers could be used to study the
66 formation and evolution of specific pollutants in the atmosphere by controlling or
67 restricting certain meteorological conditions and reactant compositions, and could also
68 be applied to obtain kinetic parameters of specific reactants (Knox, 1965; Li et al.,
69 2017a; Li et al., 2017b; McFiggans et al., 2019; Yu et al., 1997; Zhou et al., 2019).

70 According to the light sources adopted, the smog chambers were usually divided
71 to be indoor chamber and outdoor chamber; indoor chambers were equipped with
72 artificial light sources while outdoor chambers benefitted from natural solar radiation
73 (Seakins, 2010). For indoor chambers, ultraviolet lamps were used to simulate natural
74 solar radiation, thus the spectral distribution was not exactly the same as the
75 tropospheric sunlight spectrum, which made the simulation results might deviate from
76 that in nature. However, it is relatively easier to control the experimental conditions for
77 the indoor chambers, various experimental conditions (e.g. temperature, relative
78 humidity, pressure) could be precisely designed for different experimental purposes,
79 which means that the repeatability of experimental results could be ensured under
80 precise control of the reaction conditions. In comparison, since outdoor chambers
81 usually had larger size, there are relative smaller surface to volume ratio for outdoor
82 chamber, which could minimize the wall effects and wall loss of gaseous species and
83 particles. The experiments inside the outdoor chambers were performed at ambient
84 temperature and pressure, and also with natural solar radiation. Hence, the outdoor
85 chamber was an ideal reactor to simulate the atmospheric photochemical processes.
86 However, the drawbacks of the outdoor smog chamber were that the temperature,
87 humidity, and solar flux varied gradually during the experimental period, and it was
88 almost impossible to guarantee reproducible irradiation from day to day. (Johnson et
89 al., 2004; Karl et al., 2004; Seakins, 2010).

90 Many outdoor and indoor chambers had been established and applied to simulate
91 the atmospheric photochemical processes worldwide (Table S1). The construction of
92 large-size smog chamber abroad began in the 1970s, when the starting point was to
93 study near-ground ozone pollution (Akimoto et al., 1979b; Carter et al., 1982b). In the

94 following thirty years, indoor and outdoor chambers were widely used to study the
95 generation mechanism of secondary pollutants, such as ground-level-ozone (Dodge,
96 2000; Hess et al., 1992; Simonaitis et al., 1997) and SOA (Griffin et al., 1999; Leone et
97 al., 1985; Martian-Reviejo and Wirtz, 2005; McMurry and Grosjean, 1985; Odum et al.,
98 1996; Paulsen et al., 2005a; Saathoff et al., 2009). After the 1980s, many large smog
99 chambers have been transformed, rebuilt, and upgraded, to deal with the emerging
100 scientific issues of atmospheric environment and atmospheric chemistry, such as PM_{2.5}
101 pollution (Hallquist et al., 2009; Hurley et al., 2001; Johnson et al., 2004), intermediate
102 products of VOCs reaction (Bloss et al., 2005; Bohn et al., 2005; Brauers et al., 2003;
103 Ren et al., 2017), multiphase reactions (Poschl and Shiraiwa, 2015; Warneke et al.,
104 2004), reaction kinetic parameters (Karl et al., 2004; Ren et al., 2019; Rohrer et al.,
105 2005), etc.

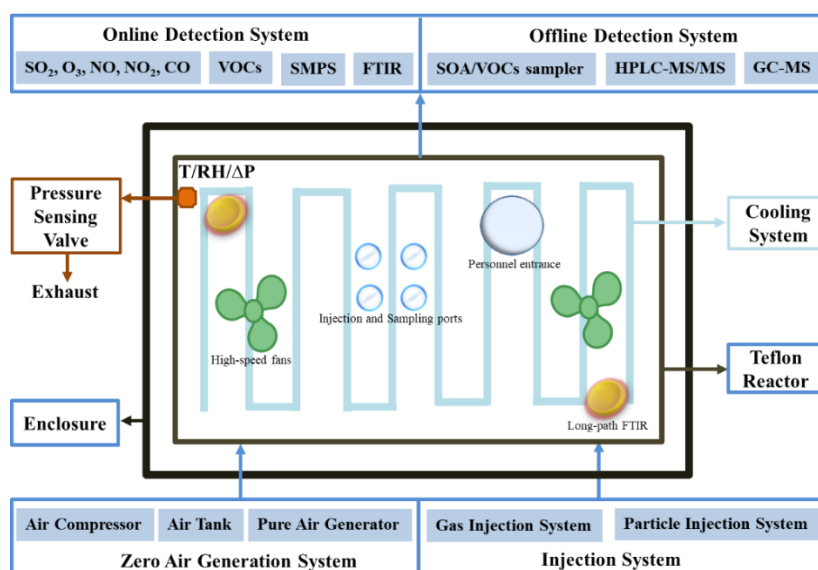
106 The domestic experimental research with the smog chamber started in the early
107 1980s, later than abroad. Peking University built the earliest indoor photochemical
108 smog chamber in 1982, in response to the photochemical smog phenomenon that
109 occurred in Lanzhou (Tang et al., 1982). A series of photochemical simulation
110 experiments of hydrocarbons and NO_x were designed and conducted according to the
111 atmospheric conditions in Lanzhou and Beijing (Zhang and Li, 1998). Then a serious
112 environmental issues were studied based on the smog chambers constructed with
113 various size in the past decades, including the mechanism of photochemical reaction
114 (Liu et al., 2017; Wang et al., 2014; Wu et al., 2007), ozone and SOA formation (Li et
115 al., 2018a; Ma et al., 2018; Wang et al., 2015), biomass burning reactions (Zhang et al.,
116 2011), the photochemical process of the gasoline and diesel (Chen et al., 2019a; Chen
117 et al., 2019b; Kamens et al., 2011), physicochemical properties of SOA formed under
118 various conditions (Li et al., 2017a; Li et al., 2020; Li et al., 2018b; Peng et al., 2018;
119 Zhang et al., 2020), et al. However, most of the chambers constructed in China were
120 indoor smog chambers, establishment large-scale outdoor smog chambers in China was
121 limited. In order to study the atmospheric pollution process close to China's actual
122 atmospheric environment, it was necessary to build a large outdoor smog chamber in
123 China.

124 This work described a new outdoor photochemical smog chamber constructed at
125 the Chinese Research Academy of Environmental Sciences (the CRAES chamber). As
126 the large-scale outdoor smog chamber in China at present, it was designed to simulate
127 the atmospheric photochemical processes at ambient temperature and radiation. A

128 series of characterization experiments were performed, including the light-transmission
 129 rate of the Teflon reactor, the mixing ability, the wall loss of gaseous pollutants and
 130 particles, and the blank photochemical background. We had also performed preliminary
 131 applications of the smog chamber, including the classic gas-phase photochemical
 132 reaction of propene, the yield of SOA derived from α -pinene ozonolysis and 1,3,5-
 133 trimethylbenzene photochemical reaction. The temperature and seed effects on vapor
 134 wall loss and SOA yield were investigated in this work.

135 1. Facility

136 The CRAES chamber was located on the rooftop of atmospheric photochemical smog
 137 chamber simulation laboratory building (40°02'27.73'N, 116°24'41.56'E), aligning in
 138 north-south direction. The chamber was mainly composed of a Teflon reactor, an
 139 enclosure, an auxiliary system and a detection system. Its schematic was illustrated in
 140 **Fig. 1**, and the pictures of the reactor and enclosure were shown in **Fig. S1**.



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Fig. 1. Schematic diagram of the CRAES chamber.

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The frame of the reactor was made of aluminum alloy, of which the bottom was made of aluminum supported by steel structure. As shown in **Fig. S1**, injection and sampling ports, air purification system import and export, and port for personnel in and out (staged manual cleaning the walls inside the chamber) were located on the bottom of the frame by using the flanges. All the connection parts on the bottom of the reactor were made of Teflon or stainless steel (covered with Teflon film) without O-rings to

149 avoid the evaporation of the organic impurities into the reactor. The reactor walls were
150 made of 0.1 mm fluorinated ethylene propylene (FEP) Teflon film (FEP 100, DuPont
151 USA), and it was suspended on the frame. The volume of the reactor was 56 m³ (3.2 m
152 × 6.2 m × 2.5 m), with a surface to volume ratio approximately 1.55 m⁻¹.

153 The enclosure consisted of a shield and an electrical control system. The main body
154 of the shield was made of stainless steel supported by a full steel frame and had a
155 rectangular parallelepiped shape. This shield could protect the reactor against adverse
156 weather conditions. The opening and closing of the shield was achieved by an electrical
157 control system. The entire system was equipped with an emergency stop device to deal
158 with sudden failures and ensured that the enclosure and Teflon reactor was not damaged.

159 The cooling system consisted of a condensing compressor (Industrial Chiller,
160 ANGES, China) and a condensing tube. The tube connected with the condensing
161 compressor being evenly distributed below the steel plate at the bottom of the reactor.
162 The water-cooling method ensured that the temperature of the reactor was within a
163 controllable range, especially under high temperature condition in summer.

164 The zero air generation system consisted of two air compressors, two air tank and
165 two AADCO pure air generators (Model 737, AADCO Instruments Inc., USA). The
166 NO, NO₂, ozone, NH₃, non-methane hydrocarbons (NMHC) (< 1 ppb, volume fraction),
167 and particles in the purified air were below detection limit, and the relative humidity
168 (RH) was less than 1%. The maximum flow rate of the purified air was 245 ± 5 L/min.
169 The purified air was used as the matrix air and carrier gas. All gas lines of the system
170 were made of stainless steel or Teflon. Gaseous species were injected into the reactor
171 through Teflon lines by cylinders connected with pressure reducing valves and mass
172 flow controllers. Most gaseous species were commercial cylinder gases, and there were
173 also gaseous species that were configured according to the experimental requirements.

174 Instrumentations of the CRAES chamber were summarized in **Table 1**. The
175 intensity of the UVA and UVB was monitored by meteorological ecological
176 environment monitoring system (Jinzhou Sunshine Technology Co. Ltd. China). Airmo
177 VOC online analyzer (GC-866, Chromato-sud, France) was used to detect the parent
178 VOCs concentrations in the chamber. Its detection limit was less than 1.0 ppb. The

179 VOCs concentrations were also monitored by a gas chromatography mass spectrometer
 180 (GC-MS, 7890A/5975C, Agilent) coupled with a model 7100 preconcentrator (Entech
 181 Instruments Inc., USA). The formed aldehyde and ketone were collected by a custom-
 182 made Aldehyde Ketone Sampler, and then the samples were analyzed by a high
 183 performance liquid chromatography-UV detector-mass spectrometry (HPLC-UV-MS;
 184 SHIMADZU, Japan, LC20AD/SPD-20A; ABSCIEX, USA, API 3200). The aerosols
 185 formed in the chamber were collected by a low flow sampler (LV 40BW, Sibata
 186 Scientific Technology Ltd., Soka, Japan) with a sample speed of 5 L/min. High
 187 performance liquid chromatography mass spectrometry (HPLC-MS, SHIMADZU,
 188 LC20A; ABsciex API3200) and high resolution electrospray ionization time-of-flight
 189 mass spectrometry (ESI-TOF-MS, micrOTOF II, Bruker) were used to detect the
 190 chemical composition of the formed aerosols. The aerosol particle size distribution was
 191 detected by a scanning mobility particle sizer (SMPS), which composed of an
 192 electrostatic classifier (EC, Model 3080, TSI Inc., USA), a differential mobility
 193 analyzer (DMA, Model 3081, TSI Inc., USA) and a condensation particle counter (CPC,
 194 Model 3772, TSI Inc., USA). The flow rates of sheath and aerosol flow were set to 3.0
 195 and 0.3 L/min, respectively, allowing for a size distribution scan ranging from 15.1 to
 196 661.2 nm within 120 s. The aerosol particles were also monitored by a nano-scanning
 197 mobility particle sizer (nano-SMPS, TSI3938E57), which was composed of an
 198 electrostatic classifier (EC, Model 3082, TSI Inc., USA), a differential mobility
 199 analyzer (DMA, Model 3086, TSI Inc., USA), a Nano Enhancer (Model 3757), and a
 200 condensation particle counter (CPC, Model 3750, TSI Inc., USA). The flow rates of
 201 sheath and aerosol flow were set to 25 and 2.5 L/min, respectively, allowing for a size
 202 distribution scan ranging from 1 to 30.5 nm within 60 s. The temperature and relative
 203 humidity inside the chamber were monitored by industrial temperature and humidity
 204 transmitter (CWS16, CCY11, Beijing Star Sensor Technology Co., LTD. China).

205 **Table 1.** Overview of Instruments of the CRAES Chamber.

Instrument	Manufacturer	Measured Parameters	Accuracy
SO ₂ analyzer	EC 9850, ECOTECH, Australia	SO ₂ concentration	0.5 ppb
O ₃ analyzer	EC 9830, ECOTECH, Australia	O ₃ concentration	0.5 ppb

NO _x analyzer	EC 9841, ECOTECH, Australia	NO _x concentration	0.5 ppb
CO analyzer	EC 9810, ECOTECH, Australia	CO concentration	50 ppb
AirmoVOC online analyzer	GC-866, Chromato-sud, France	VOC concentrations	<1.0 ppb
Long-path FTIR	NICOLET6700, Thermofisher, USA	Infrared absorption spectrum	0.09 cm ⁻¹
Aldehyde Ketone Sampler	Custom-made	Collect the aldehyde and ketone	40 ppb
SMPS	TSI Inc. USA	Particle size distribution (15-660 nm)	± 10%
nano-SMPS	TSI Inc. USA	Particle size distribution (1-30.5 nm)	± 10%
Low Flow Sampler	LV 40BW, Sibata Scientific Technology Ltd., Soka, Japan	Collect the aerosol particles	--
HPLC-UV-MS	LC20AD/SPD-20A, SHIMADZU, Japan; API 3200, ABSCIEX, USA	Chemical compositions of the aerosols	1.0 ppt
Industrial Transmitter	Beijing Star Sensor Technology Co., LTD.	Temperature, Relative Humidity, Differential Pressure	--
Meteorological Ecological Environment Monitoring System	Jinzhou Sunshine Technology Co. Ltd	UVA, UVB	--
J(NO ₂) filter radiometer	METCON, Germany	photolysis rate of NO ₂ (280~420nm)	1.5×10 ⁻⁶ sec ⁻¹ /mV

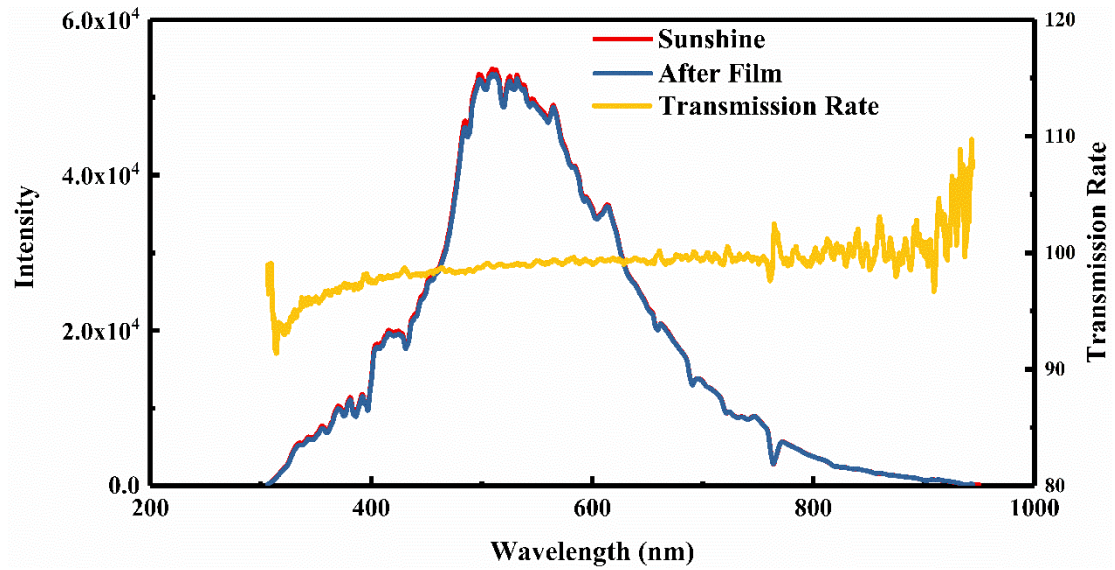
206 2. Characterization Experiments

207 In order to verify the smog chamber's utility, a series of characterization experiments
 208 were performed, including the light transmission of the Teflon film, the mixing ability,
 209 the background experiments (zero air, zero air +NO_x), and wall losses of gaseous
 210 pollutants and particles.

211 2.1 Light Transmission

212 The light densities of the solar radiation before and after the Teflon film were
 213 detected by an irradiation spectrometer (Jaz spectral sensing suite, Ocean Optics Inc.,
 214 USA), and then the light transmission of the new Teflon film was calculated.

215 **Fig. 2** showed the transmission rate of the full solar spectrum for the Teflon film.
 216 The transmission rate was above 90% at the wavelength range of 350-900 nm. The solar
 217 radiation spectra were almost identical before and after the film, which showed that this
 218 film was suitable for the Teflon reactor of the smog chamber.

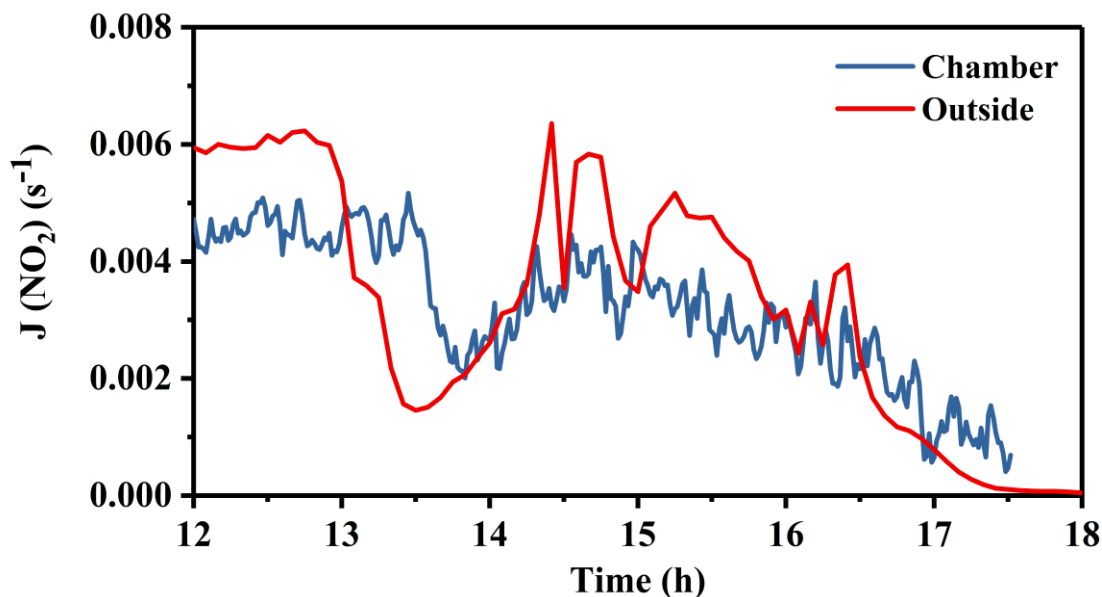


219
220 **Fig. 2.** Ultraviolet-visible transmission spectra of the Teflon film.

221 The light transmission of this chamber were also detected by comparing the NO₂
222 photolysis rate inside and outside the chamber. The NO₂ photolysis rate inside the
223 chamber was estimated by steady-state actinometry (Wang et al., 2015). NO₂ was
224 injected into the chamber and irradiated, and the resulting ozone, NO₂, and NO mixing
225 ratios were measured. The photolysis rate constant, J(NO₂), was then estimated as the
226 following equation:

$$227 \quad J = k_1[O_3][NO]/[NO_2] \quad (1)$$

228 where k_1 (cm³/molecule/sec) was the rate constant of NO and ozone reaction. The
229 measured J(NO₂) inside the chamber was compared to the NO₂ photolysis rate outside
230 the chamber, and the results were shown in **Fig. 3**. Results showed that the NO₂
231 photolysis rate inside the chamber was close to that of natural sunlight.

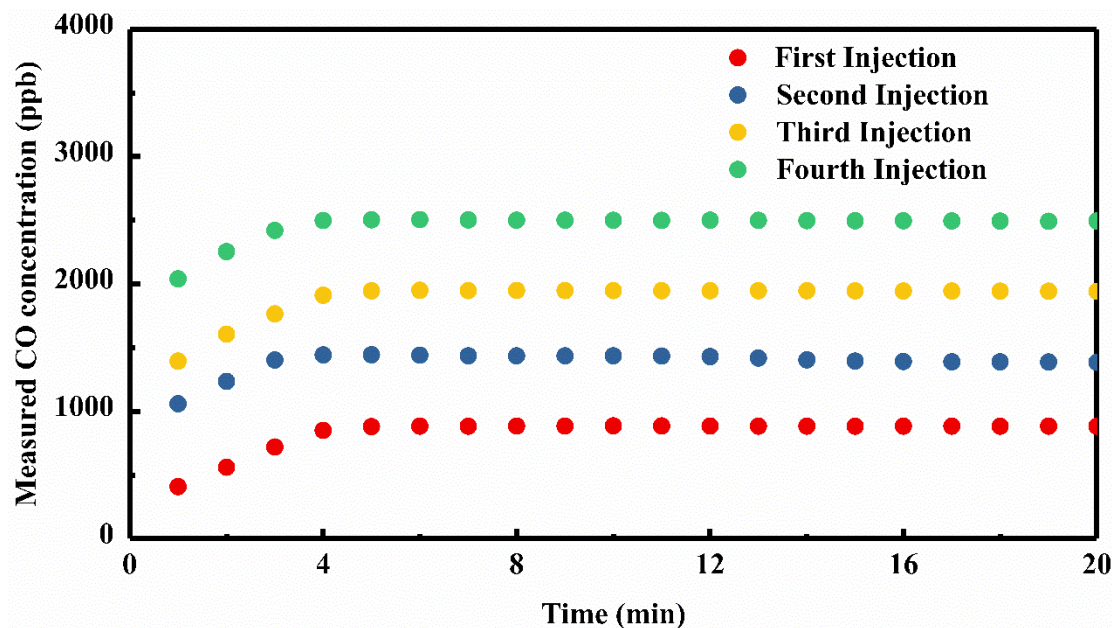


232
233 **Fig. 3.** The NO_2 photolysis rate inside and outside the chamber.

234 **2.2 Mixing Ability**

235 The mixing ability of the chamber was characterized by the length of time when
 236 the gas concentration got stable. Generally, the shorter mixing time referred to the better
 237 mixing ability of the chamber. Carbon monoxide (CO) was used as the tracer to detect
 238 the mixing ability of gaseous species inside the chamber. A known volume of CO gas
 239 was injected into the chamber by cylinder. The injection line was located in the middle
 240 of the chamber. Three high-speed fans were placed at the opposite corner of the
 241 chamber: one bracket was equipped with a vertical blown fan, and one bracket was
 242 equipped with two horizontal blown fans. The brackets supporting the fans were all
 243 covered with Teflon films. The CO concentration was measured by an EC 9810 CO
 244 analyzer (ECOTECH, Australia) with a detection limit of 50 ppb.

245 As revealed by **Fig. 4**, the CO gas entering the chamber could be mixed evenly
 246 within four min for the four injections. The mixing time was very short compared to
 247 the entire experimental process (usually several hours). This showed the good mixing
 248 ability of the chamber for experiments.



249

250 Fig. 4. Measured carbon monoxide concentration as a function of time in four injections.

251 3. Preliminary Application Experiments

252 3.1 Background Experiments

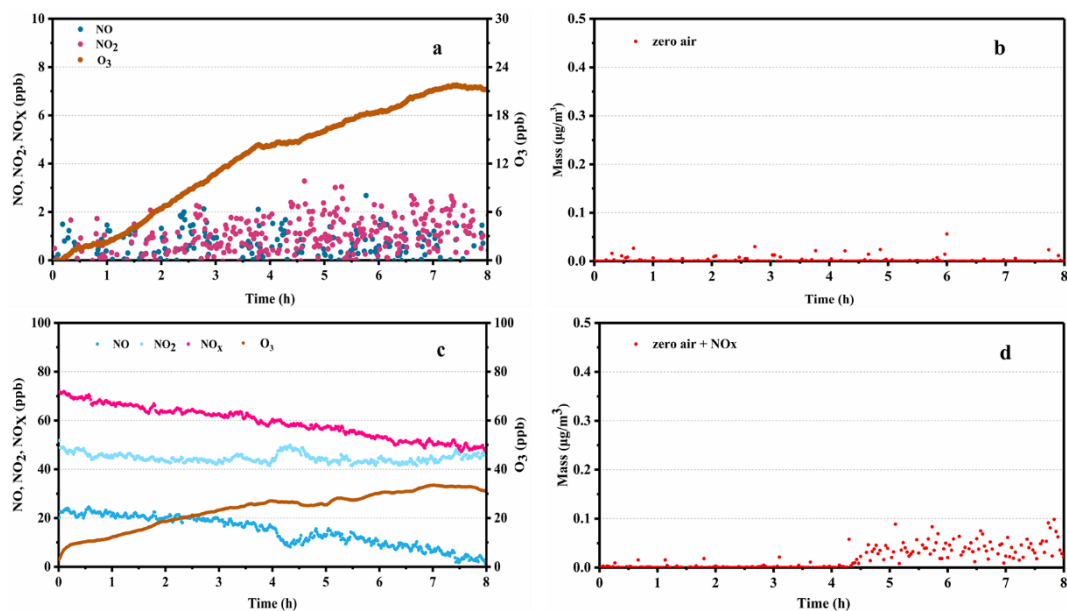
253 In order to minimize the existence of organic impurities desorbing from Teflon
 254 films (Kelly, 1982), the newly-made reactor was exposed to sunlight for 10 hours with
 255 zero air containing 1.5-2 ppm of ozone. Then the chamber was flushed for 24 hours
 256 with zero air. After the above protocols, the chamber filled with zero air was kept in the
 257 dark for more than 12 hours, and no measurable organic impurities was detected by the
 258 Airmo VOC online analyzer. Then the chamber filled with zero air or zero air + NO_x
 259 was exposed to sunlight for 8 hours. The concentrations of ozone, NO, and NO₂ were
 260 measured by EC 9830 ozone analyzer and EC 9841 NO_x analyzer (Ecotech, Australia).
 261 The detection limit of ozone and NO_x were both 0.5 ppb. The aerosol particle size
 262 distribution was detected by a SMPS.

263 The gas analyzers above were calibrated weekly by gas dilution calibration system
 264 (4010 Gas Dilution Calibrator and Model 1001 Zero Air Source, Sabio) with certified
 265 cylinders of gases. The NO, NO₂ and CO gases ($\geq 99\%$) were commercially available,
 266 and they were used without further purification. Ozone was generated by a commercial
 267 ozone generator (VMUS-4, Azco Industries Ltd, Canada), which connected the oxygen
 268 cylinder through the Teflon tube. The concentration of generated ozone could be

269 estimated based on the oxygen flow rate and time through the ozone generator.

270 **Fig. 5a and b** showed the concentration of NO, NO₂, ozone and mass of formed
271 particles for background experiments with only zero air. NO concentration was in the
272 range of 0-1 ppb with no detectable increase, while NO₂ was in the range of 0-2 ppb
273 with a slightly increasing trend, which was probably due to the release from the Teflon
274 films. Concentration of ozone increased slowly with the sunlight irradiation, up to 21
275 ppb. This was likely due to the irradiation of the purified matrix air, and was consistent
276 with the previous reported data (Grosjean, 1985). As shown in Fig 4b, the formation of
277 particles was negligible (less than 0.01 μg m⁻³).

278 The chamber filled with zero air and 71 ppb NO_x was exposed to sunlight
279 irradiation for 8 hours. As shown in **Fig. 5c and d**, concentration of NO_x slightly
280 decreased as the illumination time increases, while ozone concentration increased and
281 reached 32 ppb when the chamber was closed. After 4 h of sunlight irradiation, a small
282 amount of particles was formed, which might be from the reaction of OH radicals
283 (from NO_x cycles) with organic impurities desorbed from the Teflon films. However,
284 the particle mass concentration here (< 0.1 μg m⁻³) was much less than the particles
285 produced by reactions of volatile organic compounds discussed below.



286

287 **Fig. 5.** NO, NO₂, NO_x, and ozone concentration as a function of sunlight irradiation time with
288 zero air (a) and with zero air + NO_x (c); Mass concentration of formed particles as a function of
289 sunlight irradiation time with zero air (b) and with zero air + NO_x (d).

290 **3.2 Wall Loss of Gaseous Pollutants**

291 In the CRAES chamber, the wall loss of propene, NO, NO₂, and ozone were
 292 evaluated by injecting the gases into the chamber and monitoring their decay with
 293 duration of more than 8 hours in the dark. The wall loss rates of the gaseous pollutants
 294 were obtained by treating the gas wall losses as first order process. The temperature and
 295 relative humidity conditions during the measurement processes were 20-29 °C and less
 296 than 7%, respectively. All wall loss experiments were performed with initial
 297 concentration ranging from 80 ppb to 400 ppb.

298 As shown in **Table 2**, the wall loss rates of NO, NO₂, ozone and propene were
 299 $0.65 \times 10^{-4} \text{ min}^{-1}$, $1.01 \times 10^{-4} \text{ min}^{-1}$, $2.65 \times 10^{-4} \text{ min}^{-1}$, and $0.09 \times 10^{-4} \text{ min}^{-1}$, respectively.
 300 The wall loss rates of interested gaseous species were all within the value ranges of
 301 previous data for chambers facilities constructed from Teflon films (Bloss et al., 2005;
 302 Grosjean, 1985; Metzger et al., 2008; Wang et al., 2015; Wang et al., 2014). For the
 303 relative high wall loss rate of ozone, it might indicate the permeability of the film, and
 304 ozone might react with the reactive compounds for its high reactivity. While for propene,
 305 its wall loss rate was nearly negligible, which was consistent with the reported values:
 306 for GIG-CAS (Wang et al., 2014) smog chamber, no wall loss was detected; Wu et al.
 307 (2007) calculated the wall loss rate as $0.066 \times 10^{-4} \text{ min}^{-1}$ in a 2 m³ Teflon smog chamber;
 308 and for ICCAS (Wang et al., 2015) smog chamber, the wall loss rates were (0.30-0.31)
 309 $\times 10^{-4} \text{ min}^{-1}$, respectively.

310 **Table 2.** Summary of wall loss rates of gaseous pollutants in CRAES smog chamber and comparison
 311 with other chamber facilities.

Species	Wall Loss Rate ($\times 10^{-4} \text{ min}^{-1}$)						
	CRAES	GIG-CAS ^a	ERT ^b	EUPHORE ^c	ICCAS ^d		PSI ^e
	56 m ³	30 m ³	80 m ³	200 m ³	5×2 m ³		27 m ³
					right	left	
C ₃ H ₆	0.09	ND ^f	NA ^g	NA	0.31	0.3	NA
O ₃	2.65	1.31±0.24	1.3±0.9	1.8	3.1	2.5	1.2-4.8
NO	0.65	1.41±0.40	0-2.0	NA	3.1	3.0	NA
NO ₂	1.01	1.39±0.68	0-8.2	NA	4.5	3.8	0.13-2.52

312 a: Wang et al. (2014); b: Grosjean (1985); c: Bloss et al. (2005); d: Wang et al. (2015); e: Metzger

313 et al. (2008); f: Not detectable; g: Not applicable

314 **3.3 Wall Loss of Particles**

315 The particles inside the chamber could deposit on the chamber walls with the result
316 of turbulent, Brownian diffusion, gravitational sedimentation as a function of the
317 particle size. The wall loss rates of particles were obtained by treating the wall loss as
318 a first-order process, and the particle loss coefficient K_{dep} could be expressed as
319 following equation:

$$320 \quad \frac{dN(d_p)}{dt} = -K_{dep}(d_p)N(d_p) \quad (2)$$

321 where $N(d_p)$ was the number concentration of the particles, and $K_{dep}(d_p)$ was the loss
322 coefficient of particles in the diameter d_p .

323 Ammonium sulfate particles were used as a reference aerosol to measure the
324 particle wall losses. Ammonium sulfate solution was atomized with an atomizer (TSI,
325 Model 3079A, TSI Inc., USA), then the formed particles were passed through a
326 diffusion dryer and a neutralizer (Model 3088, TSI Inc., USA) before introducing into
327 the reactor.

328 The wall loss rate of ammonium sulfate was shown in **Table 3** and **Fig. 6**. As shown
329 in **Table 3**, the overall number wall loss rate K_{dep} was 0.23 h^{-1} , which led to a lifetime
330 of 4.4 h for particles. While for particles in the diameter range from 100 to 600 nm, as
331 shown in **Fig. 6b**, K_{dep} were determined to be in the range of $0.186\text{-}0.30 \text{ h}^{-1}$. The
332 relationship between K_{dep} and d_p was determined by optimization of four parameters (a ,
333 b , c , d) in the following equation:

$$334 \quad K_{dep}(d_p) = ad_p^b + \frac{c}{d_p^d} \quad (3)$$

335 where parameters a , b , c and d were optimized to be 6.34718×10^{-6} , 1.55745, 6.38387,
336 and 0.66596, respectively.

337 As shown in **Table 3**, the wall loss rate for the particles in different chambers were
338 various, this might due to the different environmental conditions insider the chamber
339 facilities. In addition, the relationship between K_{dep} and d_p of an aerosol in a cubic vessel
340 were theoretically expressed by Corner and Pendlebury (1951), gravitational settling
341 and diffusion are considered:

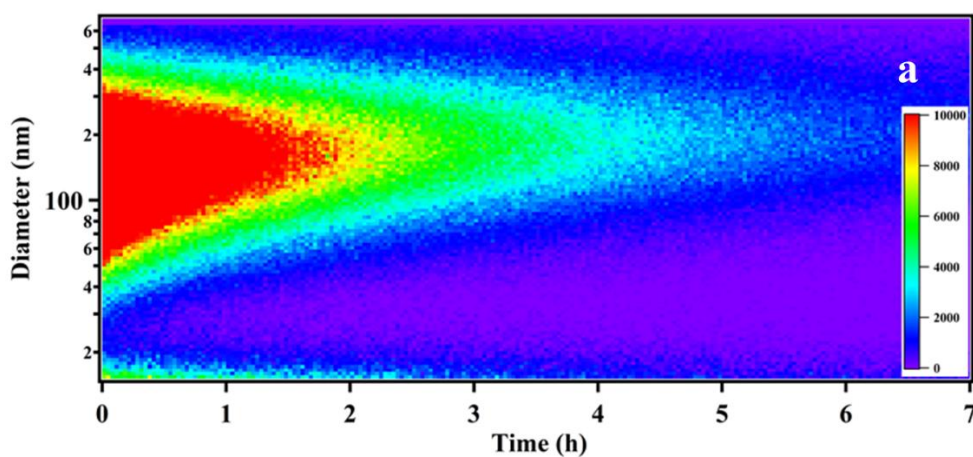
342
$$K_{dep} = \frac{1}{100} \left[\frac{6\sqrt{K_e D}}{\pi} + V \coth \frac{V\pi}{4\sqrt{K_e D}} \right] \quad (4)$$

343 where D , K_e , and V were the Brownian diffusivity, a constant for eddy diffusion, and
 344 the terminal settling velocity, respectively.

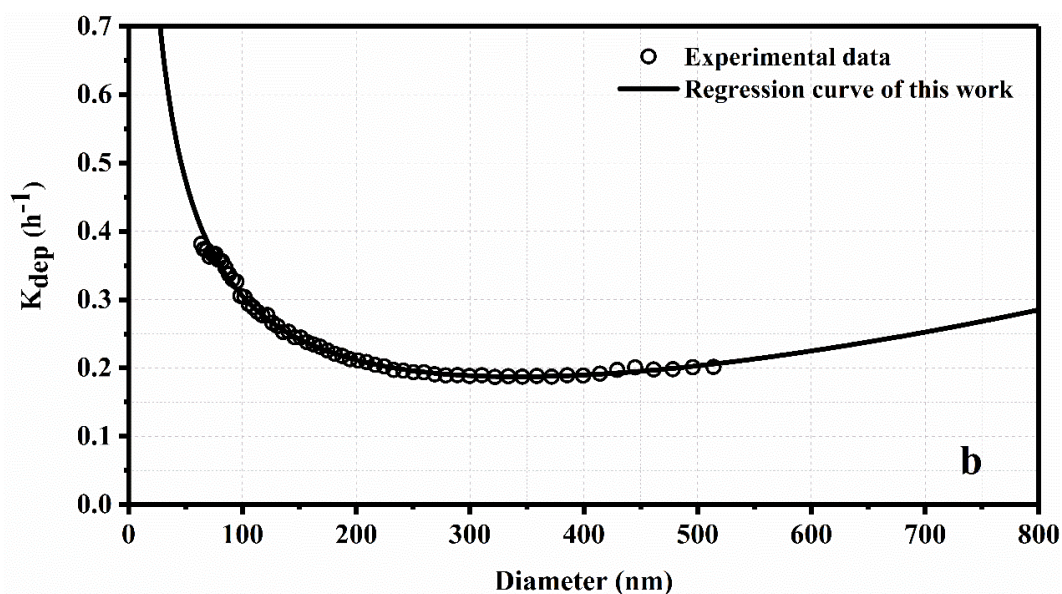
345 As mentioned above, two high-speed fans were located insider the chamber, which
 346 would affect the eddy diffusion and vibrate the wall of the chamber. The eddy diffusion
 347 and vibration of the chamber wall were likely to affect the deposition of the aerosol
 348 inside the chamber. For the experiments performed in this smog chamber in future, in
 349 order to reduce the loss of particles, the fans will be turned off after the precursors are
 350 evenly mixed.

351 **Table 3.** Summary of wall loss rates of particles in CRAES smog chamber and comparison with
 352 other chamber facilities.

Chamber	Volume (m ³)	Chamber Materials	Wall Loss Rate (h ⁻¹)	Particle Life Time (h)	References
CRAES	56	FEP	0.23	4.4	This work
GIG-CAS	30	FEP	0.17	5.9	Wang et al. (2014)
PSI	27	FEP	0.21	4.8	Paulsen et al. (2005b)
EUPHORE	200	FEP	0.18	5.6	Martian-Reviejo and Wirtz (2005)
ICCAS	5×2	FEP	0.12-0.26	3.8-8.3	Wang et al. (2015)
SAPHIR	270	FEP	0.27	3.7	Rollins et al. (2009)
CMU	12	FEP	0.40	2.5	Donahue et al. (2012)



353



354

355 **Fig. 6.** (a) Number concentration of ammonium sulfate particles as a function of time after its
 356 introduction into the chamber, the color map refers to the number concentration of the particles
 357 ($\#/cm^3$). (b) Particle wall loss rate constants for different particle diameter sizes.

358 **3.4 Preliminary Application Experiments**

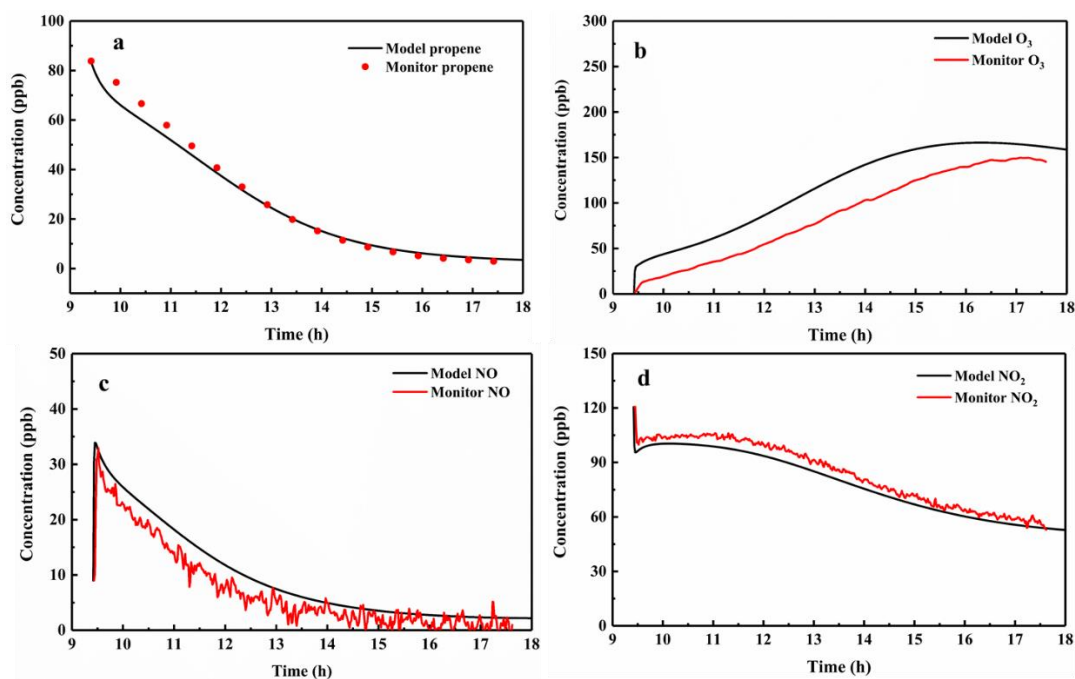
359 On the basis of characterization experiments, we carried out a series of preliminary
 360 applications experiments with the CRAES chamber, including photochemical reactions
 361 of propene- NO_x , SOA yields derived from α -pinene ozonolysis and 1,3,5-
 362 trimethylbenzene (1,3,5-TMB)- NO_x photo-oxidation.

363 **3.4.1 Propene- NO_x Experiments**

364 The propene- NO_x experiments were widely used to evaluate the ability of the smog
 365 chamber to test the chemical mechanisms (Wang et al., 2015; Wang et al., 2014). The
 366 propene- NO_x experiment was performed in the chamber close to real atmosphere. The
 367 initial concentration of propene, NO, NO_2 , and ozone were 83, 9, 120, and 2 ppb,
 368 respectively. And the HONO concentration was 8 ppb. The photolysis rate of NO_2 was
 369 measured with $J(NO_2)$ filter radiometer (METCON, Germany). The chemical
 370 mechanism of propene from the Master Chemical Mechanism (MCM) version 3.3.1
 371 was applied to simulate the propene oxidation, which was operated with Facsimile. The
 372 experiments were compared with the simulation results.

373 **Fig. 7** showed the concentration-time profiles of monitored and simulated propene,
 374 NO, NO_2 , and ozone in propene- NO_x experiment. The wall loss rates of propene, NO,

375 NO₂, and ozone obtained in Sect 3.4 were added in the model. As revealed in **Fig. 7**,
 376 good agreements were obtained for propene, NO, and NO₂, while the concentration of
 377 ozone was little over-predicted, which was also observed by previous studies, e.g.,
 378 Zador et al. (2005), Metzger et al. (2008), and Bloss et al. (2005). The results above
 379 showed that this chamber can provide valid data for gas-phase photochemical
 380 mechanism.



381

382 **Fig. 7.** Concentration-time profiles of monitored and simulated (a) propene, (b) ozone,
 383 (c) NO, and (d) NO₂ in the propene-NO_x experiment.

384 3.4.2 SOA Yields

385 A series of α -pinene ozonolysis and 1,3,5-trimethylbenzene (1,3,5-TMB)-NO_x
 386 photochemical experiments were carried in the CRAES chamber to verify its
 387 performance in studying the formation of SOA. Temperature and seed effect on the
 388 SOA yields were also investigated. All these experiments were carried out under dry
 389 conditions.

390 The aerosol yield Y was defined as the fraction of a reactive organic gas (ROG) that
 391 was converted to aerosol, which was calculated by the following equation(Odum et al.,
 392 1996):

$$393 Y = \frac{\Delta M_o}{\Delta ROG} \quad (5)$$

394 where ΔM_o was the aerosol mass concentration ($\mu\text{g}/\text{m}^3$) produced from a given amount
395 of *ROG*, and ΔROG was the mass concentration ($\mu\text{g}/\text{m}^3$) of reacted precursor.

396 The two-product model was applied to simulate the SOA yield formed in the
397 chamber, and it was calculated based on the following equation (Odum et al., 1996)
398 (Odum et al., 1996):

$$399 \quad Y = \sum_i Y_i = M_o \sum_i \left(\frac{\alpha_i K_{om,i}}{1 + K_{om,i} M_o} \right) = M_o \left(\frac{\alpha_1 K_{om,1}}{1 + K_{om,1} M_o} + \frac{\alpha_2 K_{om,2}}{1 + K_{om,2} M_o} \right) \quad (6)$$

400 where Y_i was the yield of one individual product, α_i was the proportionality constant
401 basing on the total concentration of product i , $K_{om,i}$ was the partitioning coefficient
402 basing on the organic mass concentration of species i , M_o was the overall aerosol mass
403 concentration.

404 The SOA yield was the result after particle and vapor wall loss correction. The
405 correction coefficient of the particle wall loss was calculated based on the loss after the
406 SOA mass reaches the maximum value. The details of the vapor wall loss of this
407 chamber were introduced in the Supporting Information. Briefly, as shown in **Table S2**,
408 both the temperature and seed could affect the vapor wall loss, the presence of seed in
409 the reaction system could decrease the vapor wall loss, and the increase of temperature
410 of the reaction system could decrease the vapor wall loss. Meanwhile, the vapor wall
411 loss of different reaction systems was also different.

412 **3.4.2.1 α -pinene ozonolysis experiments**

413 Four α -pinene ozonolysis experiments were performed under dry conditions. The
414 aerosol density was assumed to be $1 \text{ g}/\text{cm}^3$, which was referred to the literature values
415 (Wang et al., 2014; Wirtz and Martin-Reviejo, 2003). The details of the experimental
416 conditions were shown in **Table 4**.

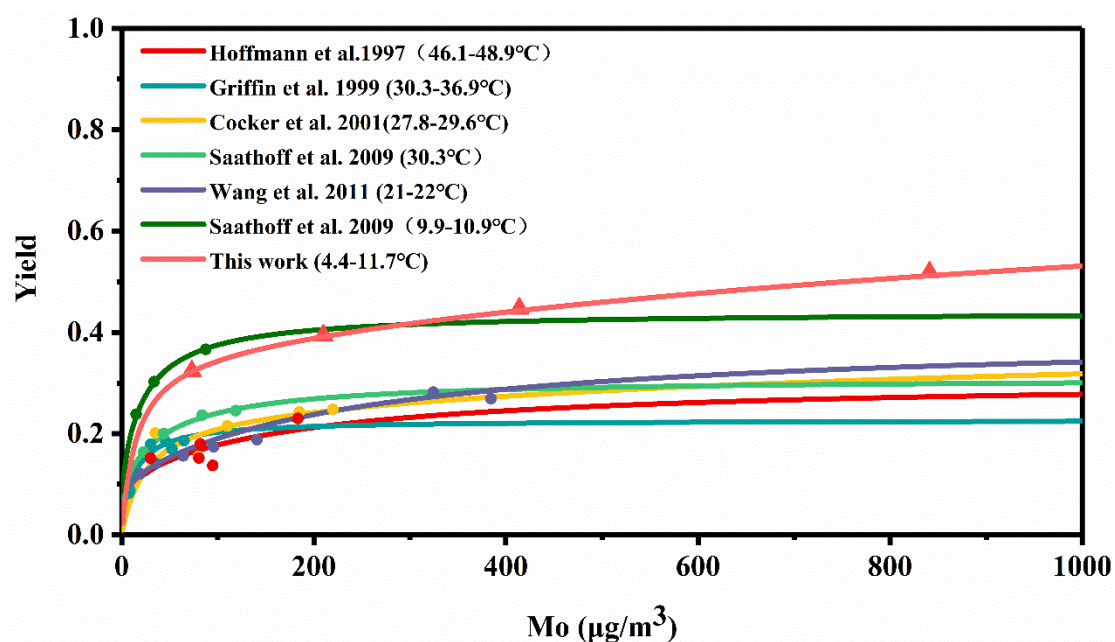
417 The SOA yields of α -pinene ozonolysis was underestimated by a factor of
418 0.32–0.78 fold when considering vapor wall loss. After considering the vapor and
419 particle wall loss, the optimal parameters α_1 , α_2 , $K_{om,1}$, and $K_{om,2}$ of this work were
420 0.3643, 0.4590, 0.0674, and 0.0006, respectively. The yield curve fitted well with the
421 experiments data. SOA yields of α -pinene ozonolysis experiments of this work and data
422 from other chamber facilities were shown in **Fig. 8**. The experiments in this work were

423 performed under low temperature (4.4-11.7°C), and the yields were comparable with the
 424 yield data obtained under similar temperature condition (9.9-10.9 °C) (Saathoff et al.,
 425 2009). Meanwhile, according to the yield values reported in other previous studies (the
 426 temperature conditions were higher than this work) (Cocker et al., 2001; Griffin et al.,
 427 1999; Hoffmann et al., 1997; Saathoff et al., 2009; Wang et al., 2015), it could be seen
 428 that temperature had important influence on the SOA yield, that a decrease in
 429 temperature could enhance the SOA yield

430 **Table 4.** Experimental conditions and resulting SOA data of the α -pinene ozonolysis
 431 experiments.

Date	Initial VOC (ppb)	Initial O ₃ (ppb)	M ₀ (μg/m ³)	Temp. (°C)	SOA yield (%)
2019.12.11	394	500	841	4.4-8.8	51.83
2019.12.13	250	390	414	6.6-11.7	44.72
2019.12.16	175	307	210	6.2-6.8	39.46
2019.12.18	95	370	73	4.7-8.6	32.31

432



433

434 **Fig. 8.** SOA yield of α -pinene ozonolysis experiments and comparison with other
 435 chamber facilities, the unit density (1 g/cm³) was used for all the experiments when
 436 comparing our results with those from previous studies.

437 3.4.2.2 1,3,5-TMB-NO_x photochemical experiments

438 For 1,3,5-TMB-NO_x photochemical experiments, the density of the formed

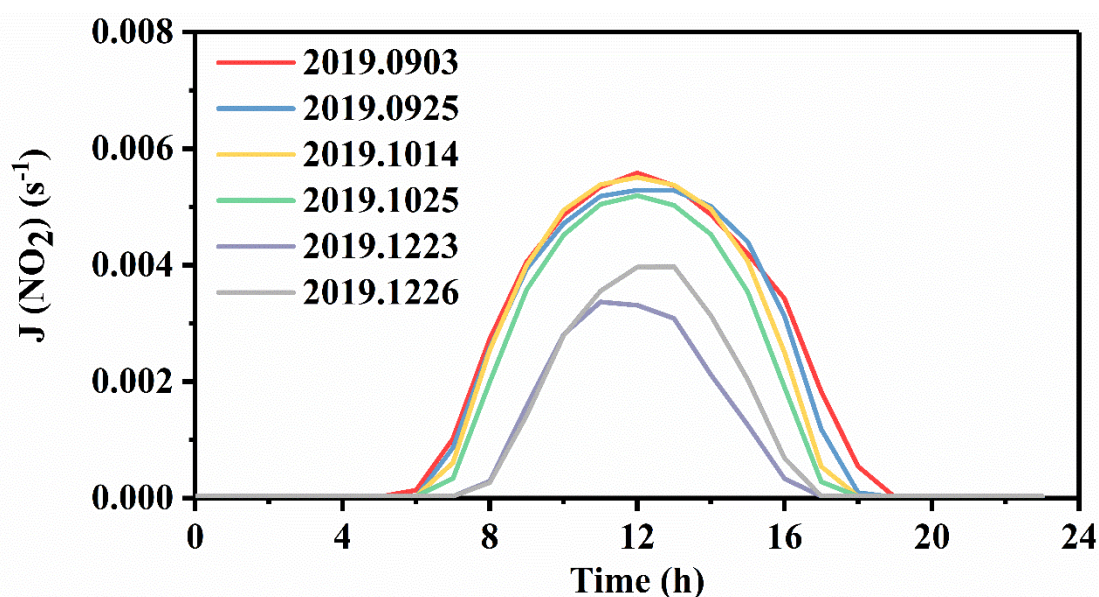
439 aerosols was assumed to be 1.4 g/cm^3 (Nakao et al., 2013), and the details were shown
440 in **Table 5**. In order to obtain the SOA yield more accurately, the vapor wall loss was
441 taken into account. Temperature and seed effect on SOA yield were all considered. As
442 shown in **Table S2**, under same temperature conditions, the presence of seed could
443 reduce timescale associated with reaching gas-particle equilibrium ($\overline{\tau_{g-p}}$), vapor could
444 be more easily partition to the particle phase, and the vapor wall loss could be reduced
445 during the photochemical processes. Under the same seed conditions, temperature
446 increase could reduce the $\overline{\tau_{g-p}}$, and the vapor wall loss would decrease.

447 As shown in **Table 5**, the SOA yields of 1,3,5-TMB-NO_x was in the range of 4.02-
448 5.43% for high temperature unseeded conditions; when the ammonium sulfate seeds
449 were introduced, the yield was increased (7.08%). Under low temperature unseeded
450 condition, the yield was 8.11%, which was higher than that under high temperature
451 condition; when the ammonium sulfate seeds were introduced, the yield was increased
452 to 11.78%. **Fig. 9** showed the photolysis rate of NO₂ ($J(\text{NO}_2)$) of the 1,3,5-TMB-NO_x
453 photochemical experiments. The $J(\text{NO}_2)$ at high temperature (in summer) was similar,
454 and it was also at low temperature (in winter), but the $J(\text{NO}_2)$ in winter was smaller
455 than that in summer. The photolysis rate was positively correlated with the intensity of
456 the photochemical reaction, indicating that the photochemical reaction in winter was
457 weak. However, the SOA yield in winter was higher than that in summer, indicating
458 that temperature was one of the main factors affecting the SOA yield. The results
459 obtained showed that both the temperature and seed could affect the SOA yield, the
460 increase of temperature could lower the SOA yield, while the presence of seed could
461 enhance the SOA yield. Im et al. (2014) reported 1,3,5-TMB SOA yield with the
462 outdoor smog chamber at high temperature unseeded condition, and the yields
463 ($4.9 \pm 0.4 \%$, $3.4 \pm 0.3 \%$) were comparable with the data we obtain under similar
464 condition.

465 According to the vapor wall loss and final SOA yields under various conditions,
466 the seed was suggested to be used in the chamber experiments, as this could minimize
467 the interaction between the gas phase and the chamber walls.

468 **Table 5.** Experimental conditions and resulting SOA data of the 1,3,5-TMB

Experiments	Seed	Initial VOC (ppb)	Initial NO _x (ppb)	VOC/NO _x (ppbC/ppb)	Temp. (°C)	SOA yield (%)
2019.0903	--	105	211	4.26	24-43	4.02
2019.0925	--	180	197	8.22	24-43	5.43
2019.1014	--	170	250	6.19	12-30	5.21
2019.1025	AS	175	285	4.32	12-28	7.08
2019.1223	--	165	795	1.87	2-17	8.11
2019.1226	AS	167	820	1.83	4-19	11.78
Im et al. (2014)	--	160	243	5.14	17-44	4.9±0.4
Im et al. (2014)	--	165	113	11.12	17-44	3.4±0.3



470

471 **Fig. 9** Photolysis rate of NO₂ ($J(\text{NO}_2)$) of the 1,3,5-TMB-NO_x photochemical experiments.472 **4. Conclusions**

473 We have constructed and characterized the CRAES chamber in this study. To our
 474 knowledge, it is the only large-scale outdoor chamber in China at present. A series of
 475 characterization experiments were performed, including the light transmission of the
 476 FEP Teflon film, the mixing ability of the chamber, the background experiments (zero
 477 air, zero air +NO_x), and wall loss of gaseous pollutants and particles. The transmission
 478 rate was above 90% for the wavelength range 350-900 nm; the mixing time was very
 479 short (within 4 min) compared to the entire experimental process (usually several hours);
 480 under both zero air and zero air + NO_x background experiments, negligible gases and
 481 particles were released from the film or formed; the wall loss rates of propene, ozone,
 482 NO, and NO₂ were 0.09×10^{-4} , 2.65×10^{-4} , 0.65×10^{-4} , and $1.01 \times 10^{-4} \text{ min}^{-1}$,

483 respectively; for inorganic ammonium sulfate particles, the wall loss rate was 0.23 h^{-1} ,
484 resulting a lifetime of 4.4 h.

485 The propene- NO_x photo-oxidation reaction was performed and the results were
486 compared with the MCM modelling results, which showed good agreement and meant
487 that it could provide valid data in studying gas-phase photochemistry reactions. For
488 dark reactions, α -pinene- O_3 experiments were performed and two product model was
489 used, the SOA yields fitted well with the model curve. For photochemical reactions,
490 1,3,5-trimethylbenzene- NO_x experiments were performed, the SOA yields were
491 compared with the data obtained from other chamber facilities. The dark and
492 photochemical reactions showed that temperature and seed could have important effect
493 on the vapor wall loss and SOA yields. Higher temperature and the presence of seed
494 could reduce the vapor wall loss, the seed were suggested to be used in the chamber to
495 reduce the interaction between the gas phase and chamber walls; SOA yield was found
496 to depend inversely on temperature, and the presence of seed could increase SOA yield.

497 Overall, the results of characterization and preliminary experiments demonstrated
498 that the chamber was in good condition and could be used to provide simulation data
499 with high quality for gas-phase chemistry and secondary air pollutants formation under
500 conditions close to the real atmosphere.

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518

519 **Appendix A. Supplementary data**

520 Supplementary data associated with this article can be found in the online version at
521 xxxxxxx

522

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