

**A Steady State Continuous Flow Chamber
for the Study of Daytime and Nighttime Chemistry
under Atmospherically Relevant NO levels**

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1 **Abstract**

2 Experiments performed in laboratory chambers have contributed significantly to the
3 understanding of the fundamental kinetics and mechanisms of the chemical reactions occurring
4 in the atmosphere. Two chemical regimes, classified as ‘high-NO’ versus ‘zero-NO’ conditions,
5 have been extensively studied in previous chamber experiments. Results derived from these two
6 chemical scenarios are widely parameterized in chemical transport models to represent key
7 atmospheric processes in urban and pristine environments. As the anthropogenic NO_x emissions
8 in the United States have decreased remarkably in the past few decades, the classic ‘high-NO’
9 and ‘zero-NO’ conditions are no longer applicable to many regions that are constantly impacted
10 by both polluted and background air masses. We present here the development and
11 characterization of the NCAR Atmospheric Simulation Chamber, which is operated in steady
12 state continuous flow mode for the study of atmospheric chemistry under ‘intermediate NO’
13 conditions. This particular chemical regime is characterized by constant sub-ppb levels of NO
14 and can be created in the chamber by precise control of the inflow NO concentration and the
15 ratio of chamber mixing to residence timescales. Over the range of conditions achievable in the
16 chamber, the lifetime of peroxy radicals (RO₂), a key intermediate from the atmospheric
17 degradation of volatile organic compounds (VOCs), can be extended to several minutes, and a
18 diverse array of reaction pathways, including unimolecular pathways and bimolecular reactions
19 with NO and HO₂, can thus be explored. Characterization experiments under photolytic and dark
20 conditions were performed and, in conjunction with model predictions, provide a basis for
21 interpretation of prevailing atmospheric processes in environments with intertwined biogenic and
22 anthropogenic activities. We demonstrate the proof of concept of the steady state continuous
23 flow chamber operation through measurements of major first-generation products, methacrolein
24 (MACR) and methyl vinyl ketone (MVK), from OH- and NO₃-initiated oxidation of isoprene.

25 1. Introduction

26 With the discovery of the role of biogenic volatile organic compounds (BVOCs) in urban
27 photochemical smog (Chameides et al., 1988), the interactions of biogenic emissions with man-
28 made pollution and their subsequent impact on the atmosphere's oxidative capacity and aerosol
29 burden have received extensive studies in the ensuing decades (De Gouw et al., 2005; Ng et al.,
30 2007; Goldstein et al., 2009; Surratt et al., 2010; Rollins et al., 2012; Shilling et al., 2013; Xu et
31 al., 2015). A particular research focus has been understanding the influence of nitrogen oxides
32 ($\text{NO}_x = \text{NO} + \text{NO}_2$) on the atmospheric oxidation cascades of BVOCs, which ultimately generate
33 ozone (O_3) and secondary organic aerosols (SOA). Nitrogen oxides alter the distribution of
34 BVOC oxidation products by primarily modulating the fate of peroxy radicals (RO_2), a key
35 intermediate produced from the atmospheric degradation of VOCs by major oxidants including
36 OH, O_3 , and NO_3 . In the absence of NO_x , RO_2 reacts predominantly with HO_2 radicals yielding
37 organic peroxides and other products, and to a lesser extent, undergoes self/cross-reactions
38 yielding carbonyls, alcohols, and multifunctional species. In the presence of elevated NO_x , the
39 dominant fate of RO_2 is to react with NO leading to ozone production, and also to organic
40 nitrates. During the night, RO_2 also reacts with NO_3 which is produced by the reaction between
41 O_3 and NO_2 . In addition, reaction of peroxyacyl radicals ($\text{RC}(\text{O})\text{O}_2$) with NO_2 produces
42 peroxyacyl nitrates that constitute a large reservoir of reactive nitrogen and a potentially
43 important SOA precursor (Singh and Hanst, 1981; Nguyen et al., 2015).

44 Much of our understanding of the extent to which NO_x mediates the oxidation chemistry of
45 BVOC in the atmosphere has been derived from measurements in laboratory chambers, where
46 two extreme experimental conditions, i.e., 'high-NO' vs. 'zero-NO', were mostly performed to
47 examine the reaction pathways of RO_2 radicals (Kroll and Seinfeld, 2008; Orlando and Tyndall,
48 2012; Ziemann and Atkinson, 2012). Results from these two chemical regimes have been widely
49 incorporated into chemical transport models to represent key atmospheric processes in urban and
50 pristine environments, respectively (Kanakidou et al., 2005). In the actual atmosphere, however,
51 the fate of RO_2 radicals is rather more complicated than simply undergoing bimolecular reactions
52 with NO/HO_2 as observed under the two extreme chamber conditions. It has been recently
53 revealed that RO_2 radicals may undergo an internal H-shift followed by sequential O_2 addition,
54 leading to highly oxygenated multifunctional peroxides (Ehn et al., 2014; Jokinen et al., 2015;
55 Kurtén et al., 2015; Kirkby et al., 2016; Zhang et al., 2017). The rate of H-shift largely depends
56 on the thermochemistry of the nascent alkyl radicals and can be reasonably fast, on a time scale
57 of seconds to minutes (Crouse et al., 2013). Further, depending on the stability of the RO_2
58 precursor (alkyl radicals), RO_2 radicals may lose O_2 in competition with bimolecular reactions
59 with NO , NO_3 , RO_2 , and HO_2 . Recent theoretical and laboratory studies have found that the
60 hydroxy peroxy radical conformers produced from isoprene photooxidation decompose readily
61 to allylic radicals on time scales faster than bimolecular processes under atmospherically relevant
62 NO/HO_2 levels (tens to hundreds of parts per trillion by volume). This highly dynamic system
63 leads to formation of distinctly different products that depend on the concentrations of
64 bimolecular reaction partners from those observed in chamber experiments under 'high-NO' and
65 'zero-NO' conditions (Teng et al., 2017).

66 Anthropogenic NO_x emissions in the United States have decreased remarkably in the past
67 few decades (EPA, 2014), resulting in significant changes in the degradation mechanisms of
68 BVOCs, especially in regions impacted by both background and polluted air masses such as the
69 Southeastern United States. However, the ultimate fate of peroxy radicals in environments with

70 sub-ppb NO levels is still poorly constrained, in part due to a lack of consistent measurements
71 under well controlled conditions. Experimental approaches targeting at a controlled NO level
72 (sub-ppb to ppb) have been introduced over the years. For outdoor chambers, experiments were
73 typically performed by exposing a gas mixture of O₃/NO_x/VOCs or HONO/NO_x/VOCs to natural
74 sunlight (Bloss et al., 2005; Karl et al., 2006). OH radicals were produced either via the
75 photolysis of ozone and subsequent reaction of O(¹D) with H₂O or directly from the photolysis
76 of HONO. NO levels ranging from a few hundreds of ppt to a few ppb over the course of several
77 hours of reactions have been reported. In the absence of any additional supply, NO will be
78 eventually depleted in a closed chamber environment, and the initial ‘moderate-NO’ condition
79 will essentially transfer to the ‘zero-NO’ condition. For indoor chambers, a ‘slow chemistry’
80 scenario initiated by photolyzing methyl nitrite (CH₃ONO) under extremely low UV intensities
81 as the OH radical source ($J_{\text{CH}_3\text{ONO}} \sim 10^{-5} \text{ s}^{-1}$) was created to study the autoxidation chemistry of
82 peroxy radicals produced from isoprene photooxidation (Crouse et al., 2011; Crouse et al.,
83 2012; Teng et al., 2017). The resulting NO and HO₂ mixing ratios are maintained at ~ppt level
84 (CH₃ONO + O₂ + *hν* → HO₂ + NO + HCHO) over the course of several hours of reaction, and
85 the average OH concentration (OH ~ 10⁵ molec cm⁻³) is approximately one order of magnitude
86 lower than that in the typical daytime ambient atmosphere. Another example relates to a recent
87 method development in the Potential Aerosol Mass (PAM) flow tube reactor where nitrous oxide
88 (N₂O) was used to produce ~ppb level of NO (O₃ + *hν* → O₂ + O(¹D); O(¹D) + N₂O → 2NO)
89 (Lambe et al., 2017). Timescales for chemical reactions and gas-particle partitioning are
90 ultimately limited to the mean residence time (~80 s) of the PAM reactor.

91 An alternative experimental platform to the batch-mode chamber and flow tube reactor
92 described above is a well-mixed steady-state chamber with continuous feed of reactants and
93 continuous withdrawal of reactor contents (Shilling et al., 2008). An attribute of the continuous
94 flow steady state chamber is that, by control of the inlet reactant concentrations and the ratio of
95 mixing to residence timescales, it is possible to simulate atmospheric oxidation under stable
96 conditions over a wide range of time periods and chemical scenarios. For example, a steady-state
97 NO level at ~1 ppb was created by the continuously mixed flow chamber operation for the study
98 of isoprene photooxidation chemistry (Liu et al., 2013). In this study, we present the
99 development and characterization of the NCAR Atmospheric Simulation Chamber, which is
100 operated in steady state continuous flow mode for simulating atmospheric daytime and nighttime
101 chemistry over chemical regimes not accessible in static chamber experiments. We focus on
102 establishing an ‘intermediate NO’ regime characterized by a constant steady-state NO level
103 ranging from tens of ppt to a few ppb in the chamber. This particular chemical regime is well
104 suited for the study of atmospheric behavior of RO₂ radicals, as they can survive up to minutes
105 and embrace various reaction possibilities as opposed to reaction with NO, NO₃, HO₂, and RO₂
106 as their dominant fate observed in most batch-mode chamber experiments. We employ the
107 ‘intermediate NO’ regimes to reexamine the daytime and nocturnal chemistry of isoprene
108 through the measurements of two first-generation products, methacrolein (MACR) and methyl
109 vinyl ketone (MVK).

110 2. Experimental

111 2.1 NCAR Atmospheric Simulation Chamber Facilities

112 The NCAR Atmospheric Simulation Chamber consists of a 10 m³ FEP Teflon (0.005” thick)
113 bag that is housed in a cubic enclosure with UV reflective surfaces and a bank of 128 wall-

114 mounted blacklight tubes (32W, Type F32T8/BL). To characterize photolytic conditions in the
115 chamber, irradiance spectra were collected in the wavelength range of 180–600 nm at ~0.8 nm
116 resolution by a custom-built spectroradiometer, as shown in Figure S1 in the Supplement
117 (Petropavlovskikh et al., 2007). Photolysis frequencies were calculated based on the measured
118 downwelling spectral actinic fluxes. The computed photolysis rate of NO₂ ($J_{\text{NO}_2} \sim 1.27 \times 10^{-3} \text{ s}^{-1}$)
119 agrees within 3% with that measured by photolyzing 18.6 ppb NO₂ in the chamber and
120 monitoring the NO production rate. The chamber is equipped with a standard set of
121 measurements, including an integrated temperature and humidity probe (Model 50U, VAISALA,
122 CO) and a Magnehelic differential pressure indicating transmitter (Model 605-11, Dwyer
123 Instruments, IN). The chamber temperature is controlled at 295 K by the building's air
124 conditioning system and increases to 305–306 K under maximum irradiation conditions. The
125 relative humidity of the chamber air is below 10% under dry conditions (the remaining water
126 vapor is generated from methane combustion during the air purification process) and can be
127 varied in the range of ~10–50% by flowing a portion of the purified dry flushing air into the
128 chamber through a temperature-controlled water reservoir. Typical temperature and relative
129 humidity profiles across the chamber under maximum irradiation conditions are given in Figure
130 S1 in the Supplement. The chamber internal pressure is maintained slightly above the ambient
131 pressure to minimize the enclosure air contamination via penetration through the Teflon film.

132 Prior to each experiment, the chamber was flushed with purified dry air from an ultra high
133 purity zero air generator (Model 737, Aadco Instruments, OH) for >12 h until ozone and NO_x
134 levels were below 1 ppb. During the operation of the steady state continuous flow mode, the
135 chamber was constantly flushed with purified dry air at 40 L min⁻¹, which gives an average
136 chamber residence time of 4.17 hours. The incoming and outgoing flows were balanced by a
137 feedback control system that maintains a constant internal pressure of 1.2–4.9×10⁻⁴ atm above
138 the ambient. The chamber is actively mixed by the turbulence created by the 40 L min⁻¹ flushing
139 air. The characteristic mixing time is defined as the time it takes for the measurement signal of a
140 tracer compound (e.g., CO₂ and NO) to stabilize following a pulse injection. The average mixing
141 time in the NCAR chamber was determined to be ~9 min, which is ~4% of the residence time.
142 Under such conditions, the gas/particle-phase composition in the outflow can be assumed
143 identical to that in the well-mixed core of the chamber.

144 To mimic daytime photochemistry in the continuous flow mode, steady-state OH mixing
145 ratio was created by photolyzing hydrogen peroxide (H₂O₂) vapor that was continuously flowing
146 into the chamber ($\text{H}_2\text{O}_2 + h\nu \rightarrow 2\text{OH}$, $J_{\text{H}_2\text{O}_2} \sim 3.93 \times 10^{-7} \text{ s}^{-1}$). Specifically, a 20 mL syringe
147 (NORM-JECT, Henke-Sass Wolf, MA) held on a syringe pump (Model 100, kdScientific, MA)
148 kept at ~4 °C was used to deliver H₂O₂ solution (1–30 wt%, Sigma Aldrich, MO) into a glass
149 bulb that was gently warmed at ~32 °C. The liquid delivery rate was sufficiently slow (100–300
150 μL min⁻¹) that all the H₂O₂ vapor was released into the glass bulb through evaporation of a small
151 droplet hanging on the needle tip. An air stream (5 L/min) swept the H₂O₂ vapor into the
152 chamber, resulting in an H₂O₂ mixing ratio in the range of 600 ppb to 16.22 ppm in the injection
153 flow as a function of the concentration of H₂O₂ aqueous solution used. A spreadsheet (Table S2)
154 for calculating the inflow H₂O₂ mixing ratio using the above input method is provided in the
155 Supplement. As H₂O₂-laden air was continuously entering the chamber, it took approximately
156 three turnover times (~12.5 hr) for the desired H₂O₂ vapor mixing ratio to reach steady state in
157 the chamber. The H₂O₂ vapor concentration in the chamber, though not measured, can be
158 estimated from the steady-state OH mixing ratio derived from the observed exponential decay of

159 a given parent hydrocarbon. Constant NO injection flow was achieved by diluting the gas flow
160 from a concentrated NO cylinder (NO = 133.16 ppm, balance N₂) to a desired mixing ratio
161 (0.1–100 ppb) using a set of mass flow controllers (Tylan FC260 and FC262, Mykrolis Corp.,
162 MA). The lowest steady-state NO level that can be achieved in the chamber is around 30 ppt
163 (unpublished, NCAR). Note that for experiments performed in the absence of any VOC
164 precursor, H₂O₂ and NO were the only two species that were continuously input into the chamber
165 for the establishment of a combination of different photochemical conditions as denoted by the
166 O₃ and NO_x measurements. For the isoprene photooxidation experiments, an isoprene standard
167 (C₅H₈ = 531 ppm, balance N₂) was constantly injected into the chamber and diluted with the
168 flushing air to achieve an inflow concentration of ~20 ppb.

169 To mimic the nighttime chemistry in the continuous flow mode, steady-state NO₃ mixing
170 ratio was created by constantly flowing diluted O₃ and NO air into the chamber (NO+O₃
171 →NO₂+O₂; NO₂+O₃→NO₃+O₂). The NO source can be replaced by NO₂, although the absolute
172 absence of NO does not necessarily represent the actual atmospheric conditions. O₃ was
173 produced by photolyzing O₂ in air at 185 nm using a mercury “Pen-Ray” lamp (UVP LLC, CA).
174 Ozone concentration in the injection flow can be controlled from 3.5 ppb to 457 ppb
175 automatically by adjusting the mercury lamp duty cycle. To study the RO₂+HO₂ pathway,
176 formaldehyde (CH₂O) was input into the chamber along with NO and O₃ to initiate HO₂
177 production (NO₃+CH₂O+O₂→HNO₃+HO₂+CO). Formaldehyde aqueous solution (37 wt%,
178 Sigma Aldrich, MO) was diluted with ultrapure water (Milli-Q, Merck Millipore, MA) to 0.2–1.0
179 wt% and continuously input into the chamber using the same method used for H₂O₂ input
180 described above. It is worth noting that the formaldehyde aqueous solution contains 10–15%
181 methanol as stabilizer to prevent polymerization. The presence of methanol in the chamber does
182 not significantly impact the nocturnal chemistry as it consumes OH and NO₃ radicals to generate
183 formaldehyde and additional HO₂ (CH₃OH+NO₃→HNO₃+CH₂O+HO₂,
184 CH₃OH+OH→H₂O+CH₂O+HO₂) (Atkinson et al., 2006). The use of formaldehyde as an HO₂
185 source mimics closely the atmospheric nighttime conditions in forest environments (Schwantes
186 et al., 2015). To study the NO₃-initiated oxidation of isoprene, an injection flow of diluted
187 isoprene (~10 ppb) was achieved using the procedure described above.

188 2.2 Analytical measurements

189 A suite of instruments was used to monitor gas-phase concentrations in the chamber
190 outflow. O₃ was monitored by absorption spectroscopy with 0.5 ppb detection limit (Model 49,
191 Thermo Scientific, CO). The O₃ monitor was calibrated using an Ozone Primary Standard in the
192 range of 0 to 200 ppb (Model 49i-PS, Thermo Scientific, CO). The O₃ monitor used for chamber
193 experiments was periodically checked with the primary standard and was shown to be stable over
194 long periods of time (less than 1 ppb drift in over 1 year). NO was monitored by
195 chemiluminescence with 0.5 ppb detection limit (Model CLD 88Y, Eco Physics, MI). Zero-point
196 and span calibrations of the NO_x monitor were performed prior to each experiment by supplying
197 the instrument with pure N₂ gas and diluted NO, respectively. Multi-point calibration was
198 performed on a weekly basis and has shown a good stability and linearity in the NO
199 measurement ranging from 1 ppb to 200 ppb. NO_x (NO+NO₂) measurements were performed
200 using a photolytic converter that selectively converts NO₂ to NO upstream of the photo-
201 multiplier tube in the CLD 88Y NO monitor. This converter uses two opposing arrays of UV
202 LEDs shining into a cylindrical quartz mixing tube to achieve approximately 50% conversion of
203 NO₂ to NO per second. The total efficiency for the equipment described here is approximately

204 70% as determined by measuring calibrated NO₂ standards. The sample path always includes
205 the photolytic converter, and typical experiments cycle the power for the LED lights to switch
206 between measuring NO (lights off) and NO_x (lights on). NO₂ concentrations were then
207 determined by subtracting the NO from the adjacent NO_x measurements.

208 A customized Proton Transfer Reaction Quadrupole Mass Spectrometer (PTR-Q-MS) was
209 used to measure volatile organic compounds including isoprene (C₅H₈), methacrolein (MACR,
210 C₄H₆O), and methyl vinyl ketone (MVK, C₄H₆O). The instrument was operated at 2.3 mbar drift
211 pressure and 560 V drift voltage. Measurements reported here were obtained at a sampling rate
212 of 10 Hz. In positive-mode operation, a given analyte [M] undergoes proton transfer reaction,
213 producing an ion of the form [M+H]⁺, that is, isoprene is detected as ion C₅H₉⁺ (*m/z* 69) and
214 MACR and MVK are both detected as ion C₄H₇O⁺ (*m/z* 71). The instrument background was
215 collected by sampling the chamber air for at least 30 min prior to each experiment. Measured ion
216 intensities for isoprene (C₅H₉⁺, *m/z* 69) and MACR and MVK (C₄H₇O⁺, *m/z* 71) were calculated
217 as the signal of each ion (counts per seconds) normalized to the total ion signal of H₃O⁺. The
218 instrument sensitivities towards isoprene, MACR and MVK were calibrated with a mixture of
219 diluted gas standards. The instrument sensitivity towards MACR is identical to that of MVK, and
220 as a result, the sum of MACR and MVK concentration in the sampling air can be calculated by
221 applying one calibration factor to the measured C₄H₇O⁺ (*m/z* 71) signal intensity. Since artifacts
222 in the measured C₄H₇O⁺ signal can be produced through thermal decomposition of isoprene
223 oxidation products, such as the peroxides, nitrates, and epoxides, on contact with hot metal
224 surface (Liu et al., 2013; Nguyen et al., 2014b; Rivera-Rios et al., 2014), a cold-trap system was
225 used to avoid bias in the interpretation of the PTR-MS data. Specifically, a 1 m section of Teflon
226 tubing was submerged in a low temperature ethanol bath (−40±2 °C) that could trap oxidized
227 products less volatile than the authentic MACR and MVK standards after steady state was
228 established in the chamber. The quantification of the sum of MACR and MVK was then based
229 on the PTR-MS measured C₄H₇O⁺ (*m/z* 71) signal downstream of the cold-trap.

230 3. Kinetic Modeling

231 Reaction kinetics and mechanisms for the gas-phase photochemistry were extracted from the
232 Master Chemical Mechanism (MCMv3.3.1, accessible at <http://mcm.leeds.ac.uk/MCM/>). The
233 inorganic reaction scheme includes 21 species and 48 reactions; and the isoprene oxidation
234 system includes 611 species and 1974 reactions. The kinetic schemes were implemented in
235 Matlab (Mathworks) to simulate the temporal profile of a given compound *i* in the chamber
236 operated in the steady state continuous flow mode:

$$237 \quad \frac{dC_i}{dt} \cdot \tau = C_{i,0} + P_i - C_i - \sum k_i \cdot \tau \cdot C_i \quad (\text{Eq1})$$

238 where *C_i* (molec cm⁻³) is the gas-phase concentration of compound *i* in the well-mixed core of
239 the chamber; *C_{i,0}* (molec cm⁻³) is the initial gas-phase concentration of compound *i* in the
240 injection flow; *k_i* (s⁻¹) is the pseudo-1st-order rate coefficient for a chemical reaction that
241 consumes compound *i*; *τ* (s) is the chamber mean residence time and can be calculated as the
242 total chamber volume divided by the incoming/outgoing flow rate; and *P_i* (molec cm⁻³) is the
243 increment in the concentration of compound *i* through chemical production during one residence
244 time. Note that two terms are neglected in Equation (1), i.e., organic vapor condensation onto
245 particles and deposition on the chamber wall. This is a reasonable simplification here owing to

246 the relatively high volatility ($\geq 10^{-1}$ atm) of compounds studied (Zhang et al., 2015b; Krechmer
247 et al., 2016; Huang et al., 2018). Incorporation of these two terms into Equation (1) is feasible
248 given the vapor pressure of compound i , suspended particle size distribution, gas-particle and
249 gas-wall partitioning coefficient, accommodation coefficients of compound i on particles and
250 walls, and the effective absorbing organic masses on the wall (Zhang et al., 2014a; Zhang et al.,
251 2015b; Huang et al., 2016; McVay et al., 2016; Nah et al., 2016).

252 Model simulations used for comparison with chamber measurements were initialized using
253 experimental conditions summarized in Table S1 in the Supplement. Model input parameters for
254 all simulations include temperature (295 at dark and 306 K under irradiation), local pressure
255 (8.6×10^4 Pa), relative humidity (8% at dark and 5% under irradiation), light intensity
256 ($J_{\text{NO}_2} = 1.27 \times 10^{-3} \text{ s}^{-1}$ under irradiation and 0 at dark), chamber mean residence time (4.17 h), and
257 input mixing ratios of H_2O_2 (0.11–16.2 ppm for photolytic experiments), NO (0.1–100 ppb for
258 photolytic experiments and 10–20 ppb for dark experiments), O_3 (22–225 ppb for dark
259 experiments), HCHO (0–600 ppb for dark experiments), and isoprene (19.9 ppb for photolytic
260 experiments and 10.2 ppb for dark experiments). The model was propagated numerically for 25 h
261 duration for each experiment.

262 4. Results and Discussions

263 4.1 Optimal operating conditions for daytime photochemistry

264 Figure 1 shows the model predicted steady-state mixing ratios of OH, HO_2 , NO_3 , NO, NO_2 ,
265 and O_3 in the chamber after 20 hours of photochemical reactions as a function of the H_2O_2 and
266 NO concentrations in the continuous injection flow. Six blank chamber experiments were
267 compared with simulations. In general, the model captures the evolution patterns of NO_x and O_3
268 well. The predicted mixing ratios of NO, NO_2 , and O_3 agree within 69%, 11%, and 33%,
269 respectively, with the measurements (see Table S1 and Figure S2 in the Supplement). The
270 relatively large NO uncertainties originate from the measurements that were performed close to
271 the instrument detection limit (0.5 ppb).

272 Simulated steady-state mixing ratios of OH radicals ($[\text{OH}]_{\text{ss}}$) range from $\sim 5 \times 10^5$ to $\sim 4 \times 10^6$
273 molec cm^{-3} , which over ~ 4 hours chamber residence time would be roughly equivalent to ~ 1 h to
274 ~ 8 h of atmospheric OH exposure ($1 \times 10^6 \text{ molec cm}^{-3}$). As expected, $[\text{OH}]_{\text{ss}}$ increases with
275 increasing NO influxes due to the enhanced NO_x/O_3 cycling but decreases with increasing H_2O_2
276 influxes owing to the overwhelming reaction $\text{OH} + \text{H}_2\text{O}_2 \rightarrow \text{H}_2\text{O} + \text{HO}_2$. As a consequence, the
277 steady-state mixing ratios of HO_2 radicals ($[\text{HO}_2]_{\text{ss}}$) reach up to $\sim 7 \times 10^9 \text{ molec cm}^{-3}$ when 16.2
278 ppm H_2O_2 is continuously injected into the chamber. If 110 ppb H_2O_2 is used instead, the
279 resulting $[\text{HO}_2]_{\text{ss}}$ levels fall close to the ambient range ($\sim 10^8 \text{ molec cm}^{-3}$).

280 Simulated steady-state NO mixing ratios in the chamber range from ~ 2 ppt to ~ 0.9 ppb from
281 combinations of 0.1–20 ppb NO and 0.11–16.22 ppm H_2O_2 in the injection flow. The ratio of
282 inflow NO concentration to the steady-state NO concentration in the chamber ranges from 5 to
283 93, demonstrating the importance of chemical removal in controlling the overall steady-state NO
284 levels. O_3 accumulation is an inevitable consequence under photolytic conditions and, for
285 example, the presence of 10 ppb O_3 leads to the chemical removal term ($k_{\text{O}_3+\text{NO}} \cdot [\text{O}_3] \cdot \tau$) in
286 Equation (1) that reduces the steady-state NO concentration by a factor of 60. It is worth noting
287 that under all simulated conditions in the continuous flow mode, O_3 (~ 1 –126 ppb) coexists with

288 NO (~0.002–0.9 ppb). This particular chemical scenario, which is impossible to achieve in
289 batch-mode reactors due to prompt conversion of NO to NO₂, could then be used to mimic
290 ambient ozonolysis chemistry, for example, in forest regions that frequently encounter polluted
291 air masses from nearby urban areas. The steady-state mixing ratios of NO₂ ([NO₂]_{ss}) exhibit a
292 strong linear correlation with NO influxes. The use of less than 20 ppb NO in the injection flow
293 results in a few to tens of ppb [NO₂]_{ss} that is higher than the range typically found in the ambient.
294 The potential ‘quenching’ effect of NO₂ on RO₂ radicals through reversible termolecular
295 reactions is discussed shortly.

296 In the so-called ‘high-NO_x’ chamber experiments, the NO₃ radical is an unavoidable side-
297 product when black lights are used as a representative of the solar radiation in mimicking the
298 daytime photochemistry in the troposphere. The photolysis of NO₃, although its primary sink in
299 the atmosphere, proceeds rather slowly ($J_{\text{NO}_3} \sim 1.8 \times 10^{-3} \text{ s}^{-1}$) under the present chamber
300 photolytic conditions, thereby leading to a significant accumulation of NO₃ radicals
301 (7.9×10^4 – $2.8 \times 10^8 \text{ molec cm}^{-3}$) at steady state. The simulated NO₃/OH ratio dictates the extent to
302 which the NO₃ (nighttime) chemistry competes with the OH-initiated (daytime) photochemistry.
303 For compounds that are highly reactive towards NO₃ such as isoprene, NO₃-initiated oxidation
304 accounts for up to ~60% of the overall isoprene degradation pathways at the highest NO₃/OH
305 ratio (~255) simulated. Low concentrations of NO (< 20 ppb) and H₂O₂ (< 2 ppm) in the
306 injection flow are therefore necessary to limit the interferences of NO₃-initiated chemistry.
307 Again, taking isoprene as an example, the NO₃ oxidation pathway contributes less than 0.1% of
308 the overall isoprene degradation kinetics at the lowest NO₃/OH ratio (~0.13) simulated here.

309 Also given in Figure 1 is the calculated lifetime (τ_{RO_2}) of an RO₂ radical with respect to
310 reactions with NO and HO₂ at 306 K. In most batch-mode chamber experiments, τ_{RO_2} of only
311 several seconds or less can be achieved, due to the presence of tens to hundreds of ppb levels of
312 NO and HO₂. Here τ_{RO_2} could extend to 60 s or even longer with the continuous input of low
313 mixing ratios of H₂O₂ (≤ 110 ppb) and NO (≤ 0.2 ppb). Note that the presence of tens of ppb
314 NO₂ in the chamber might impose a ‘quenching’ effect on the steady state RO₂ level through
315 rapid reversible reactions ($\text{RO}_2 + \text{NO}_2 + \text{M} \leftrightarrow \text{RO}_2\text{NO}_2 + \text{M}$). We evaluate this potential ‘quenching
316 effect’ using ethylperoxy radical (C₂H₅O₂) generated from OH-oxidation of ethane as an
317 example. Simulations shown in Figure S3 in the Supplement reveal that incorporation of the
318 $\text{C}_2\text{H}_5\text{O}_2 + \text{NO}_2 + \text{M} \leftrightarrow \text{C}_2\text{H}_5\text{O}_2\text{NO}_2 + \text{M}$ reaction into the mechanism in the presence of ~1–80 ppb
319 NO₂ does not notably change the behavior of C₂H₅O₂ radical. One exception is the peroxyacyl
320 radical, which combines with NO₂ yielding peroxyacyl nitrate. For example, under 0.1–16 ppb
321 [NO₂]_{ss} as displayed in Figure 1, we calculate that the time needed for peroxyacetyl radical
322 (CH₃C(O)O₂) to reach equilibrium with peroxyacetyl nitrate
323 ($\text{CH}_3\text{C}(\text{O})\text{O}_2 + \text{NO}_2 + \text{M} \leftrightarrow \text{CH}_3\text{C}(\text{O})\text{O}_2\text{NO}_2 + \text{M}$) ranges from ~1 to ~10 s, suggesting that the
324 lifetime of peroxyacyl radicals is ultimately controlled by NO₂ instead of NO/HO₂ in the reaction
325 system, and consequently, peroxyacyl radicals are not expected to be long-lived in the current
326 chamber configuration.

327 We further compare the photochemical oxidation environment created here with the
328 ‘intermediate-NO’ conditions achieved by other chambers that employed the experimental
329 approaches introduced earlier. In terms of the oxidizing power, all approaches are capable of
330 maintaining an atmospheric relevant OH level (~10⁶ molec cm⁻³), except the ‘slow chemistry’
331 scenario that limits the photolysis rate of the OH precursor and results in an average OH mixing

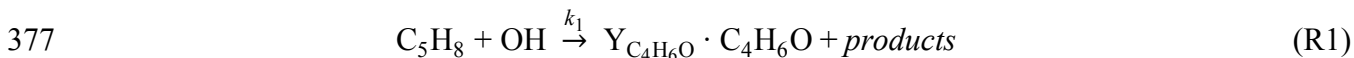
332 ratio of $\sim 10^5$ molec cm^{-3} (Crouse et al., 2012; Teng et al., 2017). At comparable OH levels, the
333 overall atmospheric OH exposure achieved in the flow tube reactor is rather limited due to the
334 short residence time (e.g., ~ 80 s in the PAM reactor). In terms of the NO_x level, precisely
335 controlled steady-state NO concentration can be achieved for an indefinite time period by
336 operating chambers in the continuously mixed flow mode. However, NO_2 accumulates during
337 the continuous oxidation process and the resulting NO_2/NO ratio can be as much as an order of
338 magnitude higher than that achieved in the static outdoor chambers.

339 4.2 Application to OH-initiated oxidation of isoprene

340 Methacrolein (MACR) and methyl vinyl ketone (MVK) are major first-generation products
341 from the OH-initiated oxidation of isoprene in the presence of NO (Wennberg et al., 2018). They
342 are produced from the decomposition of β -ISOPO alkoxy radicals that are primarily formed from
343 the reaction of β -ISOPOO peroxy radicals (β -1-OH-2-OO and β -4-OH-3-OO) with NO, see
344 mechanisms displayed in Figure 2 (A). Reactions of β -ISOPOO peroxy radicals with HO_2 and
345 RO_2 also partially yield β -ISOPO alkoxy radicals that ultimately lead to MACR and MVK,
346 although these pathways are considered to be minor in the presence of hundreds to thousands of
347 ppt NO in the atmosphere. The molar yields determined from previous studies range from
348 30–35% for MVK and 20–25% for MACR under high-NO conditions ($\text{NO} > 60$ ppb) (Tuazon
349 and Atkinson, 1990; Paulson and Seinfeld, 1992; Miyoshi et al., 1994; Ruppert and Becker,
350 2000; Sprengnether et al., 2002; Galloway et al., 2011; Liu et al., 2013). It has been recently
351 shown that the six hydroxyl peroxy radicals (ISOPOO) produced from the initial OH addition to
352 the double bonds of isoprene undergo rapid interconversion by removal/addition of O_2 that
353 competes with bimolecular reactions under atmospherically relevant NO levels (Peeters et al.,
354 2014; Teng et al., 2017). As a result, the distribution of ISOPOO radical isomers and their
355 subsequent reaction products varies with their lifetimes with respect to bimolecular reactions. In
356 the presence of hundreds of ppb NO as done by most previous experimental studies, the reaction
357 of ISOPOO radicals with NO dominates over their interconversion, and the production of β -
358 ISOPOO peroxy radical is less favored, leading the experiments to underestimate the MACR and
359 MVK yields typically obtained in ambient conditions. Measurements by Karl et al. (2006) and
360 Liu et al. (2013) conducted at NO concentrations comparable to the moderately polluted urban
361 environment (~ 0.2 ppb in Karl et al. and ~ 1 ppb in Liu et al.) found higher MACR ($\sim 27\%$ in
362 Karl et al. and $\sim 31.8\%$ in Liu et al.) and MVK ($\sim 41\%$ in Karl et al. and $\sim 44.5\%$ in Liu et al.)
363 yields than other studies.

364 Here we perform a steady-state continuous-mode experiment to measure the production of
365 MACR and MVK from the OH-initiated oxidation of isoprene in the presence of ~ 0.45 ppb NO.
366 Figure 3 shows the observed and simulated temporal profiles of NO_x , O_3 , C_5H_8 , and $\text{C}_4\text{H}_6\text{O}$ over
367 24 hours photooxidation of isoprene. In this experiment, C_5H_8 , H_2O_2 , and NO were continuously
368 fed into the chamber, with constant inflow concentrations of 19.9 ppb, 600 ppb, and 19 ppb,
369 respectively. An outgoing flow at 40 L min^{-1} continuously withdrew air from the chamber to
370 balance the pressure. After approaching steady state, the sampling tube was submerged into an
371 ethanol low temperature bath (-40 ± 2 °C) to trap oxidized products that would otherwise undergo
372 thermal decomposition introducing interferences in the $\text{C}_4\text{H}_7\text{O}^+$ (m/z 71) signal. The measured
373 concentrations of C_5H_8 and $\text{C}_4\text{H}_6\text{O}$ upon cold-trapping agree within 2.8% and 4.6% uncertainties
374 with the model simulations, see Fig.3 (C) and (D).

375 To calculate the total molar yield ($Y_{C_4H_6O}$) of MACR and MVK, two reactions are
 376 considered:



379 where k_1 is the rate constant for OH reaction with isoprene, and k_2 is taken as the average of rate
 380 constants for OH reactions with MACR and MVK. Uncertainties associated with the
 381 simplification of k_2 in calculating the MACR and MVK yields will be discussed shortly. Note
 382 that the ozonolysis and NO_3 -initiated oxidation in total account for less than 6% of isoprene
 383 degradation pathway under current experimental conditions and are neglected in the calculation.
 384 The ozonolysis and photolysis in total account for ~6% of the C_4H_6O degradation pathway and
 385 are neglected here as well.

386 In the continuous-mode operation, two mass conservation equations are satisfied at steady
 387 state:

$$388 \quad \frac{d[C_5H_8]_{ss}}{dt} = [C_5H_8]_0/\tau - [C_5H_8]_{ss}/\tau - k_1 \cdot [OH]_{ss} \cdot [C_5H_8]_{ss} = 0 \quad (Eq2)$$

$$389 \quad \frac{d[C_4H_6O]_{ss}}{dt} = Y_{C_4H_6O} \cdot k_1 \cdot [OH]_{ss} \cdot [C_5H_8]_{ss} - k_2 \cdot [OH]_{ss} \cdot [C_4H_6O]_{ss} - [C_4H_6O]_{ss}/\tau = 0 \quad (Eq3)$$

390 where $[C_5H_8]_{ss}$ and $[C_4H_6O]_{ss}$ are the PTRMS measured steady-state concentrations of isoprene
 391 and the sum of MACR and MVK when using the cold trap, respectively, $[C_5H_8]_0$ is the initial
 392 concentration of isoprene, and τ is the chamber mean residence time and can be calculated as the
 393 total chamber volume divided by the incoming/outgoing flow rate. The steady state OH radical
 394 concentration ($[OH]_{ss}$) can be derived by solving Equation (2). The calculated $[OH]_{ss}$ (3.13×10^6
 395 molec cm^{-3}) is 12% higher than the model prediction (2.74×10^6 molec cm^{-3}). The molar yield of
 396 the sum of MACR and MVK from isoprene OH oxidation pathway in the presence of ~0.45 ppb
 397 NO is thus given by Equation (4) and calculated as $76.7 \pm 5.8\%$:

$$398 \quad Y_{C_4H_6O} = \frac{[C_4H_6O]_{ss} + k_2 \cdot [OH]_{ss} \cdot \tau \cdot [C_4H_6O]_{ss}}{k_1 \cdot [OH]_{ss} \cdot \tau \cdot [C_5H_8]_{ss}} \times f_{\beta\text{-ISOPOO}+NO} \quad (Eq4)$$

399 Here a 5.8% uncertainty originates from the assumption that MACR+OH and MVK+OH
 400 proceed with equal reaction rate, although the rate constant for MVK+OH is ~31% lower than
 401 that of MACR+OH. Another potential uncertainty relates to the accuracy of the simulated steady
 402 state HO_2 and RO_2 concentrations and the contribution of $\beta\text{-ISOPOO}+HO_2$ and $\beta\text{-ISOPOO}+RO_2$
 403 reaction pathways to the overall $\beta\text{-ISOPOO}$ fate. The fraction of $\beta\text{-ISOPOO}$ radicals that reacts
 404 with NO ($f_{\beta\text{-ISOPOO}+NO}$) was predicted as 0.88, which was used here to scale the final
 405 MACR+MVK yield, see Eq(4).

406 In summary, the measured yield of the sum of MACR and MVK in this study is close to that
 407 reported by Karl et al. (2006) and Liu et al. (2013), but ~27–52% higher than the majority of
 408 previous measurements performed under high-NO conditions ($NO > 60$ ppb). This is consistent
 409 with the dynamic nature of the six ISOPOO radical isomers that undergo rapid interconversion
 410 by addition/removal of O_2 . In the presence of ~0.45 ppb NO as performed in this study, lifetimes
 411 of the $\beta\text{-1-OH-2-OO}$ peroxy radical with respect to reaction with NO and loss of O_2 are

412 estimated as 9.4 s and 0.2 s, respectively, implying that the rapid interconversion between β -
413 ISOPOO and δ -ISOPOO radicals essentially governs their distribution, and under such
414 conditions, the production of thermodynamically more stable β -ISOPOO isomers is favored,
415 leading to higher yields of MACR and MVK. Here the reported MACR and MVK yield from
416 isoprene OH oxidation in the presence of ~ 0.45 ppb NO represents an illustration of chamber
417 operation at steady state continuous flow mode for the establishment of certain experimental
418 conditions that are not easily accessible from traditional batch-mode chamber experiments. A
419 complete measurement of first-generation oxidation products from isoprene OH reaction under a
420 wide range of NO levels (ISOPOO bimolecular lifetimes) will be forthcoming in a future
421 publication.

422 **4.3 Optimal operating conditions for nighttime chemistry**

423 Figure 4 shows the model simulated steady-state mixing ratios of HO₂, NO₃, NO, NO₂, and
424 O₃ after 16 hours of dark reactions in the chamber as a function of the HCHO concentration and
425 O₃/NO ratio in the continuous chamber inflow. Blank experiments were compared with
426 simulations in five cases (see Table S1 in the Supplement). The model captures the evolution
427 patterns of NO_x and O₃ well. The observed mixing ratios of NO₂ and O₃ agree with the
428 simulations to within 11% and 6%, respectively (Figure S4 in the Supplement).

429 Compared with the photochemical reaction schemes discussed earlier, the nocturnal
430 chemistry is rather straightforward; that is, the inflow O₃/NO ratio governs the steady-state
431 concentrations of NO₃, NO_x, and O₃, while the inflow HCHO concentration ultimately controls
432 the steady-state HO₂ level. Increasing the O₃/NO ratio from 1 to 9 in the continuous inflow leads
433 to increased NO₃ from 2.4×10^5 to 1.1×10^9 molec cm⁻³, but decreased NO from 1.8 ppb to 20 ppt
434 and decreased NO₂ from 18 to 7 ppb. At a fixed inflow O₃/NO ratio, doubling the NO and O₃
435 concentrations leads to elevated NO₃, NO_x, and O₃ by a factor of 2.0–3.2, 1.5–2.0, and 1.4–2.0,
436 respectively. The use of HCHO as an effective dark HO₂ source does not significantly impact the
437 steady-state mixing ratios of NO_x and O₃, but slightly weakens the NO₃ production.

438 The calculated RO₂ lifetime (τ_{RO_2}) with respect to reactions with NO, NO₃, and HO₂ at 295
439 K ranges from 3 to 225 s. The highest τ_{RO_2} was achieved in the absence of any HCHO source
440 and corresponds to a chemical regime that can be employed to study the intramolecular
441 isomerization (autoxidation) pathway of RO₂ radicals, if any. Adding a continuous flow of
442 HCHO to the system leads to the production of 10^7 – 10^9 molec cm⁻³ HO₂ radicals that then
443 constitute a significant sink of RO₂ radicals and represents prevailing forest environments during
444 nighttime.

445 **4.4 Application to NO₃-initiated oxidation of isoprene**

446 NO₃-initiated oxidation of isoprene proceeds by the NO₃ addition to the carbon double
447 bonds followed by O₂ addition, yielding six distinct nitrooxy peroxy radicals (INOO), including
448 two isomers (β -INOO) with O₂ added on the β -carbon to the nitrate group (see Figure 2B for
449 schematic illustration). The β -INOO radicals react further with NO₃, HO₂, NO, and RO₂,
450 producing nitrooxy alkoxy radicals (β -INO) with molar yields of 1.00, 0.53, 0.97, and 0.40,
451 respectively (Wennberg et al., 2018). The further decomposition of β -INO radicals produces
452 MACR and MVK, together with HCHO and NO₂. Depending on the actual fate of β -INOO
453 radicals, the yields of β -INO radicals can then vary from 0.4 to 1.0, resulting in a distinct
454 distribution of final oxidation products. It is thus important to specify the ultimate fate of INOO

455 radicals during quantification of oxidation products from isoprene reaction with NO₃. As an
456 illustration, we performed one continuous mode experiment that targets on controlling the
457 steady-state fate of INOO radicals to be their reaction with NO and HO₂ (46% and 38% INOO
458 radicals are predicted to react with NO and HO₂, respectively, as shown in Fig.5). Note that by
459 adjusting the concentrations and fractions of inflow reactants (O₃, NO, HCHO, and C₅H₈),
460 different chemical fates and lifetimes of INOO radicals can be achieved.

461 Figure 5 shows the observed and predicted temporal profiles of NO_x, O₃, C₅H₈, and C₄H₆O
462 over 25 hours of isoprene oxidation by NO₃, with continuous input of 10.2 ppb C₅H₈, 205 ppb
463 O₃, and 59 ppb NO into the chamber and a balancing outgoing flow at 40 L min⁻¹ carrying well-
464 mixed reactants and products. It took >16 hours to reach steady state for all the species
465 displayed. In general, the model captures the trends of O₃ and NO well, while underpredicting
466 the steady state NO₂ by ~26%. After ~18 hours of dark reaction, the PTR-MS sampling tubing
467 was submerged into an ethanol cold bath (- 40±2 °C) to trap artifacts in the PTR-MS measured
468 C₄H₇O⁺ (*m/z* 71) signal. The simulated steady-state concentration of isoprene agrees within 9%
469 with the measurements. The derived concentration of the sum of MACR and MVK from the
470 measured C₄H₇O⁺ ion intensity upon cold-trapping is ~1.1 ppb, which is ~129% higher than the
471 model predictions (~0.48 ppb). This disagreement can be attributed, to a large extent, to the
472 oversimplified representation of the six different INOO radicals as one δ-INOO isomer in the
473 MCMv3.3.1 mechanism. As a result, the production of β-INOO radical, the important precursor
474 of MACR and MVK, from NO₃-initiated oxidation of isoprene is suppressed in the simulations.
475 The measured molar yield of the sum of MACR and MVK is 36.3±12.1%, with uncertainties
476 arising from the fact that 10.5% isoprene is predicted to react with OH as an additional source of
477 MACR and MVK. Using this value, the fraction of β-INOO over the sum of nitrooxy peroxy
478 radicals is estimated as 48.6±16.2%, which is close to that (~46.3%) reported by Schwantes et al.
479 (2015), although the estimated bimolecular lifetime of INOO radical in that study (~30 s) is
480 lower than that predicted in the present work (~50 s). As discussed above, the hydroxyl peroxy
481 radicals produced from OH-oxidation of isoprene could undergo rapid interconversion through
482 addition/removal of O₂ at atmospherically relevant lifetimes. This interconversion significantly
483 impacts the subsequent chemistry of individual ISOPOO radical isomers in terms of reaction
484 rates and product distributions. It is likely that the INOO radicals follow similar interconversion
485 due to the small R-OO bond dissociation energy, although no experimental evidence exists. A
486 full examination of the INOO chemistry, i.e., their kinetic and thermodynamic properties as well
487 as their chemical fate at different lifetimes, will be the focus of future studies using this
488 continuous flow chamber operation method.

489 5. Conclusions

490 We report here the development and characterization of the NCAR Atmospheric Simulation
491 Chamber operated at steady state continuous flow mode for simulating daytime and nocturnal
492 chemistry under atmospherically relevant NO levels. The chamber is designed to achieve a well-
493 controlled steady-state environment by continuous inflow of reactants and continuous
494 withdrawal of reactor contents. We use a combination of kinetic modeling and chamber
495 experiments to characterize the ‘intermediate-NO’ chemical regime (tens of ppt to a few ppb)
496 that can be achieved by precisely controlling the inlet reactant concentrations and the
497 mixing/residence timescales of the chamber.

498 To mimic daytime photochemistry, continuous input of H₂O₂ and NO gases is required,
499 resulting in steady state OH mixing ratios of 10⁵–10⁶ molec cm⁻³ under irradiation. Under such
500 conditions, the lifetime of a peroxy radical with respect to reaction with NO and HO₂ can be
501 extended to 60 s or even longer, thus providing a unique environment to study all reaction
502 possibilities of RO₂ radicals including the intramolecular isomerization (autoxidation) pathway.
503 When studying OH-initiated chemistry, care needs to be taken to avoid a range of experimental
504 conditions (e.g., inflow H₂O₂ > 2 ppm and NO > 20 ppb) where NO₃-oxidation might account for
505 a large fraction of the overall degradation pathway of certain parent hydrocarbons such as
506 alkenes.

507 To mimic nighttime chemistry, continuous input of NO (or NO₂) and O₃ is needed to
508 produce steady state NO₃ radicals in the range of 10⁶–10⁹ molec cm⁻³ in the dark. Under such
509 conditions, an RO₂ radical can live up to 4 min prior to finding a bimolecular reaction partner
510 (e.g., NO, NO₃, and HO₂), which were the dominant fates of RO₂ radicals in most batch-mode
511 chamber experiments. Again, the long lifetime of RO₂ radicals achieved by the steady state
512 continuous mode operation opens an avenue for close examination of RO₂ unimolecular
513 (isomerization) pathways in nocturnal environments.

514 In simulating both daytime and nighttime chemistry with continuous flow operation method,
515 O₃ accumulation is unavoidable. The extent to which ozonolysis interferes with OH- or NO₃-
516 initiated oxidation chemistry depends on the steady state O₃ concentration achieved in the
517 chamber and its reactivity towards various parent VOCs. Taking isoprene as an example,
518 ozonolysis accounts for <1% and <0.1% of the overall isoprene degradation kinetics,
519 respectively, under established steady-state photolytic and dark conditions described above.

520 In atmospheric chemistry, the terms ‘zero-NO’ versus ‘high-NO’ have been widely used to
521 classify photooxidation conditions and delineate the gas-phase fate of the peroxy radicals (RO₂)
522 generated from VOCs oxidation (Zhang et al., 2010; He et al., 2011; Cappa et al., 2013; Zhang
523 and Seinfeld, 2013; Loza et al., 2014; Nguyen et al., 2014a; Schilling Fahnstock et al., 2014;
524 Zhang et al., 2014b; Krechmer et al., 2015; Zhang et al., 2015a; Gordon et al., 2016; Riva et al.,
525 2016; Thomas et al., 2016; Schwantes et al., 2017a; Schwantes et al., 2017b). In the so-called
526 ‘high-NO’ regime, reaction with NO dominates the fate of RO₂ radicals, whereas in the ‘zero-
527 NO’ regime, the RO₂ radicals primarily undergo reaction with HO₂ and, perhaps to a much lesser
528 degree, self/cross-combination. The importance of the ‘intermediate-NO’ regime lies in the fact
529 that at sub-ppb levels of NO, the RO₂+NO and RO₂+HO₂ reactions are expected to co-exist and
530 the RO₂ radical could survive up to several minutes before encountering a partner (NO/HO₂) for
531 bimolecular reactions. Under such conditions, the RO₂ radical isomers may undergo
532 interconversion by addition/removal of O₂ and intramolecular isomerization (autoxidation)
533 through H-shift. Here we use isoprene as an illustrative VOC to explore the fate of RO₂ radicals
534 under sub-ppb NO. Future work will focus on detailed characterization of oxidation products
535 from isoprene day- and nighttime chemistry with particular attention given to the controlled RO₂
536 fates and lifetimes.

537 **Data Availability**

538 Data presented in this manuscript are available upon request to the corresponding author.

539 **Competing interests**

540 The authors declare that they have no conflict of interest.

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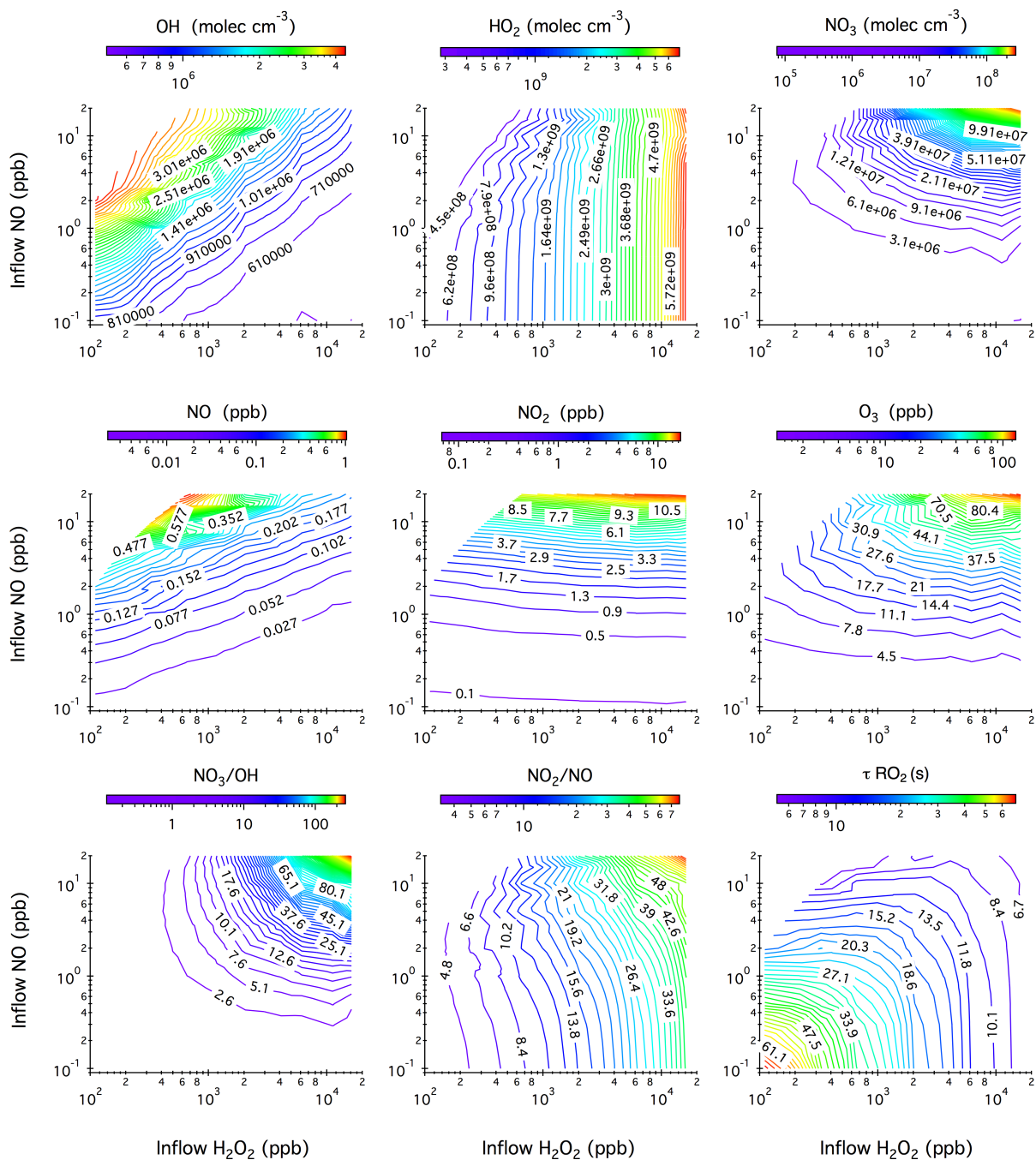


Figure 1. Contour plots showing the model predicted steady-state mixing ratios of OH, HO_2 , NO_3 , NO, NO_2 , and O_3 after 20 hours of photochemical reactions in the chamber as a function of the concentrations of H_2O_2 and NO in the continuous injection flow. Also given here are the simulated NO_3 to OH ratio, NO_2 to NO ratio, and the lifetime of an RO_2 radical (τ_{RO_2}) with respect to reactions with NO and HO_2 . Note that the ripples on the contour lines originate from the limited simulation datasets that are used to generate iso-response values.

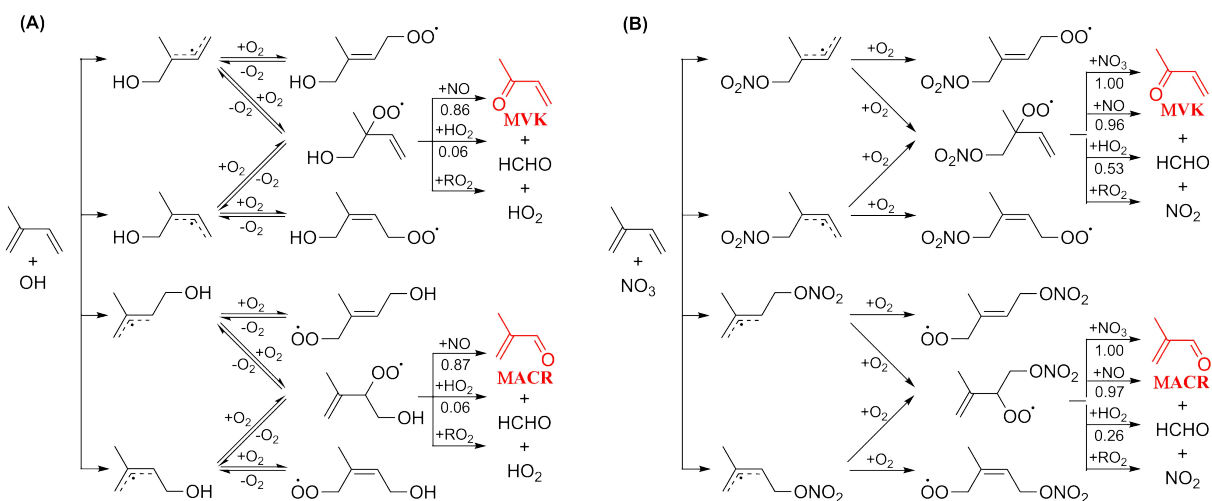


Figure 2. Representative mechanism for (A) OH- and (B) NO₃-initiated oxidation of isoprene that leads to the formation of MACR and MVK.

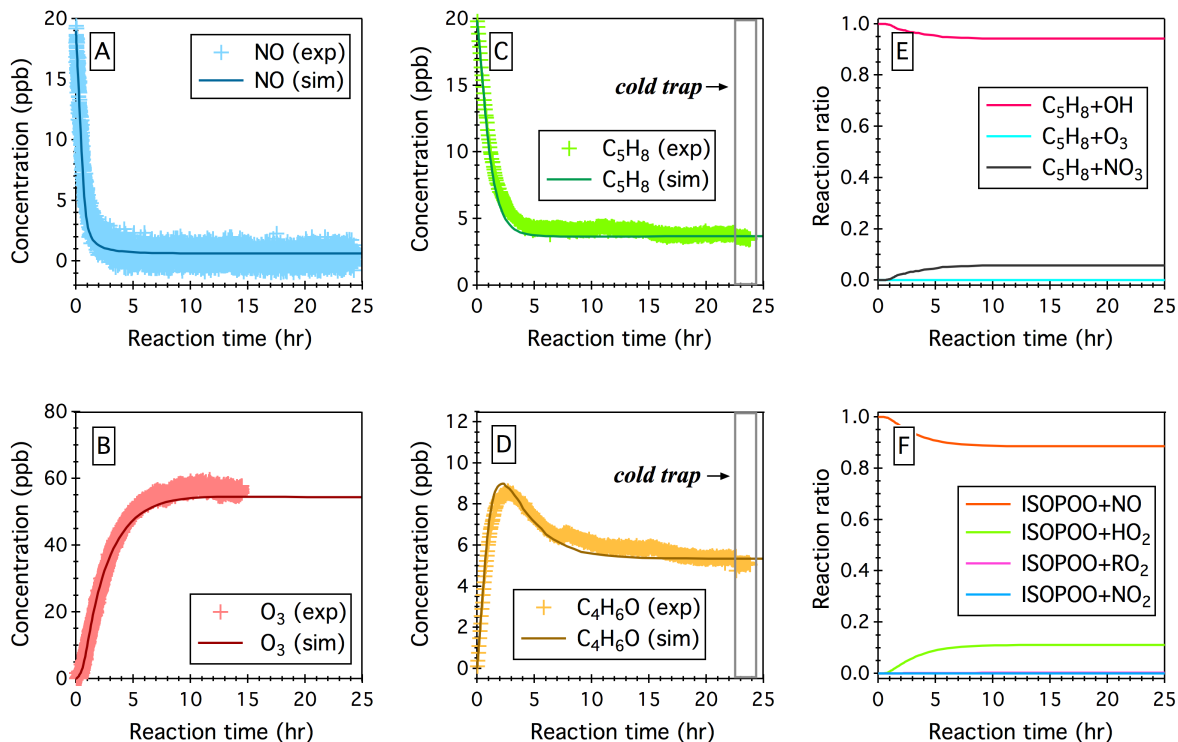


Figure 3. Simulated (sim.) and observed (exp.) temporal profiles of (A) NO, (B) O₃, (C) isoprene (C₅H₈), and (D) the sum of MACR and MVK (C₄H₆O) over 24 hours OH-initiated oxidation of isoprene in the continuous-flow mode chamber operation. Also displayed here include (E) simulated fractions of OH-oxidation, ozonolysis, and NO₃-oxidation as the removal pathways of isoprene, and (F) simulated fractions of ISOPPOO radicals that react with NO, HO₂, RO₂, and NO₃. Time 0 is the point at which the chamber lights are turned on. Initial experimental conditions are 19 ppb NO, 0 ppb NO₂, 0 ppb O₃, 600 ppb H₂O₂, and 19.9 ppb C₅H₈, with continuous input of 600 ppb H₂O₂, 19 ppb NO, and 19.9 ppb C₅H₈ over the course of 24 hour photochemical reactions.

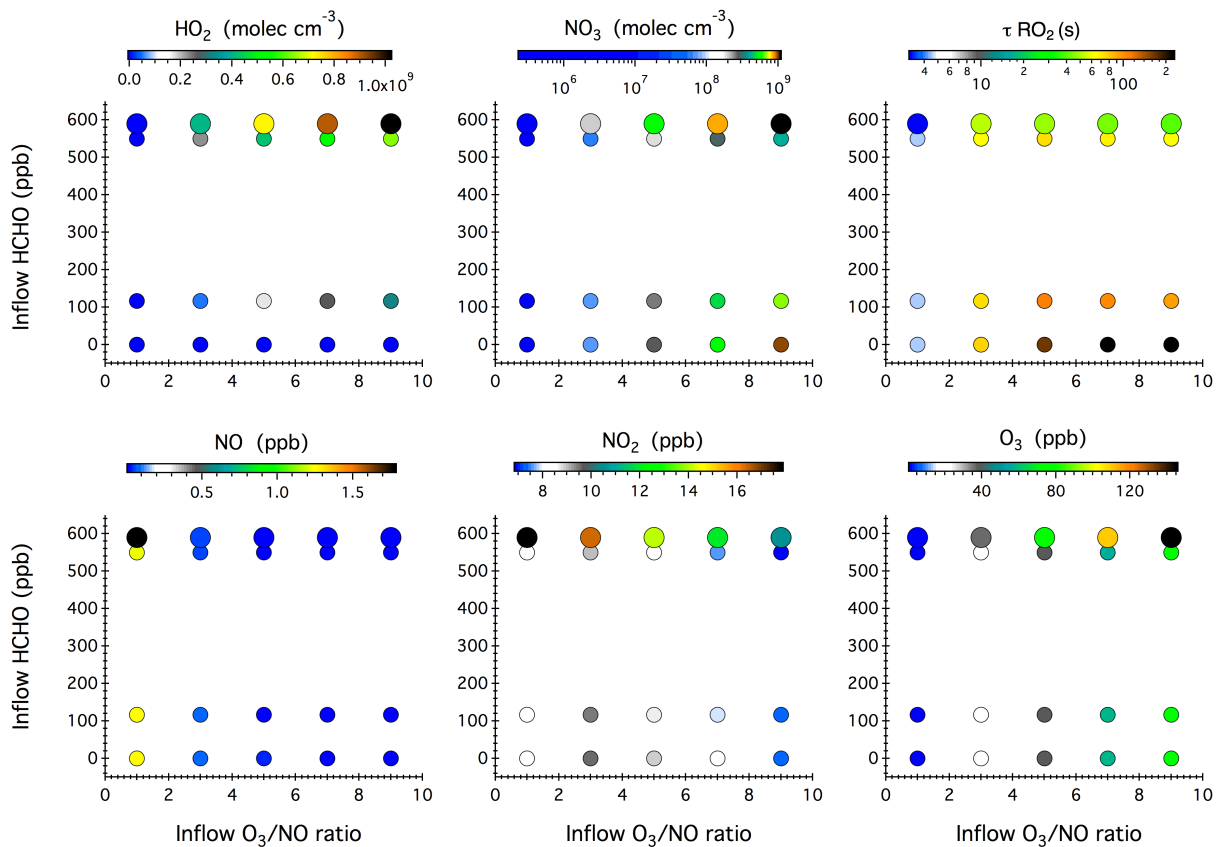


Figure 4. Simulated steady-state mixing ratios of HO_2 , NO_3 , NO , NO_2 , and O_3 after 16 hours of dark reactions in the chamber as a function of the concentrations of NO and O_3 in the continuous injection flow. The symbol size denotes different inflow NO concentrations, i.e., 10 ppb and 20 ppb. Also given here is the calculated lifetime of an RO_2 radical (τ_{RO_2}) with respect to reactions with NO , NO_3 , and HO_2 .

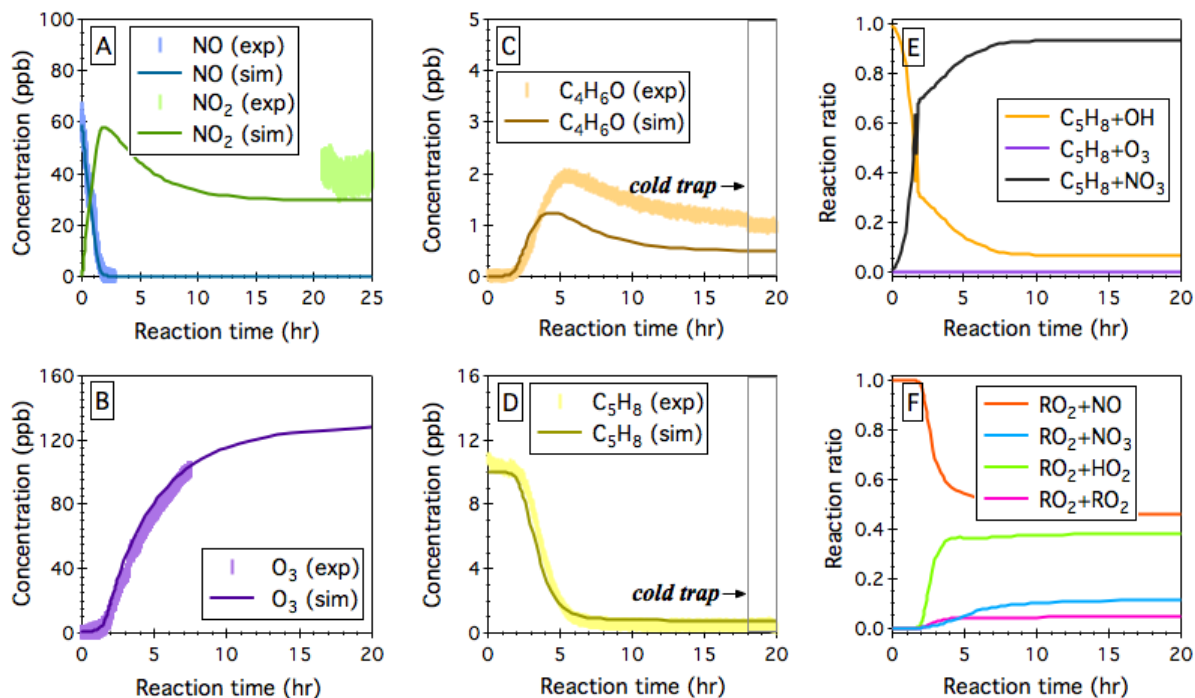


Figure 5. Simulated (sim.) and observed (exp.) evolution patterns of (A) NO_x, (B) O₃, (C) the sum of MACR and MVK (C₄H₆O), and (D) isoprene (C₅H₈) over 25 hours NO₃-initiated oxidation of isoprene under continuous-flow mode chamber operation. The fractions of isoprene that react with OH, O₃, and NO₃ are given in panel (E), and the fractions of INOO radical that undergo bimolecular reactions with NO, NO₃, HO₂, and RO₂ are given in panel (F). Initial experimental conditions are 0 ppb O₃, 59 ppb NO_x, and 10.2 ppb C₅H₈, with continuous input of 205 ppb O₃, 59 ppb NO, and 10.2 ppb C₅H₈ over the course of 25 hour dark reactions.