



1 **Hourly-Resolved temperature inflection points of ozone formation: Chemical**
2 **pathways and precursor sensitivity in Zhengzhou, China**

3
4 Mingkai Wang^{1,2}, Shenbo Wang^{2,3}, Luqi Shang^{1,2}, Jie Tao⁴, Yifei Xu⁴, Ruiqin
5 Zhang^{2,3,*}, ZhenTao Xu^{1,2}, WenSheng Wang^{2,3}, Xinyu Wang^{1,2}, and Yan Yu^{1,2}

6 ¹ School of Chemistry, Zhengzhou University, Zhengzhou 450000, China

7 ² Research Institute of Environmental Sciences, Zhengzhou University, Zhengzhou
8 450000, China

9 ³ School of Ecology and Environment, Zhengzhou University, Zhengzhou, 450000,
10 China

11 ⁴ Zhengzhou Ecological Environment Monitoring Center of Henan Province,
12 Zhengzhou 450000, China

13

14 *Corresponding author Email:

15 Ruiqin Zhang: rqzhang@zzu.edu.cn.

16



17 **Abstract:**

18 Ground-level ozone (O_3) is a key secondary pollutant. Its formation is
19 nonlinearly modulated by temperature, an effect amplified under climate warming.
20 However, the chemical mechanisms by which temperature influences the diurnal O_3
21 cycle and its synergistic interactions with other parameters remain inadequately
22 understood. By integrating observational data from a typical inland city in China with
23 model simulations and machine learning, this study identifies the temperature
24 inflection point for O_3 formation and elucidates the underlying chemical mechanisms
25 and dominant controlling factors. The net O_3 production rate ($P_{net}(O_3)$) peaks at 31°C.
26 The rapid formation between 25 and 31°C is driven by the HO_2+NO and RO_2+NO
27 pathways, with enhanced nitrogen dioxide photolysis rate ($J(NO_2)$) and elevated
28 isoprene as the main drivers. From 31 to 36°C, $P_{net}(O_3)$ declines because the HO_2+NO
29 pathway is weakened and decreasing photolysis rates become the dominant limiting
30 factor. Above 36°C, nitrous acid (HONO) and formaldehyde (HCHO) concentrations
31 decrease, weakening radical cycling and further suppressing O_3 formation. Sensitivity
32 and two-factor analyses support a temperature-dependent dynamic control strategy: in
33 the low-temperature range (22–31°C), priority should be given to controlling
34 anthropogenic alkenes with nitrogen oxides (NO_x) reductions to avoid diminishing
35 returns from single-species cuts; in the high-temperature range (32–40°C), NO_x
36 reductions should be intensified, and synergistic precursors such as HONO and
37 oxygenated volatile organic compounds (OVOCs) should be reduced with emphasis,
38 enhancing the O_3 reduction benefit per unit emission and mitigating O_3 pollution risks
39 under a warming climate.

40 **Keywords:** ground-level ozone, temperature, influencing factors, chemical
41 mechanism, ozone formation sensitivity

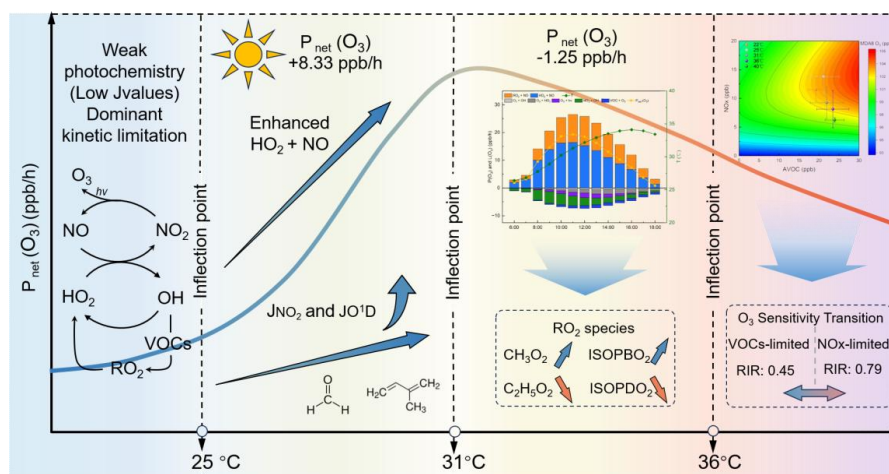
42

43

44



45 **Graphical abstract:**



46

47



48 **1. Introduction**

49 Tropospheric ozone (O_3) not only induces respiratory diseases and impairs
50 cardiovascular function, thereby harming human health, but also disrupts plant
51 photosynthesis, suppresses ecosystem productivity, and participates in tropospheric
52 oxidation processes that promote secondary aerosol formation (Chen et al., 2026; Liu
53 et al., 2023; Wu et al., 2024). The formation of O_3 depends on complex chain
54 photochemical reactions involving volatile organic compounds (VOCs) and nitrogen
55 oxides (NO_x) that are initiated by shortwave radiation, and is synergistically
56 modulated by emission source strengths, meteorological conditions, and the
57 atmospheric chemical environment (Hu et al., 2024; Porter and Heald, 2019; Qiu et al.,
58 2025).

59 The diurnal variation of ground-level O_3 represents the most direct temporal
60 signature of atmospheric photochemical processes, and observations from numerous
61 monitoring stations worldwide have established its fundamental unimodal behavior. A
62 study based on 33 monitoring stations in Beijing showed that O_3 concentrations
63 exhibit a typical unimodal diurnal cycle, with the minimum occurring at 06:00–07:00
64 and the maximum at 14:00–15:00 (Xie et al., 2021). Cheng et al. (2025) drawing on
65 statistics from 1605 sites across China in 2019, similarly indicated that the diurnal O_3
66 cycle peaks in the afternoon at 15:00–16:00 and reaches its minimum at 07:00–08:00.

67 Among the various meteorological factors influencing the diurnal variation of O_3 ,
68 temperature is recognized as the most important driving variable (Wang et al., 2026b,
69 a), and its action pathways can be categorized into direct and indirect effects. The
70 direct effect is primarily manifested as an acceleration of photochemical reactions,
71 thereby enhancing O_3 formation. Coates et al. (2016) demonstrated that under high-
72 NO_x urban atmospheric conditions, a temperature increase from 20°C to 40°C can
73 contribute approximately 20 ppb to O_3 concentrations through the enhancement of
74 photochemical reaction rates alone. Li et al. (2024) reported that within the 20–40°C
75 range, high temperatures directly accelerate photochemical reactions, leading to



76 increases in urban O₃ column concentrations of 8.5 mg/m² and 1.7 mg/m² during the
77 heatwaves of 2013 and 2022, respectively. The indirect effect is closely associated
78 with the enhanced emissions of volatile organic compounds under heat stress (Wang
79 et al., 2024, 2026a; Yang et al., 2026). Yang et al. (2026) clarified that under moderate
80 warming from 30 to 40°C, plant metabolic activities are significantly enhanced,
81 driving a substantial increase in BVOC emission fluxes and consequently affecting O₃
82 formation. Lu et al. (2019) through source apportionment, revealed that driven by
83 high summer temperatures, BVOC emissions can enhance surface O₃ concentrations
84 in eastern China by more than 15 ppb. Beyond BVOCs, temperature-driven emissions
85 of anthropogenic volatile organic compounds (AVOCs) also exacerbate urban O₃
86 pollution during heatwaves. Based on observations in Shanghai, Qin et al. (2025)
87 showed that as temperature increases from 25°C to 35°C, AVOC concentrations
88 roughly double, driving an 82% increase in the OH reactivity of VOCs and a 4.6 ppb
89 rise in O₃ concentration.

90 It is noteworthy that the effect of temperature on O₃ is not always positive;
91 instead, an inflection temperature exists beyond which O₃ concentrations no longer
92 increase linearly with temperature but level off or decline. Li et al. (2025a) examined
93 the statistical relationship between daily maximum temperature ($T_{\max}$) and the
94 maximum daily 8-hour average O₃ concentration (MDA8 O₃) using a random forest
95 model, revealing response inflection points between temperature and O₃. Their results
96 identified inflection temperatures in 49 of the 63 cities studied, ranging from 28.0 to
97 34.5 °C, with inflection points in coastal cities approximately 2–4°C lower than those
98 in inland cities. Observations during the 2013 heatwave in the Yangtze River Delta
99 showed that O₃ increased at a rate of 4–5 ppb/K within the 28–38°C range, but
100 declined at a rate of –1.3 ~ –1.7 ppb/K once temperature exceeded 38°C (Pu et al.,
101 2017). A study in the Sichuan Basin in 2022 further confirmed the nonlinear response
102 of O₃ to temperature. With a threshold of 39.4°C, each 1°C increase in temperature
103 below this threshold led to a 22.5% increase in O₃ concentration, whereas above the



104 threshold, each 1 °C increase resulted in a 4.7% decline, exhibiting a “promotion–
105 inhibition” two-stage transition with distinct spatial heterogeneity Xu et al. (2025).
106 Previous studies have attributed such inflection points to the joint regulation of
107 photochemical kinetic saturation, precursor emission changes, and boundary layer
108 processes. Among these, the “hormetic” emission response of BVOCs to temperature
109 is particularly critical (Li et al., 2025b), which may participate in O₃ suppression
110 during high-temperature episodes by weakening the atmospheric oxidative capacity.
111 However, current understanding of the dominant chemical mechanism shifts across
112 the inflection point remains inadequate. Furthermore, most empirical analyses of the
113 temperature inflection point to date rely on statistical relationships between daily
114 maximum temperature and daily maximum O₃ (or MDA8 O₃). This daily-scale
115 aggregation approach masks the diurnal-stage-specific differences in O₃ response to
116 temperature within the diurnal cycle, thereby hindering a refined characterization of
117 the chemical mechanism transitions before and after the inflection point.

118 To address this deficiency, this study identifies the temperature inflection point in
119 the diurnal O₃ cycle based on long-term observational and modeling data. By
120 designing sensitivity experiments involving meteorological factors and precursors, it
121 systematically quantifies the synergistic effects of temperature and its coupled factors
122 on O₃ formation, and establishes the response relationships between various
123 parameters and O₃ under different temperature conditions. The results can provide a
124 scientific basis for the refined control of urban O₃ pollution under a warming climate
125 and fill the gap in the quantitative understanding of the inflection temperature at the
126 diurnal cycle scale.

127 **2. Materials and Methods**

128 **2.1 Observational dates and locations**

129 Observations were conducted in June of each year from 2015 to 2024 at an
130 atmospheric comprehensive observation station in the Zhengzhou High-tech Zone



131 (34.75 °N, 113.60 °E). The monitoring site was located on the rooftop of the station
132 building, approximately 20 m above ground level. It is a typical urban site,
133 surrounded by residential areas, schools, commercial districts, and office buildings.
134 Within a 1 km radius, there are no point sources of air pollution, although the site may
135 be affected by vehicle emissions.

136 2.2 Sample Collection and Analysis

137 Concentrations of non-methane volatile organic compounds (NMHCs) were
138 measured online using a gas chromatography–mass spectrometry system (GC–MS;
139 TH-PKU 300B, Wuhan Tianhong Instruments Co., Ltd., China) that combines ultra-
140 low-temperature pre-concentration with gas chromatography–mass
141 spectrometry/flame ionization detection (FID). The instrument operates at a time
142 resolution of 1 h with a flow rate of 60 mL/min. Air samples were collected during the
143 first 5 minutes of each hour and subsequently pre-concentrated through a cold trap to
144 remove H₂O and CO₂. An empty capillary column was used for sample introduction.
145 After pre-concentration, the sample was rapidly desorbed by heating and introduced
146 into the analytical system. Following chromatographic separation, the sample was
147 detected using FID (for C₂–C₅ hydrocarbons) and MS (for C₅–C₁₂ hydrocarbons,
148 halocarbons, and oxygenated volatile organic compounds (OVOCs)). The correlation
149 coefficients of the calibration curves for the target compounds were ≥0.99, and the
150 method detection limits were ≤0.1 nmol/mol. A total of 115 NMHC species were
151 monitored, including 29 alkanes, 11 alkenes, 1 alkyne, 17 aromatics, 35 halocarbons,
152 21 OVOCs, and 1 sulfide (carbon disulfide). Detailed information on this setup can be
153 found in our previous study (Zhang et al., 2024). In addition, hourly concentrations of
154 particulate matter (PM_{2.5} and PM₁₀), trace gases (CO, O₃, NO, SO₂, HONO, and
155 HCHO), meteorological parameters (temperature (T), relative humidity (RH),
156 pressure (P), wind speed (WS), and wind direction (WD)), and photolysis rates
157 (J(O¹D), J(NO₂), J(HCHO)) were simultaneously measured in this study. Detailed
158 information on the instrument models is provided in Table S1 of the Supporting



159 Information.

160 **2.3 Machine Learning**

161 To identify the key drivers influencing O₃ concentrations, we adopted an
162 Extreme Gradient Boosting (XGBoost) model. The model incorporated input data
163 including concentrations of O₃ and other pollutants, as well as meteorological
164 parameters, to establish a predictive model for O₃ levels. The model was further
165 interpreted using the Shapley Additive Explanations (SHAP) framework, which
166 evaluates the importance of each influencing factor in predicting O₃ concentrations.
167 The XGBoost model is a machine learning algorithm based on gradient boosted
168 decision trees. It is a highly scalable and optimized version of gradient boosting
169 machines, with improvements in both speed and predictive performance. XGBoost
170 possesses several advantages, such as the ability to handle missing values, reduce
171 overfitting, and enhance computational speed and accuracy. It has been widely
172 applied to the prediction of air pollutant concentrations (Fang et al., 2025; Sun et al.,
173 2025).

174 To validate the reliability of the model, we used it to simulate and predict O₃
175 concentrations during the observation period. Prior to model input, the data were
176 preprocessed by removing extreme outliers and missing values. The dataset was split
177 into training and validation sets at an 8:2 ratio, and the prediction results are shown in
178 Figure S1. The correlation coefficient R² was 0.98, indicating that the model exhibits
179 reliable predictive capability and confirming its feasibility in predicting pollutant
180 concentrations.

181 **2.4 Observation-Based Model (OBM)**

182 In this study, a zero-dimensional (0-D) box model incorporating the latest Master
183 Chemical Mechanism (MCMv3.3.1, <https://mcm.york.ac.uk/MCM>) was applied to
184 simulate the photochemical formation of O₃ and to diagnose the relationship between
185 O₃ and its precursors (Jiang et al., 2025; Xue et al., 2026). The 0-D box model (e.g.,
186 the Framework for 0-D Atmospheric Modeling, F0AM) is widely used to simulate



187 atmospheric photochemical processes, with ambient measurements serving as model
188 constraints. Numerous studies have employed 0-D box models coupled with different
189 chemical mechanisms to calculate O₃ production; details of the OBM can be found in
190 our previous study (Zhang et al., 2024). Briefly, the OBM is a zero-dimensional
191 model that assumes a well-mixed atmosphere and incorporates atmospheric chemical
192 mechanisms to simulate O₃ production rates and the corresponding O₃ concentrations
193 at a specific time. Hourly monitoring data for air pollutants (O₃, CO, NO, NO₂, and
194 SO₂), VOCs, meteorological parameters (T, RH, and P), and photolysis rates (J(NO₂),
195 J(O¹D), J(HONO), and J(HCHO)) were input into the OBM as constraints for the
196 model simulations. Photolysis rates for other species were determined by the solar
197 zenith angle. The index of agreement (IOA) was used to evaluate the model
198 performanc (Huang et al., 2005), calculated according to Eq. (1):

199
$$\text{IOA} = 1 - \frac{\sum_{i=1}^n (O_i - S_i)^2}{\sum_{i=1}^n (|O_i - \bar{O}| + |S_i - \bar{O}|)} \quad (1)$$

200 where S_i , O_i , and $\bar{O}$ represent the observed, simulated, and mean observed
201 hourly values, respectively. To assess the reliability of the model simulation, we
202 analyzed the atmospheric O₃ concentrations and calculated the IOA and R². The IOA
203 and R² values for O₃ were 0.95 and 0.96, respectively (Figure S2), indicating that the
204 model simulation results are reliable.

205

206 **3. Results and Discussion**

207 **3.1 The temperature inflection point for O₃ changes**

208 Based on long-term observational data during the daytime hours (06:00–18:00)
209 in June from 2015 to 2024 in Zhengzhou, the statistical relationship between hourly
210 O₃ concentration and air temperature (T) and its variation characteristics were
211 analyzed. The nonlinear dependence of O₃ formation on temperature was revealed
212 through the response characteristics of the rate of change of O₃ concentration with



213 time (dO_3/dt) and the rate of change of O_3 concentration per unit temperature
214 (dO_3/dT).

215 As shown in Figure 1a, the O_3 concentration exhibits a continuously increasing
216 trend with rising temperature, enters a rapid increase phase at approximately 25°C ,
217 and tends to level off or even decline when the temperature exceeds 36°C . This
218 characteristic is largely consistent with reports in the literature (Xu et al., 2025).

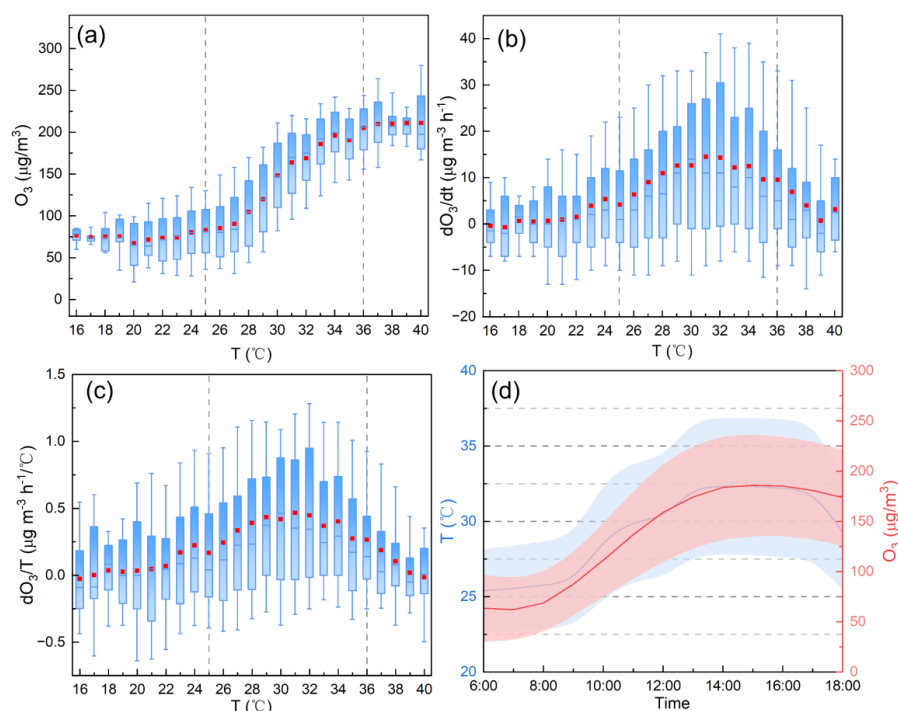
219 Examining the response relationships of the rate of change of O_3 concentration
220 with time (dO_3/dt) and the rate of change of O_3 concentration per unit temperature
221 (dO_3/T) with temperature (Figure 1b–c), when the temperature is below 25°C , the
222 mean dO_3/dt ranges from -0.38 to $4.8 \mu\text{g}\cdot\text{m}^{-3}\cdot\text{h}^{-1}$, with an average of
223 $2.71 \pm 4.46 \mu\text{g}\cdot\text{m}^{-3}\cdot\text{h}^{-1}$. Combined with the diurnal variation characteristics at the
224 same temperature (Figure 1d), this temperature range primarily corresponds to the
225 period from 06:00 to 10:00. During this stage, dO_3/dT ranges from -1.26 to
226 $2.11 \mu\text{g}\cdot\text{m}^{-3}\cdot\text{h}^{-1}/^\circ\text{C}$, indicating that the growth rate of O_3 concentration within this
227 time window is relatively small and that O_3 formation is weakly influenced by the
228 temperature increase.

229 When the temperature exceeds 36°C , the mean dO_3/dt ranges from 0.52 to 7.58
230 $\mu\text{g}\cdot\text{m}^{-3}\cdot\text{h}^{-1}$, with an average of $4.58 \pm 7.09 \mu\text{g}\cdot\text{m}^{-3}\cdot\text{h}^{-1}$; the mean dO_3/dT stabilizes
231 between -0.01 and $0.19 \mu\text{g}\cdot\text{m}^{-3}\cdot\text{h}^{-1}/^\circ\text{C}$, with an average of $0.12 \pm 0.59 \mu\text{g}\cdot\text{m}^{-3}\cdot\text{h}^{-1}/^\circ\text{C}$.
232 In terms of temporal distribution, the period with temperatures above 36°C is mainly
233 concentrated between 13:00 and 16:00.

234 Within the temperature range of 25°C to 36°C , O_3 formation exhibits the
235 strongest temperature dependence. The mean dO_3/dt ranges from 3.12 to 14.51
236 $\mu\text{g}\cdot\text{m}^{-3}\cdot\text{h}^{-1}$, indicating rapid accumulation of O_3 concentration over time; the mean
237 dO_3/dT ranges from 0.12 to $0.47 \mu\text{g}\cdot\text{m}^{-3}\cdot\text{h}^{-1}/^\circ\text{C}$, with an average of 0.31 ± 0.63
238 $\mu\text{g}\cdot\text{m}^{-3}\cdot\text{h}^{-1}/^\circ\text{C}$. This temperature range primarily corresponds to the period from late
239 morning to afternoon (10:00–16:00), which represents the rapid growth phase of O_3 .
240 Notably, 31°C is a key inflection point for O_3 formation. At this temperature, both



241 dO_3/dt and dO_3/dT reach their peak values, at $14.51 \pm 12.65 \mu\text{g}\cdot\text{m}^{-3}\cdot\text{h}^{-1}$ and
 242 $0.47 \pm 0.58 \mu\text{g}\cdot\text{m}^{-3}\cdot\text{h}^{-1}/^\circ\text{C}$, respectively, indicating that the temperature sensitivity of
 243 O_3 formation is highest at this point. A temperature of 31°C typically corresponds to
 244 11:00–12:00 at noon in June in Zhengzhou; under this critical state, the combination
 245 of solar radiation, precursor concentrations, and reactivity is most favorable for net O_3
 246 production.
 247



248
 249 **Figure 1.** (a) Box plots of O_3 concentration as a function of temperature in June from
 250 2015 to 2024; (b) box plots of hourly rate of change of O_3 concentration (dO_3/dt)
 251 versus temperature; (c) box plots of rate of change of O_3 concentration per unit
 252 temperature (dO_3/dT) versus temperature; (d) diurnal variations of temperature and O_3
 253 concentration, (Time: UTC+8).

254 To further verify the inflection point in the O_3 –temperature response relationship,
 255 a one-month comprehensive observation was conducted in June 2024 (Figure S3).
 256 The analysis of the data (Figure S4) indicates that, similar to the characteristics



described above, inflection temperatures exist for O_3 concentration, dO_3/dt , and dO_3/dT , at 25°C, 31°C, and 36°C, respectively.

Based on the OBM model simulations, the net O_3 production rate ($P_{net}(O_3)$) was obtained. As shown in Figure 2a, within the 22–25°C range, the $P_{net}(O_3)$ is at a relatively low level, averaging 3.43 ± 2.45 ppb/h. In the 25–31°C range, with increasing temperature, the $P_{net}(O_3)$ begins to rise significantly, reaching a peak of 15.05 ± 7.09 ppb/h at 31°C. In the 31–36°C range, although $P_{net}(O_3)$ declines somewhat, it remains at a relatively high level, with an average rate of 13.90 ± 8.51 ppb/h during this stage. When the temperature exceeds 36°C, the $P_{net}(O_3)$ exhibits fluctuations or even a decreasing trend.

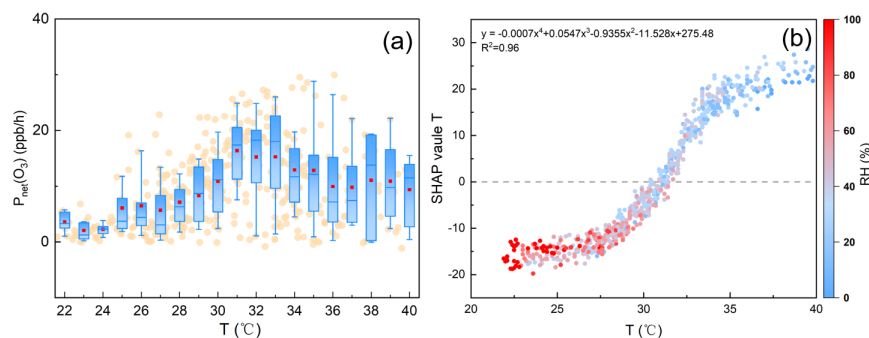
Using the XGBoost machine learning model coupled with SHAP interpretability analysis, T was identified as the primary factor influencing O_3 concentration during the study period (Figure S5). Furthermore, the SHAP dependence plot of T (Figure 2b) further reproduces the nonlinear effect of T on O_3 concentration.

When the temperature is in the range of 22–25°C, the SHAP values are predominantly negative with small fluctuations, indicating that the model-predicted O_3 concentration is below the average level under low-temperature conditions, where the atmospheric photochemical reaction rate is relatively slow and clearly limited by kinetics. Entering the 25–36°C range, the SHAP values exhibit the steepest slope of variation, rapidly shifting from negative to positive with warming and crossing the zero axis at 31°C. The curve is particularly steep between 28 and 31°C, suggesting that a unit increase in temperature can bring about a substantial enhancement in the predicted O_3 value. Especially in the 28–31°C range, the curve rises sharply, meaning that each unit increase in temperature leads to a notable increase in the predicted O_3 concentration. When the temperature is in the range of 36–40°C, the SHAP values remain positive, but the increase stagnates or even shows a slight decline, indicating that O_3 formation is further suppressed under extreme high temperatures.

In summary, the response of O_3 concentration to temperature exhibits three key



285 inflection points (25°C, 31°C, and 36°C). Identifying these inflection points helps
286 precisely target the sensitive stages of photochemical reactions and provides scientific
287 support for pollution control decision-making.



288
289 **Figure 2.** (a) Box plot of net O₃ production rate ($P_{\text{net}}(\text{O}_3)$) versus temperature; (b)
290 SHAP dependence plot of temperature with respect to O₃.

291 3.2 Differences in O₃ formation among temperature regimes

292 3.2.1 O₃ budget analysis

293 Adverse meteorological conditions are generally favorable for O₃ accumulation;
294 however, box plot statistics in Figure S6 show that both wind speed (WS) and
295 boundary layer height (BLH) increase significantly with rising temperature, indicating
296 that horizontal and vertical dispersion conditions are actually better during high-
297 temperature periods. Therefore, the high O₃ concentrations under high temperatures
298 should be primarily attributed to intense photochemical production, which is largely
299 consistent with previous studies (Song et al., 2026).

300 Figure 3a illustrates the O₃ production mechanism resolved by the OBM model.
301 The O₃ budget analysis based on the OBM model shows that, in terms of average
302 rates, the mean rates of the O₃ sources RO₂+ NO and HO₂+ NO are 6.06 ± 3.36 ppb/h
303 and 9.36 ± 5.29 ppb/h, respectively. The O₃ sinks are dominated by the NO₂+ OH
304 reaction and photolysis, with mean rates of 2.27 ± 1.24 ppb/h and 0.68 ± 0.56 ppb/h,
305 respectively. The average $P_{\text{net}}(\text{O}_3)$ is 10.55 ± 6.45 ppb/h. The diurnal variations of both
306 sources and sinks exhibit a unimodal pattern, peaking at 11:00, at which time the



307 corresponding temperature and $P_{\text{net}}(\text{O}_3)$ are $31.31 \pm 3.06^\circ\text{C}$ and 19.3 ± 8.96 ppb/h,
308 respectively.

309

310 Based on the O_3 budget across the identified temperature inflection points
311 (Figure 3b), the dominant O_3 source at all stages is the $\text{HO}_2 + \text{NO}$ pathway, followed
312 by $\text{RO}_2 + \text{NO}$. When the temperature increases from 25°C to 31°C , the $P_{\text{net}}(\text{O}_3)$ rises
313 sharply from 6.72 ppb/h to 15.05 ppb/h, an increase of 8.33 ppb/h. During this
314 interval, the $\text{HO}_2 + \text{NO}$ and $\text{RO}_2 + \text{NO}$ pathways are enhanced by 6.40 ppb/h and 4.47
315 ppb/h, respectively. When the temperature continues to rise from 31°C to 36°C , the
316 $P_{\text{net}}(\text{O}_3)$ exhibits a notable turning point, decreasing from 15.05 ppb/h to 13.80 ppb/h,
317 a reduction of 1.25 ppb/h. This declining trend is mainly attributed to the significant
318 attenuation of the $\text{HO}_2 + \text{NO}$ pathway: its rate drops from 12.74 ppb/h to 11.09 ppb/h,
319 a decrease of 1.65 ppb/h, which may result from the thermal depletion of HO_2 radicals
320 at elevated temperatures. In contrast, the $\text{RO}_2 + \text{NO}$ pathway continues to increase
321 over this temperature range, from 7.22 ppb/h to 8.96 ppb/h, a rise of 1.74 ppb/h.

322 Analysis of the top five RO_2 species (CH_3O_2 , $\text{C}_2\text{H}_5\text{O}_2$, ISOPBO_2 , ISOPDO_2 ,
323 HMKBO_2) in terms of their reaction rates with NO (Table S2) revealed that they
324 exhibit distinctly different temperature responses around 31°C . The $\text{CH}_3\text{O}_2 + \text{NO}$ and
325 $\text{ISOPBO}_2 + \text{NO}$ pathways increase continuously across the entire temperature range,
326 with increments of 0.38 and 0.11 ppb/h, respectively, in the $31\text{--}36^\circ\text{C}$ interval. In
327 contrast, the $\text{C}_2\text{H}_5\text{O}_2 + \text{NO}$ and $\text{ISOPDO}_2 + \text{NO}$ pathways decrease by 0.10 and 0.04
328 ppb/h, respectively. The $\text{HMKBO}_2 + \text{NO}$ pathway shows a slight increase of 0.08
329 ppb/h from 31 to 36°C but declines again toward 40°C . Such differences can be
330 attributed to the distinct molecular structures of different RO_2 species, which lead to
331 varying temperature sensitivities of their competing consumption channels (Wennberg
332 et al., 2018). For structurally simple peroxy radicals (RO_2 , e.g., CH_3O_2), the lack of
333 efficient unimolecular reaction channels such as intramolecular hydrogen shift means
334 that their consumption is absolutely dominated by the $\text{RO}_2 + \text{NO}$ bimolecular reaction;



therefore, enhanced precursor oxidation driven by rising temperature can be directly translated into an increase in the rate of this pathway. In contrast, complex RO₂ species bearing functional groups such as hydroxyl (e.g., ISOPDO₂) possess intramolecular hydrogen shift channels with relatively low energy barriers. These channels are highly temperature-sensitive and can be accelerated exponentially upon warming, thereby strongly competing with the RO₂ + NO reaction and reducing the chain propagation efficiency (Li et al., 2023). Moreover, the decline in NO concentration under high-temperature conditions further limits the rate of the RO₂ + NO reaction. Thus, the conversion efficiency of reactive precursors to O₃ is dually constrained by competing chemical pathways, dictated by the molecular structure of the precursors, and by NO_x availability (Anand et al., 2025; Fittschen et al., 2014; Yan et al., 2016).

Therefore, although some RO₂ branches remain active at elevated temperatures, their combined positive contributions are still insufficient to offset the attenuation of the dominant HO₂ + NO pathway, leading to an inflection point in the P_{net}(O₃) after 31°C.

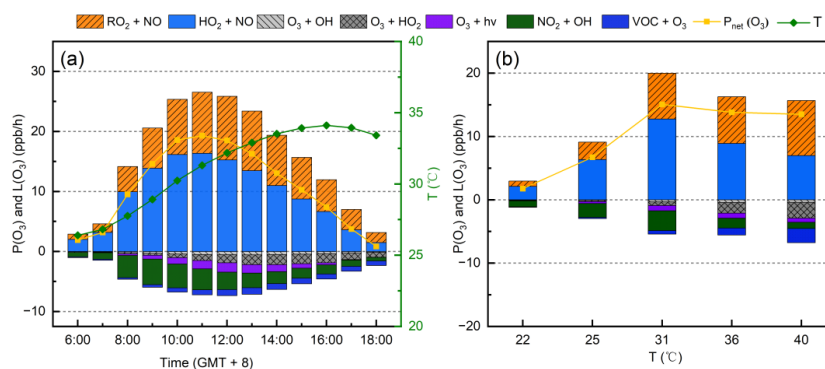


Figure 3. (a) O₃ budget analysis for the daytime of the observation period; (b) O₃ budget analysis at different temperatures.

3.2.2 Analysis of dominant influencing factors

To quantify the contributions of various precursors and meteorological parameters to O₃ formation, single-factor sensitivity analyses were conducted based



357 on the OBM. With all other input parameters fixed at their mean values during the
358 observation period (Table S3), each target parameter (e.g., temperature, VOCs, and
359 NO_x) was varied uniformly from its minimum to maximum observed value. This
360 approach isolates the influence of other factors, thereby simulating the response of the
361 $P_{\text{net}}(\text{O}_3)$ to changes in a single variable.

362 The results show that the driving capacities of various factors on $P_{\text{net}}(\text{O}_3)$ differ
363 considerably (Figure S7). Among the meteorological parameters, all exert positive
364 effects except for boundary layer height. This is primarily because the OBM is a zero-
365 dimensional box model that does not include vertical mixing and transport processes
366 of the boundary layer and thus cannot reflect the influence of boundary layer
367 dynamics on O_3 . Among the meteorological factors with positive effects, the
368 photolysis rate $J(\text{NO}_2)$ has the greatest impact on $P_{\text{net}}(\text{O}_3)$. In terms of precursors,
369 $P_{\text{net}}(\text{O}_3)$ exhibits strong positive responses to HONO, HCHO, and C_5H_8 , while the
370 effects of species such as alkanes and aromatics are relatively small. Nitrogen oxides
371 (NO_x) display a nonlinear characteristic, initially increasing and then decreasing.

372 Based on the responses of $P_{\text{net}}(\text{O}_3)$ to different parameters, we quantified the
373 impacts of individual factors during the temperature rise, as shown in Table S4 and
374 Figure 4. When the temperature increased from 22°C to 25°C , the observed values of
375 $J(\text{NO}_2)$ and $J(\text{O}^1\text{D})$ rose from $1.17 \times 10^{-3} \text{ s}^{-1}$ and $9.7 \times 10^{-7} \text{ s}^{-1}$ to $4.11 \times 10^{-3} \text{ s}^{-1}$ and
376 $7.9 \times 10^{-6} \text{ s}^{-1}$, respectively, contributing to increases in $P_{\text{net}}(\text{O}_3)$ of 2.25 ppb/h and
377 0.73 ppb/h. This is primarily attributed to the enhancement of morning solar radiation,
378 where the increase in photolysis rates directly accelerates radical initiation reactions.
379 The temperature increase itself contributed only 0.45 ppb/h to the rise in $P_{\text{net}}(\text{O}_3)$, a
380 relatively minor effect. Furthermore, although alkane concentrations increased by
381 2.03 ppb, $P_{\text{net}}(\text{O}_3)$ increased by merely 0.26 ppb/h. These results indicate that during
382 the 06:00–10:00 period, O_3 formation is primarily driven by the enhancement of
383 photolysis efficiency, which lifts the kinetic limitation.

384 When the temperature increases from 25°C to 31°C , the rise in $P_{\text{net}}(\text{O}_3)$ is



385 primarily driven by a 0.63 ppb increase in isoprene concentration (contributing +4.29
386 ppb/h). This is attributed to the high OH reactivity of isoprene (C_5H_8) and the strong
387 temperature dependence of its emissions; warming leads to an exponential growth in
388 vegetation emission fluxes, providing abundant precursors for the reactions. The
389 further enhancement of $J(NO_2)$ contributes an additional +2.66 ppb/h. Notably,
390 although NO_x concentrations decrease during this stage (NO from 3.24 to 0.95 ppb,
391 NO_2 from 17.39 to 7.39 ppb), mainly due to accelerated photolytic loss and the
392 substantial consumption of OH by reactive VOCs altering the NO_x cycling pathways,
393 the net contribution of NO_x to $P_{net}(O_3)$ remains +1.52 ppb/h. Additionally, the increase
394 in temperature itself raises $P_{net}(O_3)$ by 1.19 ppb/h through the enhancement of
395 chemical reaction rate constants (Atkinson et al., 1997). Overall, O_3 formation in this
396 temperature regime mainly results from the synergistic effect of warming-driven
397 biogenic VOC emission increases and enhanced photolysis.

398 When the temperature increases from 31°C to 36°C, $P_{net}(O_3)$ declines to
399 13.80 ± 6.12 ppb/h. During this stage, the significant decrease in photolysis rates
400 becomes the dominant limiting factor. Although this period corresponds to the
401 afternoon high-temperature hours (~13:00–15:00), biogenic emissions remain
402 elevated, with isoprene concentration rising to 1.33 ppb (contributing +2.83 ppb/h),
403 and the thermodynamic effect of temperature contributes +1.05 ppb/h, sustaining the
404 reactivity; however, the weakening of photolysis directly reduces $P_{net}(O_3)$ by 2.60
405 ppb/h. Concurrently, HONO and HCHO concentrations already exhibit a declining
406 trend during this warming interval, yielding negative contributions of -1.12 and -0.14
407 ppb/h, respectively.

408 When the temperature further increases from 36°C to 40°C, $P_{net}(O_3)$ declines
409 further to 13.50 ± 6.07 ppb/h. During this stage, the limiting factors shift: the
410 persistent and substantial decreases in HONO and HCHO concentrations, along with
411 their pronounced negative effects, become the dominant cause. Intense solar radiation
412 at high temperatures accelerates the photolytic loss of both species, and the abundant



HO_x radicals generated fail to efficiently drive O₃ formation under low-NO_x conditions, instead exacerbating radical termination reactions. Notably, in this temperature range, isoprene concentration further increases and peaks at 1.85 ppb, contributing +2.04 ppb/h, and no suppression of BVOC emissions by high temperature is observed (Figure S8). However, the negative contributions of HONO and HCHO expand to −2.87 and −1.06 ppb/h, respectively, completely offsetting the positive effects of the precursors. This indicates that under extreme high temperature and low-NO_x conditions, as key intermediates such as HONO and HCHO are depleted, photochemical reactions are constrained by either the NO_x titration effect or VOC saturation effects.

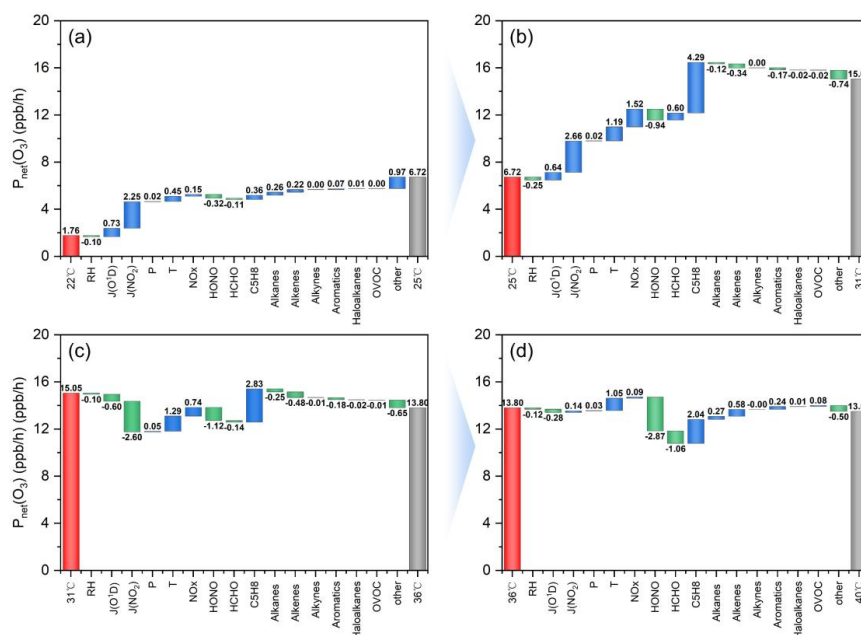


Figure 4. Contributions of individual precursors and meteorological factors to the $P_{\text{net}}(\text{O}_3)$ during temperature increase.

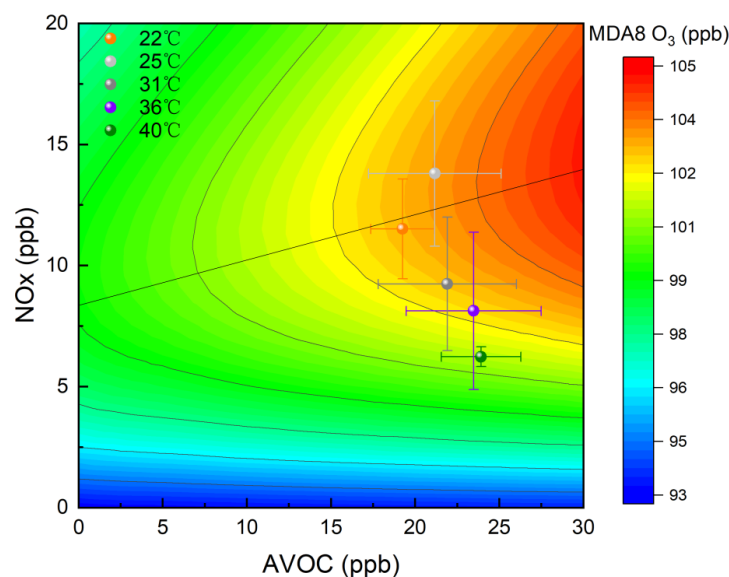
3.3 O₃ management strategies for different temperature phases

This study constructed an Empirical Kinetic Modeling Approach (EKMA) curve based on the OBM model (Figure 5). The formation of O₃ exhibits a highly nonlinear relationship with AVOCs and NO_x. By mapping the pollutant concentrations



430 corresponding to characteristic temperature points onto this curve to identify the O₃
431 formation regime, the results show that at 22°C and 25°C, O₃ formation is generally in
432 the VOC-limited regime near and above the ridge line; as temperature increases, the
433 O₃ sensitivity gradually shifts from the VOC-limited regime toward the NO_x-limited
434 regime, and by 40°C it has completely fallen into the NO_x-limited regime below the
435 ridge line.

436 The relative incremental reactivity (RIR) analysis for different temperature
437 ranges (Figure S9) further corroborates this transition. In the 22–25°C and 26–31°C
438 ranges (Figure S9a–b), alkenes exhibit the highest RIR (0.52 and 0.56, respectively),
439 followed by C₅H₈ and HONO, whereas the RIR of NO_x remains at relatively low
440 levels (0.19 and 0.11), indicating that O₃ formation during these stages is primarily
441 VOC-limited. When the temperature rises to 32–36°C (Figure S9c), the RIR of NO_x
442 increases sharply to 0.56, surpassing that of alkenes (0.48) and becoming the
443 dominant contributing species. In the 37–40°C range (Figure S9d), the RIR of NO_x
444 further increases to 0.79, while the RIR of alkenes and isoprene decrease to 0.45 and
445 0.22, respectively, revealing a significantly enhanced sensitivity of O₃ formation to
446 NO_x at high temperatures and a shift of the control regime from VOC-limited toward
447 NO_x-limited or transitional conditions. The above changes demonstrate that
448 temperature drives a shift in the key precursor to O₃ formation from alkene VOCs to
449 NO_x by influencing photolysis rates, radical cycling, and the NO_x–VOC partitioning.



450

451 **Figure 5.** Sensitivity response surface of O₃ formation to AVOC and NO_x and the
 452 distribution of temperature points.

453 3.4 Synergistic effects of temperature and influencing factors

454 To further investigate the synergistic effects between temperature and other
 455 factors on O₃ formation, this study conducted two-factor simulations (Figure 6) and
 456 employed two approaches for quantifying O₃ concentration increments (ΔO_3) (Figure
 457 S10): (1) For a fixed variation range of a given factor, the change in ΔO_3 when
 458 temperature increases from 293K to 314K is compared; a larger increase indicates a
 459 positive synergistic effect of warming on that factor, whereas a smaller increase
 460 suggests suppression. (2) For a fixed warming magnitude, the difference in ΔO_3
 461 across the variation range of the factor is compared; if ΔO_3 increases with rising factor
 462 levels, it indicates that the factor exerts a positive synergistic effect on the warming
 463 response, and conversely, a suppression effect.

464 Among the meteorological factors, J(NO₂), J(O¹D), and RH exhibit significant
 465 positive synergy with temperature, with J(NO₂) showing the strongest synergistic
 466 effect. When J(NO₂) increases from $2.07 \times 10^{-4} \text{ s}^{-1}$ to $8.96 \times 10^{-3} \text{ s}^{-1}$, ΔO_3 rises from
 467 28.45% at 293 K to 40.92% at 314 K; under a fixed warming magnitude, ΔO_3



468 increases from -1.69% at low $J(\text{NO}_2)$ to 7.86% at the maximum $J(\text{NO}_2)$ value. $J(\text{O}^1\text{D})$
469 and RH rank next. The underlying mechanism is that $J(\text{NO}_2)$ directly controls NO_2
470 photolysis and the $\text{NO} + \text{O}_3$ equilibrium, while $J(\text{O}^1\text{D})$ and RH enhance OH
471 production via the $\text{O}^1\text{D} + \text{H}_2\text{O} \rightarrow 2\text{OH}$ reaction, accelerating VOC oxidation, though
472 their contributions are less pronounced than that of the core photolysis cycle.

473 Among the gaseous precursors, HONO, aromatics, halocarbons, and OVOCs
474 generally exhibit positive synergy with temperature, and are the reactive precursors
475 that should be preferentially controlled during high-temperature periods. In the
476 synergy analysis with a fixed concentration range, HONO shows the largest effect
477 ($0.04 \rightarrow 3.99$ ppb, ΔO_3 rises from 18.28% at 293 K to 19.98% at 314 K), followed by
478 aromatics, halocarbons, and OVOCs. In the synergy analysis with a fixed warming
479 magnitude, OVOCs show the largest effect ($0.6 \rightarrow 7.43$ ppb, ΔO_3 increases from 3.96%
480 to 5.92%).

481 Among the gaseous precursors, HONO, aromatics, halocarbons, and OVOCs
482 generally exhibit positive synergy with temperature, and are the reactive precursors
483 that should be preferentially controlled during high-temperature periods. In the
484 synergy analysis with a fixed concentration range, HONO shows the largest effect
485 ($0.04 \rightarrow 3.99$ ppb, ΔO_3 rises from 18.28% at 293 K to 19.98% at 314 K), followed by
486 aromatics, halocarbons, and OVOCs. In the synergy analysis with a fixed warming
487 magnitude, OVOCs show the largest effect ($0.6 \rightarrow 7.43$ ppb, ΔO_3 increases from 3.96%
488 to 5.92%).

489 In contrast, alkenes, HCHO, and alkynes mainly exhibit suppression, with
490 alkenes showing the strongest overall suppression ($0.28 \rightarrow 10.75$ ppb, ΔO_3 decreases
491 from 23.86% to 22.29%). However, in the synergy analysis with a fixed warming
492 magnitude, a concentration inflection point exists for alkenes: as the concentration
493 increases from 0.28 ppb to 2.37 ppb, ΔO_3 rises from 4.50% to 4.85% , but a further
494 increase to 10.75 ppb causes ΔO_3 to drop to 3.18% . This indicates that excessively
495 high alkene concentrations lead to RO_2 accumulation through substantial NO_x



496 consumption, thereby weakening the positive temperature effect (Whalley et al.,
497 2021). It suggests that simply emphasizing alkene reduction may not be consistently
498 effective at high temperatures—once alkene concentrations have fallen into the NO_x -
499 limited regime, further alkene reduction yields diminishing returns, and NO_x co-
500 control should be strengthened instead. The synergy between alkanes and temperature
501 exhibits a temperature inflection point (304 K): over the range of 2.88 → 43.42 ppb,
502 ΔO_3 increases from 6.00% at 293 K to 6.20% at 304 K, then decreases to 6.05% at
503 314 K. This is because warming initially accelerates alkane oxidation, whereas above
504 304 K, enhanced RO_2 self-reactions and reactions with HO_2 reduce the conversion
505 efficiency of additional alkanes to O_3 (Donahue et al., 1998; Meng et al., 2023). This
506 implies that above a certain high-temperature threshold, the O_3 reduction benefit from
507 alkane emission cuts will decline, and the control focus should shift more toward
508 other species with sustained positive synergy. The synergy between temperature and
509 NO_x is nonlinear (Figure S11): moderate concentrations (approximately 5–12 ppb)
510 promote O_3 formation, whereas excessively high concentrations suppress it due to the
511 NO titration effect, further suggesting that dynamic emission reduction strategies
512 should be formulated based on actual NO_x concentration levels during high-
513 temperature periods.

514

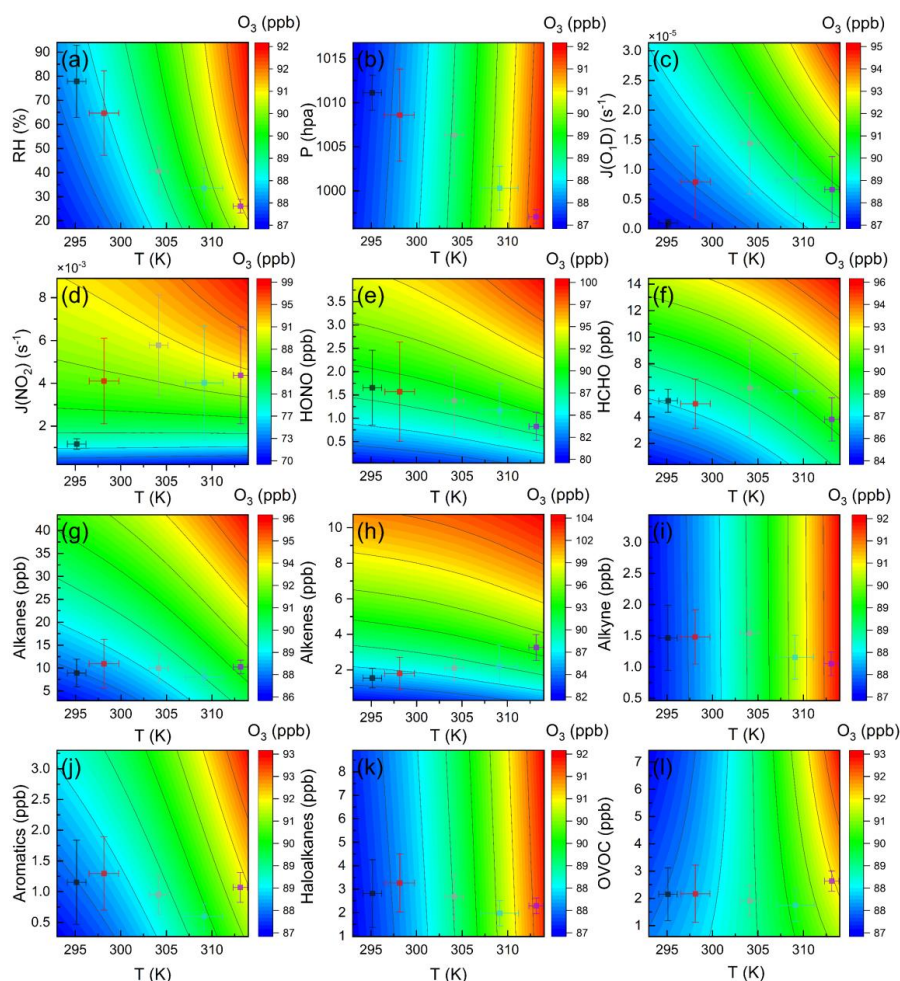


Figure 6. Analysis of O_3 concentration changes under different temperatures and various influencing factors. The five data points represent the values of the respective factors at each of the five temperature levels.

4 Conclusions

Based on summertime observations in Zhengzhou, this study coupled an observation-based box model (OBM) with machine learning to systematically elucidate the nonlinear response of ozone (O_3) to temperature within the diurnal cycle. We identified three critical temperature inflection points at 25°C, 31°C, and 36°C. The net ozone production rate, $P_{net}(O_3)$, peaked at 31°C. The rapid increase between 25



525 and 31°C was dominated by the HO₂+NO and RO₂+NO pathways, driven primarily
526 by elevated isoprene and J(NO₂), with O₃ formation remaining in the VOC-limited
527 regime. From 31 to 36°C, P_{net}(O₃) declined, primarily due to the significant
528 attenuation of the HO₂+NO pathway and decreasing photolysis rates, shifting the
529 formation regime toward NO_x-limited conditions. Above 36°C, substantial decreases
530 in HONO and HCHO promoted reservoir species formation (e.g., PAN) and radical
531 termination, further suppressing O₃ production and intensifying NO_x sensitivity.
532 Furthermore, two-factor analysis revealed that temperature exhibited positive
533 synergies with J(NO₂), J(O¹D), and RH that strengthened with rising temperatures,
534 alongside an antagonistic relationship with pressure. Notably, alkane synergy
535 displayed a temperature threshold (~31°C), whereas alkene synergy exhibited a
536 concentration threshold; HONO and OVOCs were identified as strongly synergistic
537 reactive precursors under high temperatures.

538 This hourly-scale, multi-inflection-point mechanism significantly advances our
539 understanding of O₃ formation. It complements and refines previous statistical
540 conclusions that were limited to a single threshold based on daily maximum values,
541 providing a more dynamic and precise depiction of diurnal atmospheric chemistry.

542 These mechanisms collectively support the establishment of a temperature-
543 graded dynamic control strategy. In the low-temperature range (22–31°C), the highest
544 RIR of isoprene and alkenes suggests that priority should be given to controlling
545 anthropogenic alkenes (e.g., from vehicle emissions and solvent use); however, this
546 must be coordinated with NO_x reduction to avoid the diminished marginal returns
547 caused by excessive alkene consumption of NO_x. Entering the high-temperature range
548 (32–40°C), the sharply increasing RIR of NO_x dictates a shift toward NO_x-limited
549 control, targeting a moderate concentration window (approximately 5–12 ppb) to
550 maximize the O₃ reduction benefit per unit of emission reduction. Simultaneously,
551 intensified co-reduction of NO_x, HONO, and OVOCs should be implemented to
552 suppress their strong positive synergies with temperature, while the control priority



553 for alkanes should be lowered due to the weakened emission reduction benefits
554 beyond 31°C. This provides a robust quantitative basis for the refined management of
555 urban O₃ pollution under a warming climate.

556 It should be noted that this study is based on observational data from a single city.
557 Due to spatial heterogeneities in emission structures, meteorological backgrounds,
558 and vegetation types, the specific values of the temperature inflection points and the
559 dominant mechanisms may vary across regions (Figure S12). Therefore, future
560 research should extend to multi-city and multi-season observations and modeling to
561 establish temperature–O₃ response relationships covering different climatic zones and
562 pollution regimes, thereby providing a more robust foundation for deepening
563 mechanistic understanding and improving models.

564
565



566 **Data availability**

567 The data supporting the findings of this study are available within the paper and
568 its supplementary information files. Additional atmospheric observation data are
569 available from <https://doi.org/10.5281/zenodo.23252602> (Wang and Zhang, 2026).

570 **Author contributions**

571 M.W.: Writing—original draft, visualization, data curation. S.W.: Conceptualization,
572 supervision, data curation. L.S.: Investigation, data curation. J.T.: Data curation. Y.X.:
573 Investigation. R.Z.: Funding acquisition, supervision. Z.X.: Investigation. W.W.:
574 Investigation. X.W.: Investigation. Y.Y.: Investigation.

575 **Competing interests**

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

577 **Acknowledgments**

578 This work was supported by the National Key R&D Program of China (No.
579 2024YFC3713700), the National Natural Science Foundation of China (No.
580 42505100) and Key Research Project Plan for Higher Education Institutions in Henan
581 Province (No. 26A610019).

582

583 **Supplementary information**

584 Attached please find supplementary information associated with this article.

585



References

- Anand, V. J., Rai, P. K., and Kumar, P.: Criegee + HONO reaction: a bimolecular sink of criegee, and the missing non-photolytic source of OH, *Atmos. Chem. Phys.*, 25, 16713–16727, <https://doi.org/10.5194/acp-25-16713-2025>, 2025.
- Atkinson, R., Baulch, D. L., Cox, R. A., Hampson, R. F., Jr., Kerr, J. A., Rossi, M. J., and Troe, J.: Evaluated kinetic, photochemical and heterogeneous data for atmospheric chemistry: supplement V. IUPAC subcommittee on gas kinetic data evaluation for atmospheric chemistry, *J. Phys. Chem. Ref. Data*, 26, 521–1011, <https://doi.org/10.1063/1.556011>, 1997.
- Chen, J., Tang, J., Rinnan, R., and Zhu, B.: Global variability in isoprenoid emissions: divergent responses to warming and drought driven by physiochemical controls, *Plant Cell Environ.*, 49, 5294–5312, <https://doi.org/10.1111/pce.70536>, 2026.
- Cheng, F., Li, Z., Yang, Z., Li, R., Wang, D., Jia, A., Li, K., Zhao, B., Wang, S., Yin, D., Li, S., Xue, W., Cribb, M., and Wei, J.: First retrieval of 24-hourly 1-km-resolution gapless surface ozone (O_3) from space in China using artificial intelligence: diurnal variations and implications for air quality and phytotoxicity, *Remote Sens. Environ.*, 316, 114482, <https://doi.org/10.1016/j.rse.2024.114482>, 2025.
- Coates, J., Mar, K. A., Ojha, N., and Butler, T. M.: The influence of temperature on ozone production under varying NO_x conditions – a modelling study, *Atmos. Chem. Phys.*, 16, 11601–11615, <https://doi.org/10.5194/acp-16-11601-2016>, 2016.
- Donahue, N. M., Anderson, J. G., and Demerjian, K. L.: New rate constants for ten OH alkane reactions from 300 to 400 K: an assessment of accuracy, *J. Phys. Chem. A*, 102, 3121–3126, <https://doi.org/10.1021/jp980532q>, 1998.
- Fang, H., Xu, H., Wu, T., Jia, Q., Li, J., Ruan, Z., Li, F., Li, Y., Shi, Y., and Wang, X.: Unveiling the drivers of ozone pollution rebound at an urban site in the Yangtze River Delta since 2020, *Atmospheric Research*, 325, 108264, <https://doi.org/10.1016/j.atmosres.2025.108264>, 2025.
- Fittschen, C., Whalley, L. K., and Heard, D. E.: The reaction of CH_3O_2 radicals with OH radicals: a neglected sink for CH_3O_2 in the remote atmosphere, *Environ. Sci. Technol.*, 48, 7700–7701, <https://doi.org/10.1021/es502481q>, 2014.
- Hu, T., Lin, Y., Liu, R., Xu, Y., Ouyang, S., Wang, B., Zhang, Y., and Liu, S. C.: What



- 619 caused large ozone variabilities in three megacity clusters in eastern China
620 during 2015–2020?, *Atmos. Chem. Phys.*, 24, 1607–1626,
621 <https://doi.org/10.5194/acp-24-1607-2024>, 2024.
- 622 Huang, J., Fung, J. C. H., Lau, A. K. H., and Qin, Y.: Numerical simulation and
623 process analysis of typhoon-related ozone episodes in Hong Kong, *J. Geophys.*
624 *Res.*, 110, 2004JD004914, <https://doi.org/10.1029/2004JD004914>, 2005.
- 625 Jiang, Z., Tang, M.-X., He, L., Li, J.-H., Hong, Y., He, L.-Y., and Huang, X.-F.:
626 Unveiling the HONO Offsetting Effect: Rethinking NO_x Emission Controls
627 during Urban Ozone Pollution Episodes, *Environ. Sci. Technol.*, 59, 22050–
628 22059, <https://doi.org/10.1021/acs.est.5c04831>, 2025.
- 629 Li, M., Huang, X., Yan, D., Lai, S., Zhang, Z., Zhu, L., Lu, Y., Jiang, X., Wang, N.,
630 Wang, T., Song, Y., and Ding, A.: Coping with the concurrent heatwaves and
631 ozone extremes in China under a warming climate, *Sci. Bull.*, 69, 2938–2947,
632 <https://doi.org/10.1016/j.scib.2024.05.034>, 2024.
- 633 Li, N., Liang, J., Liu, W., Gu, C., Li, J., Xu, Y., Tang, K., Liao, H., and Hu, J.:
634 Mechanisms of high-temperature ozone suppression in eastern China: a
635 meteorological perspective, *Environ. Res. Lett.*, 20, 094001,
636 <https://doi.org/10.1088/1748-9326/adf1ba>, 2025a.
- 637 Li, S., Yuan, X., Li, S., Zhou, Y., Wang, S., Zhang, K., Agathokleous, E., Blande, J. D.,
638 and Feng, Z.: Extreme heat event alters BVOC responses to elevated ozone: from
639 physiology to emission patterns, *Environ. Sci. Technol.*, 59, 12132–12144,
640 <https://doi.org/10.1021/acs.est.5c01132>, 2025b.
- 641 Li, Y., Zhang, R. M., and Xu, X.: Theoretical kinetics studies of isoprene peroxy
642 radical chemistry: the fate of Z- δ -(4-OH, 1-OO)-ISOPOO radical, *Ecotoxicol.*
643 *Environ. Saf.*, 266, 115553, <https://doi.org/10.1016/j.ecoenv.2023.115553>, 2023.
- 644 Liu, Y., Geng, G., Cheng, J., Liu, Y., Xiao, Q., Liu, L., Shi, Q., Tong, D., He, K., and
645 Zhang, Q.: Drivers of increasing ozone during the two phases of clean air actions
646 in China 2013–2020, *Environ. Sci. Technol.*, 57, 8954–8964,
647 <https://doi.org/10.1021/acs.est.3c00054>, 2023.
- 648 Lu, X., Zhang, L., Chen, Y., Zhou, M., Zheng, B., Li, K., Liu, Y., Lin, J., Fu, T.-M.,
649 and Zhang, Q.: Exploring 2016–2017 surface ozone pollution over China: source
650 contributions and meteorological influences, *Atmos. Chem. Phys.*, 19, 8339–
651 8361, <https://doi.org/10.5194/acp-19-8339-2019>, 2019.



- 652 Meng, X., Jiang, J., Chen, T., Zhang, Z., Lu, B., Liu, C., Xue, L., Chen, J., Herrmann,
653 H., and Li, X.: Chemical drivers of ozone change in extreme temperatures in
654 eastern China, *Sci. Total Environ.*, 874, 162424,
655 <https://doi.org/10.1016/j.scitotenv.2023.162424>, 2023.
- 656 Porter, W. C. and Heald, C. L.: The mechanisms and meteorological drivers of the
657 summertime ozone–temperature relationship, *Atmos. Chem. Phys.*, 19, 13367–
658 13381, <https://doi.org/10.5194/acp-19-13367-2019>, 2019.
- 659 Pu, X., Wang, T. J., Huang, X., Melas, D., Zanis, P., Papanastasiou, D. K., and
660 Poupkou, A.: Enhanced surface ozone during the heat wave of 2013 in Yangtze
661 River delta region, china, *Sci. Total Environ.*, 603–604, 807–816,
662 <https://doi.org/10.1016/j.scitotenv.2017.03.056>, 2017.
- 663 Qin, M., She, Y., Wang, M., Wang, H., Chang, Y., Tan, Z., An, J., Huang, J., Yuan, Z.,
664 Lu, J., Wang, Q., Liu, C., Liu, Z., Xie, X., Li, J., Liao, H., Pye, H. O. T., Huang,
665 C., Guo, S., Hu, M., Zhang, Y., Jacob, D. J., and Hu, J.: Increased urban ozone in
666 heatwaves due to temperature-induced emissions of anthropogenic volatile
667 organic compounds, *Nat. Geosci.*, 18, 50–56, [https://doi.org/10.1038/s41561-](https://doi.org/10.1038/s41561-024-01608-w)
668 024-01608-w, 2025.
- 669 Qiu, Y., Li, X., Chai, W., Liu, Y., Song, M., Tian, X., Zou, Q., Lou, W., Zhang, W., Li,
670 J., and Zhang, Y.: Insights into ozone pollution control in urban areas by
671 decoupling meteorological factors based on machine learning, *Atmospheric*
672 *Chemistry and Physics*, 25, 1749–1763, [https://doi.org/10.5194/acp-25-1749-](https://doi.org/10.5194/acp-25-1749-2025)
673 2025, 2025.
- 674 Song, Y., Wang, P., Yang, Y., Tang, J., and Liao, H.: Meteorological conditions and
675 physicochemical processes amplifying ozone pollution during heatwaves in
676 major city clusters of China, *Atmos. Res.*, 330, 108580,
677 <https://doi.org/10.1016/j.atmosres.2025.108580>, 2026.
- 678 Sun, C., Tao, J., Xu, Y., Zhang, Y., Yang, W., Wang, W., Dong, Z., Wang, S., Wang, M.,
679 and Zhang, R.: Machine Learning-Driven Source Apportionment of HONO in
680 High-Ammonia Street Canyon Microenvironments, *ACS EST Air*, 2, 2680–2691,
681 <https://doi.org/10.1021/acsestair.5c00286>, 2025.
- 682 Wang, N., Wang, H., Huang, X., Chen, X., Zou, Y., Deng, T., Li, T., Lyu, X., and Yang,
683 F.: Extreme weather exacerbates ozone pollution in the pearl river delta, china:
684 role of natural processes, *Atmos. Chem. Phys.*, 24, 1559–1570,



- 685 <https://doi.org/10.5194/acp-24-1559-2024>, 2024.
- 686 Wang, W., Su, H., Parrish, D. D., Ni, R., Li, X., Bao, F., Wang, H., Huang, C.,
687 Williams, J., Liao, H., Lu, K., Zhang, Y., and Cheng, Y.: Global warming makes
688 nitrogen oxide abatement key to ozone pollution mitigation, *Sci. Adv.*, 12,
689 eaca4124, <https://doi.org/10.1126/sciadv.aea4124>, 2026a.
- 690 Wang, W., Su, H., Huang, X., Zeng, C., Parrish, D. D., Zhang, Y., Ding, A., and
691 Cheng, Y.: The dominant role of temperature in seasonal ozone sensitivity
692 changes in China, *Nat. Geosci.*, 1–7, [https://doi.org/10.1038/s41561-026-02036-](https://doi.org/10.1038/s41561-026-02036-8)
693 8, 2026b.
- 694 Wennberg, P. O., Bates, K. H., Crounse, J. D., Dodson, L. G., McVay, R. C., Mertens,
695 L. A., Nguyen, T. B., Praske, E., Schwantes, R. H., Smarte, M. D., St Clair, J. M.,
696 Teng, A. P., Zhang, X., and Seinfeld, J. H.: Gas-phase reactions of isoprene and
697 its major oxidation products, *Chem. Rev.*, 118, 3337–3390,
698 <https://doi.org/10.1021/acs.chemrev.7b00439>, 2018.
- 699 Whalley, L. K., Slater, E. J., Woodward-Massey, R., Ye, C., Lee, J. D., Squires, F.,
700 Hopkins, J. R., Dunmore, R. E., Shaw, M., Hamilton, J. F., Lewis, A. C., Mehra,
701 A., Worrall, S. D., Bacak, A., Bannan, T. J., Coe, H., Percival, C. J., Ouyang, B.,
702 Jones, R. L., Crilley, L. R., Kramer, L. J., Bloss, W. J., Vu, T., Kotthaus, S.,
703 Grimmond, S., Sun, Y., Xu, W., Yue, S., Ren, L., Acton, W. J. F., Hewitt, C. N.,
704 Wang, X., Fu, P., and Heard, D. E.: Evaluating the sensitivity of radical
705 chemistry and ozone formation to ambient VOCs and NO_x in Beijing, *Atmos.*
706 *Chem. Phys.*, 21, 2125–2147, <https://doi.org/10.5194/acp-21-2125-2021>, 2021.
- 707 Wu, W., Fu, T.-M., Arnold, S. R., Spracklen, D. V., Zhang, A., Tao, W., Wang, X., Hou,
708 Y., Mo, J., Chen, J., Li, Y., Feng, X., Lin, H., Huang, Z., Zheng, J., Shen, H., Zhu,
709 L., Wang, C., Ye, J., and Yang, X.: Temperature-Dependent Evaporative
710 Anthropogenic VOC Emissions Significantly Exacerbate Regional Ozone
711 Pollution, *Environ. Sci. Technol.*, 58, 5430–5441,
712 <https://doi.org/10.1021/acs.est.3c09122>, 2024.
- 713 Xie, J., Shi, S., Wu, L., and Zhang, X.: Spatiotemporal changes of near-surface ozone
714 concentration from 2015 to 2018 in Beijing, *Front. Environ. Sci.*, 9,
715 <https://doi.org/10.3389/fenvs.2021.593220>, 2021.
- 716 Xu, T., Gao, X., Jiang, S., Hu, K., Peng, Z., Zhao, X., and Tang, X.: Nonlinear ozone
717 response to extreme high temperature in a subtropical megacity basin: integrated



718 observation and modeling analysis, *Environ. Res.*, 285, 122274,
 719 <https://doi.org/10.1016/j.envres.2025.122274>, 2025.

720 Xue, L., Zhu, Y., Gao, J., Zhong, X., Cui, C., Wang, S., Jiang, Z., Sun, Y., Li, Q.,
 721 Zhang, Y., Li, H., Zhang, Y., Wang, S., Zhao, M., Shen, H., Zhang, Y., Tang, G.,
 722 Wang, T., and Wang, W.: Critical transition of urban ozone formation regime in
 723 the north China plain, *Natl. Sci. Rev.*, 13, nwaf596,
 724 <https://doi.org/10.1093/nsr/nwaf596>, 2026.

725 Yan, C., Kocевska, S., and Krasnoperov, L. N.: Kinetics of the reaction of CH_3O_2
 726 radicals with OH studied over the 292–526 K temperature range, *J. Phys. Chem.*
 727 *A*, 120, 6111–6121, <https://doi.org/10.1021/acs.jpca.6b04213>, 2016.

728 Yang, Y., Sun, F., Chen, Y., Yang, S., Dai, Y., Qin, Y., Zhang, N., Shu, Z., Yan, H., Ge,
 729 X., and Wang, J.: Impact of temperature on the biogenic volatile organic
 730 compound (BVOC) emissions in China: a review, *J. Environ. Sci.*, 159, 649–660,
 731 <https://doi.org/10.1016/j.jes.2025.03.054>, 2026.

732 Zhang, D., Li, X., Yuan, M., Xu, Y., Xu, Q., Su, F., Wang, S., and Zhang, R.:
 733 Characteristics and sources of nonmethane volatile organic compounds
 734 (NMVOCs) and O_3 – NO_x –NMVOC relationships in Zhengzhou, China,
 735 *Atmospheric Chemistry and Physics*, 24, 8549–8567,
 736 <https://doi.org/10.5194/acp-24-8549-2024>, 2024.

737