

1 **Insights into the significant increase of ozone during COVID-** 2 **19 in a typical urban city of China**

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17 **Abstract**

19 The outbreak of COVID-19 promoted strict restrictions to human activities in China, which led to
20 dramatic decrease in most air pollutant concentrations (e.g., PM_{2.5}, PM₁₀, NO_x, SO₂, and CO).
21 However, obvious increase of ozone (O₃) concentrations was found during the lockdown period in
22 most urban areas of China. In this study, we conducted a field measurement targeting ozone and its
23 key precursors by utilizing a novel proton transfer reaction time-of-flight mass spectrometer (PTR-
24 TOF-MS) in Changzhou, which is representative for the Yangtze River Delta (YRD) city cluster of
25 China. We further applied the integrated methodology including machine learning, observation-based
26 model (OBM), and sensitivity analysis to get insights into the reasons causing the obvious increase of

27 ozone. Major findings include: (1) By deweathered calculation, we found changes in precursor
28 emissions contributed 1.46 ppbv to the increase in the observed O₃ during the Full-lockdown period in
29 2020, while meteorology constrained 3.0 ppbv of O₃ in the Full-lockdown period of 2019. (2) By
30 using an OBM model, we found that although significant reduction of O₃ precursors was observed
31 during Full-lockdown period, the photochemical formation of O₃ was stronger than that during the
32 Pre-lockdown period. (3) The NO_x/VOCs ratio dropped dramatically from 1.84 during Pre-lockdown
33 to 0.79 in Full-lockdown period, which switched O₃ formation from VOCs-limited regime to the
34 boundary of NO_x- and VOC-limited regime. Additionally, box model results suggested that the
35 decrease in NO_x/VOCs ratio during Full-lockdown period could increase the MeanO₃ by 2.4 ppbv.
36 Results of this study give insights into the relationship between O₃ and its precursors in urban area,
37 and demonstrate reasons causing the obvious increase of O₃ in most urban areas of China during the
38 COVID-19 lock-down period. This study also underlines the necessity of controlling anthropogenic
39 OVOCs, alkenes, and aromatics in the sustained campaign of reducing O₃ pollution in China.

40 **Keywords:** Ozone; VOCs; PTR-TOF-MS; COVID-19

41 **1. Introduction**

42 At the end of 2019, a tragic coronavirus (COVID-19) occurred, which has caused over 271
43 million global infection and over 4.51 million deaths as of this writing (12th Feb 2022). To protect
44 people's health, China adopted strict measures to control the spread of this pandemic. Thirty provinces,
45 autonomous regions and municipalities have launched Full-lockdown response (also known as Level I
46 response, roughly from 24th Jan to 25th Feb 2020) as early as 24th Jan 2020 (Shen et al., 2021; Li et al.,
47 2020; Huang et al., 2020). With the effective control of COVID-19 in China, the emergency response
48 level in most provinces (except Hubei province, the hardest-hit region) gradually downgraded to
49 Partial-lockdown (Level II and Level III response, roughly after 25th Feb 2020) (Li et al., 2020), and
50 work resumption started. During Full-lockdown period, all the social events that may cause crowds
51 (excluding transportation and industries that maintained the basic operation of society) were severely
52 restricted. Affected by the pandemic, many factories were shut down, and the on-road traffic volume

53 and construction activities have been reduced significantly (Zheng et al., 2020). During Full-lockdown
54 period, dramatic decrease of air pollutants (e.g., PM_{2.5}, NO₂, BC) were found in China, especially in
55 urban areas (Fan et al., 2021; Gao et al., 2021; Li et al., 2020; Xu et al., 2020). Surprisingly, marginal
56 increases of O₃ were observed during the lockdown period in YRD region, and this seems to be
57 contradictory to the decrease of most air pollutants (Li et al., 2020). However, as suggested by
58 previous studies, the formation of O₃ is significantly influenced by NO_x/VOCs ratio and
59 meteorological conditions (temperature, relative humidity and actinic flux) (Zhang et al., 2020a;
60 Zhang et al., 2020b). Therefore, it is essential to investigate the changes of meteorological and
61 emissions conditions to figure out reasons causing the increase of O₃ during this pandemic.

62 Previous studies on the O₃ pollution in the YRD region have often focused on the more populated
63 metropolitan areas, such as Shanghai and Nanjing, which are considerably far away from the
64 industrial zones that are essentially responsible for the sources of O₃ precursors (Li et al., 2019; Zhang
65 et al., 2020b). Changzhou, located in the center of the Yangtze River Delta (YRD) region, is a typical
66 city with fast urbanization, heavy industrial structure, huge energy consumption, increasing vehicle
67 stocks and frequent air pollution. Therefore, it provides a more representative environment to fully
68 elucidate the mechanism underlying the O₃ pollution in the YRD region (Shi et al., 2020). In a
69 companion paper (Jensen et al., 2021), we also demonstrated that Changzhou is representative for the
70 region by analyzing both surface observations and satellite data. According to previous studies, the
71 anthropogenic VOCs emission in Changzhou was around 9~12.6×10⁴ tons/year, among which
72 industries was the dominant source, accounting for 27~47% of the total VOC emissions (Cheng et al.,
73 2016; Fu et al., 2013). It is notable that industrial sources together contributed over 80% of
74 anthropogenic VOC emissions (Sun et al., 2019). Apart from industrial sources, vehicle exhaust
75 accounted for 9%~14% of total VOC emissions (Sun et al., 2019). However, rare observation
76 regarding VOCs characteristics during COVID-19 in Changzhou has been conducted.

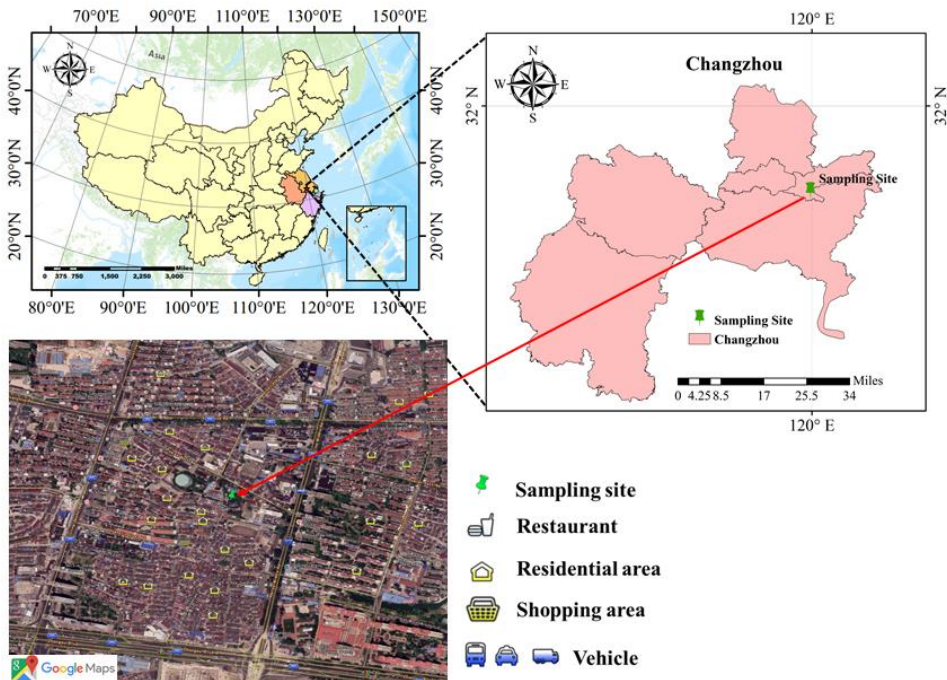
77 Highly time-resolved measurements of VOCs are generally much sparse and could not be easily
78 expanded during the lockdowns. This limits our understanding of how VOCs changed and how the
79 formation of ozone was affected. Here, we used a novel proton transfer reaction time-of-flight mass

80 spectrometer (PTR-TOF-MS, Tofwerk, Model Vocus Elf, CHE) to conduct online observation of
81 VOCs in Changzhou. The characteristics of VOCs and the variations of general air pollutants in each
82 emergency response period were analyzed. Additionally, ozone formation during each period was
83 investigated by an OBM model. Although terrifying impact has been caused by the COVID-19, it
84 provided a rare experiment to analyze the variations of VOCs and NO_x due to changes of
85 anthropogenic activities in a typical city of China. Furthermore, results of this study offer theoretical
86 support for formulating refined ozone management policy in China.

87 **2. Methodology**

88 **2.1 Field measurement**

89 The field campaign was conducted from 8th Jan to 31st Mar 2020 at a sampling site located on the
90 rooftop of a building at Changzhou Environmental Monitoring Center (CEMC, 31.76° N, 119.96° E),
91 which was approximately 15 m above ground level. As a typical urban monitoring station, this site is
92 in the center of Changzhou city, surrounded by residential and commercial area, which is also adjacent
93 to the main transportation junction in Changzhou (Figure 1). According to local epidemic prevention
94 policies, we roughly classified the measurement periods into three stages: Pre-lockdown (8th January
95 to 23rd January 2020), Full-lockdown (25th January to 24th February 2020), Partial-lockdown (25th
96 February to 28th March 2020) as defined in a study of the Yangtze River Delta (Li Li et al., 2020).



97
98 **Figure 1. Location of the sampling site in Changzhou.**

99 From Jan 8th to Mar 27th, 2020, the concentrations of traditional air pollutants (PM_{2.5}, PM₁₀, NO_x,
100 SO₂, CO, O₃) as well as meteorological parameters were monitored by a series of analyzers (Table 1).
101 In particular, 87 VOCs species were quantified, 59 of which were identified, by a PTR-TOF-MS with
102 time resolution of 1 min. Detailed measurement techniques and quality assurance and control has been
103 documented in detail in our companion paper (Jensen et al., 2021). Here, we just briefly introduce the
104 measurement. The air samples were directly drawn into a 3 m-long tube connected to the instrument.
105 A priming pump, with flow rate of 4 L/min, was used to reduce the retention time of the gas sample in
106 the tube. To avoid blocking of inlet tube caused by particles, a particulate filter was assembled at the
107 front of the inlet tube. The pressure of the ion source was set as 2 mbar and the temperature of the
108 reaction chamber was set to 90 °C during the observation. VOCs are ionized by reactions with H₃O⁺
109 ions from a discharge, and the product ions are detected by a time-of-light mass analyzer (m/Δm
110 FMHW of 950 at m/Q 107). The PTR-TOF-MS can detect most unsaturated hydrocarbons and VOCs
111 with functional groups but cannot detect species with proton affinities lower than that of water,
112 namely alkanes and small alkenes. Eighteen standard gases (including acetonitrile, acetaldehyde,
113 acrolein, acetone, isoprene, butanone, 2-butanone, benzene, 2-pentanone, ethyl acetate, toluene,

114 methyl isobutyl ketone, styrene, xylene, trimethylbenzene, naphthalene, α -pinene, and 1,3-
 115 dichlorobenzene) with concentrations of 1 ppmv were used for the calibration of the PTR-TOF-MS. In
 116 addition, a built-in calibration system was used to control the zero and standard gases.

117 **Table 1 Measurements performed during the field campaign.**

Species/Parameter	Experimental Technique
T, RH, WS, WD and P	2000WX, Airmax, USA
O ₃	400E, API, USA
NO _x (NO and NO ₂)	T200, API, USA
SO ₂	T100, API, USA
CO	T300, API, USA
PM _{2.5}	5030, Thermo Fisher, USA
PM ₁₀	5030, Thermo Fisher, USA
VOCs	Vocus Elf, ToFwerk, CHE

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119 2.2 Observation-based model

120 An OBM model coupled with MCM v3.3.1 was utilized to investigate the atmospheric oxidation
 121 capability and the radical chemistry. Detailed information about the chemistry mechanism is available
 122 on MCM website (<http://mcm.leeds.ac.uk/MCM/>, last access 8 Jul 2021). More than 5800 chemical
 123 species and 17000 reactions are included in this mechanism. The photolysis frequencies (J values)
 124 were calculated as a function of solar zenith angle, altitude using lookup tables, calculated using the
 125 Tropospheric Ultraviolet and Visible (TUV) model (Wolfe et al., 2016). Dilution mixing within the
 126 boundary layer is considered. However, as a 0-D model, vertical or horizontal transport of airmasses
 127 are not involved. The observed meteorological parameters (T, RH, P), trace gases (NO, NO₂, CO, SO₂,
 128 and VOCs) were used to constrain the model. Before each simulation, the model was run 3 days as
 129 spin-up to reach a stable state. According to the definition of atmospheric oxidation capability (AOC),
 130 AOC is quantified by Eq (1) (Geyer et al., 2001).

$$AOC = \sum_{i=1} k_{Y_i-X} [Y_i] [X] \quad (1)$$

131 where Y_i are the primary pollutants (e.g., VOCs, CH₄, and CO); X are atmospheric oxidants (OH, O₃,

132 NO₃); k_{Y_i} are the bimolecular rate constants for the reactions of Y_i and X. A high value of AOC
133 indicates fast scavenge of primary air pollutants. Additionally, OH reactivity (k_{OH}), defined as the
134 reaction rate coefficients multiplied by the concentrations of the reactants with OH, is also widely
135 used as an indicator of AOC. The value of k_{OH} depends on both the abundances and compositions of
136 primary pollutants and can be calculated by Eq (2).

$$k_{OH} = \sum_i k_{OH+X_i} \times [X_i] \quad (2)$$

137 where k_{OH+X_i} are the reaction rate coefficients of reaction OH+ X_i ; X_i are the concentrations of
138 pollutants (VOC, NO₂, CO, OVOC etc.) (Zhu et al., 2020).

139 **2.3 Trend Analysis**

140 Mann-Kendall (MK) trend test is a widely used non-parametric test method (Pathakoti et al.,
141 2021; Zhang et al., 2013). It is applicable to all distributions (that is, the data does not need to meet the
142 assumption of normal distribution), but the data should have no serial correlation. If the data has serial
143 correlation, it will have an impact on the significance level (p value). In this study, the MK trend
144 analysis was performed for individual VOC concentrations during Pre-lockdown and Full-lockdown
145 period. By using the “feast” R package, no obvious serial correlation of individual VOC is found.
146 Therefore, the observed VOC data is suitable for MK test. Detailed description and the calculation
147 formula of MK trend test could be found in the study of Pathakoti et al. (2021) and Alhathloul et al.
148 (2021). A positive z value from the MK test indicates increasing trend of the target compound. On the
149 contrary, a negative z value suggests the target compound was decreasing.

150 Sen’s slope, a non-parametric test proposed by Sen (1968), is used in this study to assess the rate
151 of change in individual VOC concentrations. The Sen’s slope is selected since it is insensitive to
152 outliers, and does not require a normal distribution of residuals. Sen’s slope (Q) is mathematically
153 represented by the following equations.

$$Q = \text{median}(SS_{ij}) \quad (3)$$

$$SS_{ij} = \frac{x_j - x_i}{j - i}, 1 \leq i < j \leq n \quad (4)$$

154 where x_j and x_i are concentrations of VOC specie x at time j and i ($1 \leq i \leq j \leq n$), respectively. SS_{ij} is the
155 linear slope between time i and j , and Q is the median of SS_{ij} . Positive and negative Q values indicate
156 increasing or decreasing trend of VOC specie x , respectively.

157 **2.4 Deweathered model**

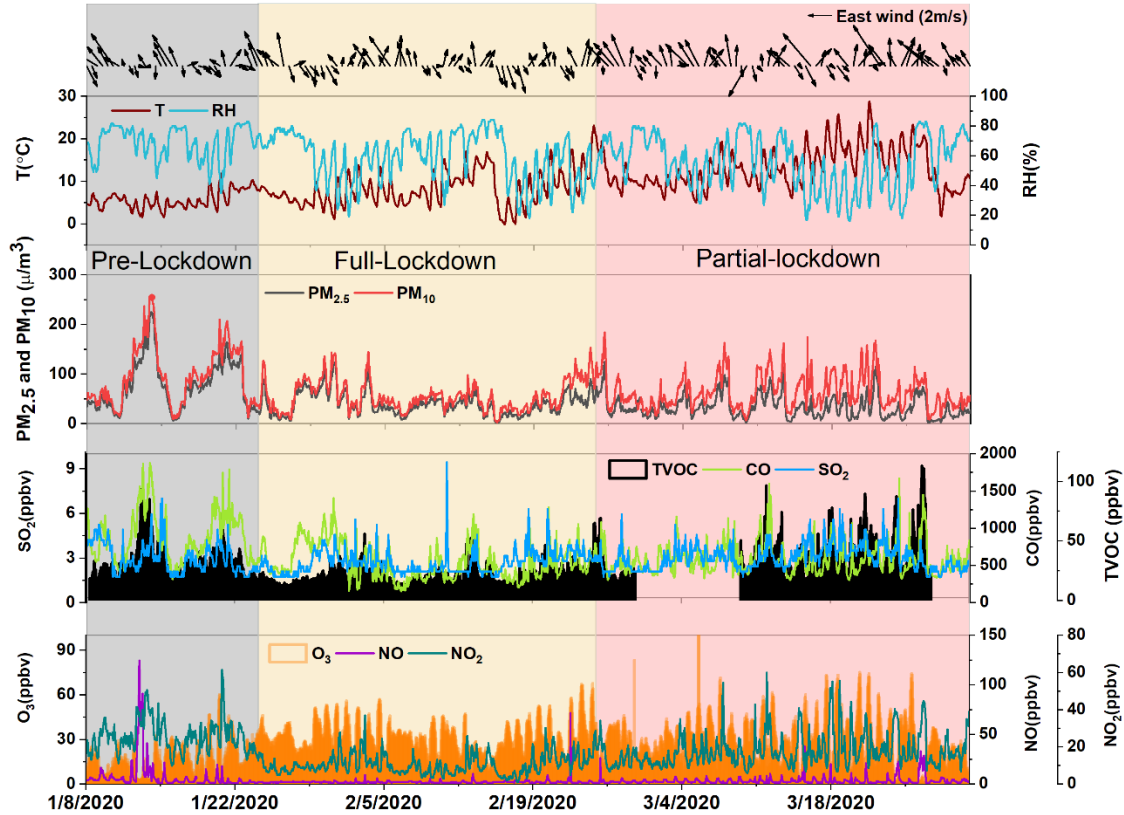
158 The observed concentrations of O_3 could be influenced by meteorological conditions, emissions
159 and/or chemistry. The emissions and chemistry are being treated together and separated from
160 meteorology by the deweathered approach based on the random forest (RF). Hourly data of Unix date
161 (number of seconds since 1970-01-01), Julian day, weekday, hour of day, wind speed (WS), wind
162 direction (WD), temperature (T), relative humidity (RH), and pressure (P), which are available during
163 the whole observation, were used for the deweathered calculation of O_3 . The missing data was
164 replaced by linear interpolation. Training of the models was conducted on 80% of the input data and
165 the other 20% was withheld from training. To avoid the disadvantage of overfitting during the training
166 of RF, a process called bagging (or bootstrap aggregation) was adopted. Bagging results in new,
167 sampled set called out-of-bag (OOB) data. A decision tree is then grown on the OOB data. Therefore,
168 all the decision trees are grown on different observations and avoid the overfitting (Grange and David
169 (2019)). To determine the value of number of trees (ntree), number of samples (nsample), and the
170 minimal node size, a series of random forests were performed under different choices of ntree,
171 nsample, and minimal node size. The results suggest that the highest coefficient of determination (R^2 ,
172 0.84) was obtained when ntree, nsample and minimal node size was set as 300, 300, and 5,
173 respectively (Table S1 and S2). More details of this model could be found in the study of Grange and
174 David (2019). The uncertainty of the deweather model is obtained by growing 50 random forest
175 models with the hyperparameters described above, which is the same method as Grange and Carslaw
176 (2019). The mean and standard error of the predicted O_3 concentrations is shown in Figure S1, and
177 results of the model are stable during the 50 runs. The differences in observed O_3 concentrations
178 ($O_{3,Obs}$) and deweathered O_3 concentrations ($O_{3,Normal}$) were regarded as the concentrations contributed
179 by meteorology ($O_{3,Met}$), which is consistent with the definition in Li et al. (2021). Correspondingly,
180 the differences in $O_{3,Normal}$ concentrations in different periods represent the influence of emissions,

181 since the $O_{3,Normal}$ has already removed the influence of meteorological conditions.

182 **3. Results and discussion**

183 **3.1 Overview of the field campaign**

184 Figure 2 shows the meteorological conditions during the observation. During the whole
185 experiment, the prevailing WD was southeast. The average T and RH was $9.9 \pm 5.1^\circ\text{C}$ and $58.9 \pm$
186 17.1% , respectively. Compared to Pre-lockdown period, the concentrations of $PM_{2.5}$, PM_{10} , SO_2 , NO ,
187 NO_2 , TVOC and CO during Full-lockdown period decreased by 48%, 42%, 11%, 65%, 58%, 33% and
188 39%, respectively. It should be noted that the decreasing ratio of VOC/NO_x is around 1.75, suggesting
189 that the lockdown policy has stronger influence on NO_x emissions than VOC emissions. The O_3
190 concentrations during the same period in 2020 and 2019 are summarized in Table 2. Considering the
191 influence of Chinese New Year, the corresponding period in 2019 was decided according to lunar
192 calendar. It should be noted that, compared to Full-lockdown period in 2019, the mean O_3
193 concentration in 2020 is obviously higher (5.5 ppbv, Figure 2). Meanwhile, the average O_3
194 concentrations in Full-lockdown period in 2020 was 67% higher than that during Pre-lockdown period
195 in 2020. To roughly analyze the cause of the obvious increase of O_3 during Full-lockdown period in
196 2020, we summarized the temperature (T) and relative humidity (RH) in Table 2. The T and RH in
197 Full-lockdown period in 2020 was $\sim 1.6^\circ\text{C}$ higher and 6.1% lower than that in the same period in 2019,
198 while the P and WS were comparable during the same period in 2020 and 2019 (Table 2). The
199 relatively higher T was in favor of O_3 formation during the Full-lockdown period in 2020. As for RH,
200 the influence on O_3 is nonlinear (Zhang et al., 2020), and based on our sensitivity test, lower RH could
201 lead to decrease or increase of O_3 concentration (Figure S2). Overall, changes in O_3 concentrations
202 could be a result of the joint effect of meteorological conditions and emissions/chemistry, the
203 following sections would discuss these influences respectively.



204

205 **Figure 2** Time series of meteorological parameters and air pollutants during the whole observation.

206 **Table 2** Comparison of average meteorological conditions during Pre-lockdown, Full-lockdown, and Partial-
 207 **lockdown in 2020 and the same period in 2019.**

Periods	Date	P (hPa)	RH (%)	T (°C)	Precipitation (mm)	WS (m/s)
Pre-lockdown	(2020.1.8-1.24)	1025.4	84.9	4.8	0.13	1.8
Same period in 2019	(2019.1.19-2.4)	1025.6	72.7	5.2	0.05	1.9
Full-lockdown	(2020.1.25-2.24)	1025.6	73.0	7.3	0.09	2.1
Same period in 2019	(2019.2.5-3.7)	1024.1	79.1	5.7	0.15	2.1
Partial-lockdown	(2020.2.25-3.31)	1018.9	69.5	12.1	0.11	2.4
Same period in 2019	(2019.3.8-4.12)	1017.6	64.0	13.8	0.02	2.0

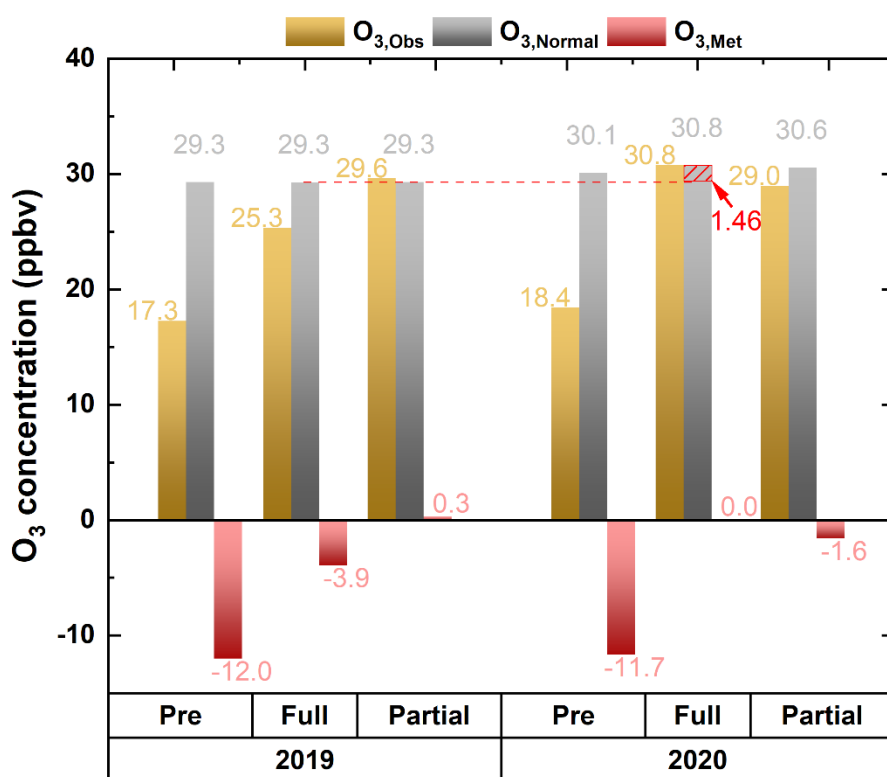
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209 **3.2 Mechanism affecting the obvious O₃ increase**

210 **3.2.1 Meteorological perspective**

211 Deweathered O₃ concentrations were calculated based on the model described in Section 2.4. The
 212 difference between O_{3,Obs} and O_{3,Normal} can be regarded as the meteorological influence (O_{3,Met}). In

213 addition, the difference between $O_{3,Normal}$ concentrations in different years could be considered as the
 214 influence of emissions ($O_{3,Emi}$). Figure 3 exhibited the average $O_{3,Obs}$, $O_{3,Normal}$, $O_{3,Met}$ during the same
 215 periods in 2019 and 2020, respectively. It is obvious that the $O_{3,Obs}$ during Pre-lockdown period is
 216 much lower than that during Full-lockdown period in both years, which was partly attributed to
 217 negative influence of meteorological condition during Pre-lockdown period (Figure 3). This is
 218 consistent with the increasing temperature and solar radiation, which could significantly contribute to
 219 the increase in ozone concentration, from Pre-lockdown to Full-lockdown period. It should be noted
 220 that meteorology constrained O_3 concentrations by 3.9 ppbv during the Full-lock down period in 2019.
 221 Apart from the influence of meteorological condition, the $O_{3,Normal}$ in Full-lockdown period in 2020 is
 222 still 1.46 ppbv and 0.64 ppb higher than that during Full-lockdown period in 2019 and that during Pre-
 223 lockdown period in 2020, indicating that improper decline of precursor emissions was possibly the
 224 key reason for the obvious increase of O_3 during Full-lockdown period in 2020.



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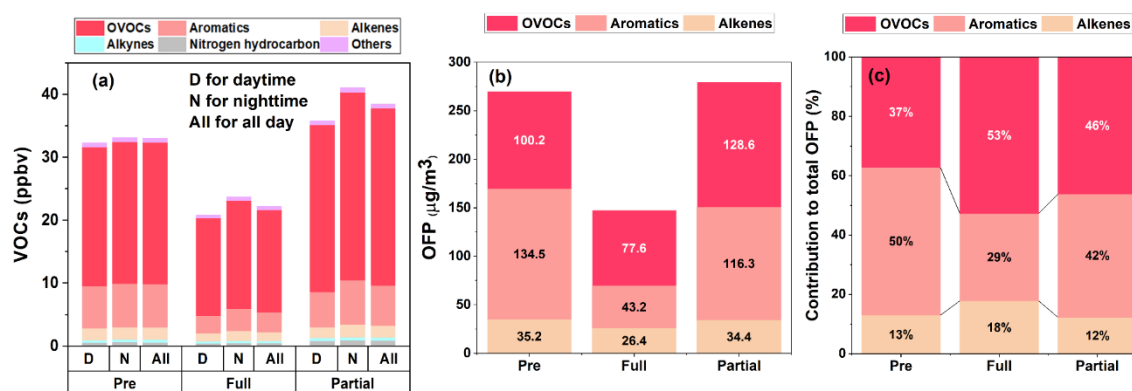
Figure 3. Comparison of observed (Obs), weather-normalized (Normal), and meteorological-factors-infected

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(Met) O₃ concentrations during the same period in 2019 and 2020.228 **3.2.2 Ambient VOCs**

229 As mentioned above, the changes in O₃ precursor emissions strongly affected the O_{3,Obs}, and the
 230 changes in VOCs and NO_x emissions would eventually be reflected by the observed concentrations of
 231 individual VOCs and NO_x. Therefore, the concentrations of each VOC group in different periods were
 232 summarized (Figure 4). OVOCs dominated the total VOCs (TVOC) concentrations during the whole
 233 observation, with a daily average concentration of 21.44 ± 10.27 ppbv. During Full-lockdown period,
 234 the TVOC dropped to 22.19 ± 7.9 ppbv from 32.78 ± 13.81 ppbv, which was mainly affected by the
 235 decrease in industrial activities and traffic volume. This is proved by the trend of traffic volume,
 236 VOCs emission and traffic/industrial-derived VOCs (Text S1 and Figure S3). In addition, Jensen et al.
 237 (2021) found the VOC emissions from most industries in Changzhou share the same “U-shape” trend
 238 as our study. The most obvious drop was found in aromatics (~54%), followed by OVOCs (~27%),
 239 alkenes (~26%), nitrogen hydrocarbon (~25%), and other VOCs (~21%). Additionally, the
 240 discrepancy of daytime and nighttime VOCs concentrations during different periods were compared
 241 (Figure 4 (A)). The concentration of each VOCs group exhibited higher values during nighttime,
 242 which was caused by the low atmospheric oxidation condition and the low atmospheric boundary
 243 layer height (Maji et al., 2020; Valach et al., 2015).

244



245 **Figure 4. Comparison of daytime and nighttime VOCs concentrations (A), average OFP (B), and contribution**
 246 **to total OFP (C) during different periods.**

247 Furthermore, the average concentrations of individual VOCs during different periods were

248 summarized in Figure 5. Total 42 VOC species exhibited an ‘U’ shape trend during the whole
249 observation, while formaldehyde (HCHO) and methanol showed an obvious increasing pattern. It
250 should be noted that the measurement of HCHO could be strongly influenced by humidity. Since
251 within the drift tube, the back reaction, which converse the protonated HCHO back into HCHO, is
252 highly humidity dependent (Inomata et al., 2008; Warneke et al., 2011).

253 To quantitatively evaluate the changes of individual VOC concentrations from Pre-lockdown to
254 Full-lockdown period, when the variations of each VOCs are obvious, we applied MK trend test and
255 Sen’s slope analysis based on the hourly average VOCs concentration data (Table S3). Table 3 lists the
256 top 10 VOCs species with decreasing pattern (with negative Q value) from Pre-lockdown to Full-
257 lockdown period. Toluene, benzene and xylene exhibited the most significant decreasing pattern, with
258 a slope of 7.73×10^{-4} , 7.36×10^{-4} , and 7.20×10^{-4} ppbv h^{-1} , respectively. As for NO_x and TVOC, the slope
259 was -1.62×10^{-2} and 5.48×10^{-3} ppb h^{-1} (Table S3). This result is consistent with the drastic drop of
260 industrial activities and traffic volumes, which are key sources of aromatics and NO_x , from Pre-
261 lockdown to Full-lockdown period. Other VOCs, such as ethyl-acetate, acetic acid, acetaldehyde,
262 diethyl sulfide, ethanol, butanol and acrolein are also tightly associated with industrial processes,
263 thereby showed decreasing trend from Pre-lockdown to Full-lockdown period. Additionally, the
264 average diurnal variations of acetonitrile, dimethyl formamide (DMF), and styrene, which are tracers
265 of biomass burning and industrial emission, respectively, exhibited significant reduction during Full-
266 lockdown period (Figure S4), also indicating strong decrease in these emissions. However,
267 formaldehyde and methanol exhibited increasing trend, with a slope of 12.78×10^{-4} and 6.35×10^{-4} ppbv
268 h^{-1} , respectively. This could be explained by the secondary formation of HCHO and methanol, which
269 was promoted under better oxidation condition in Full-lockdown period.

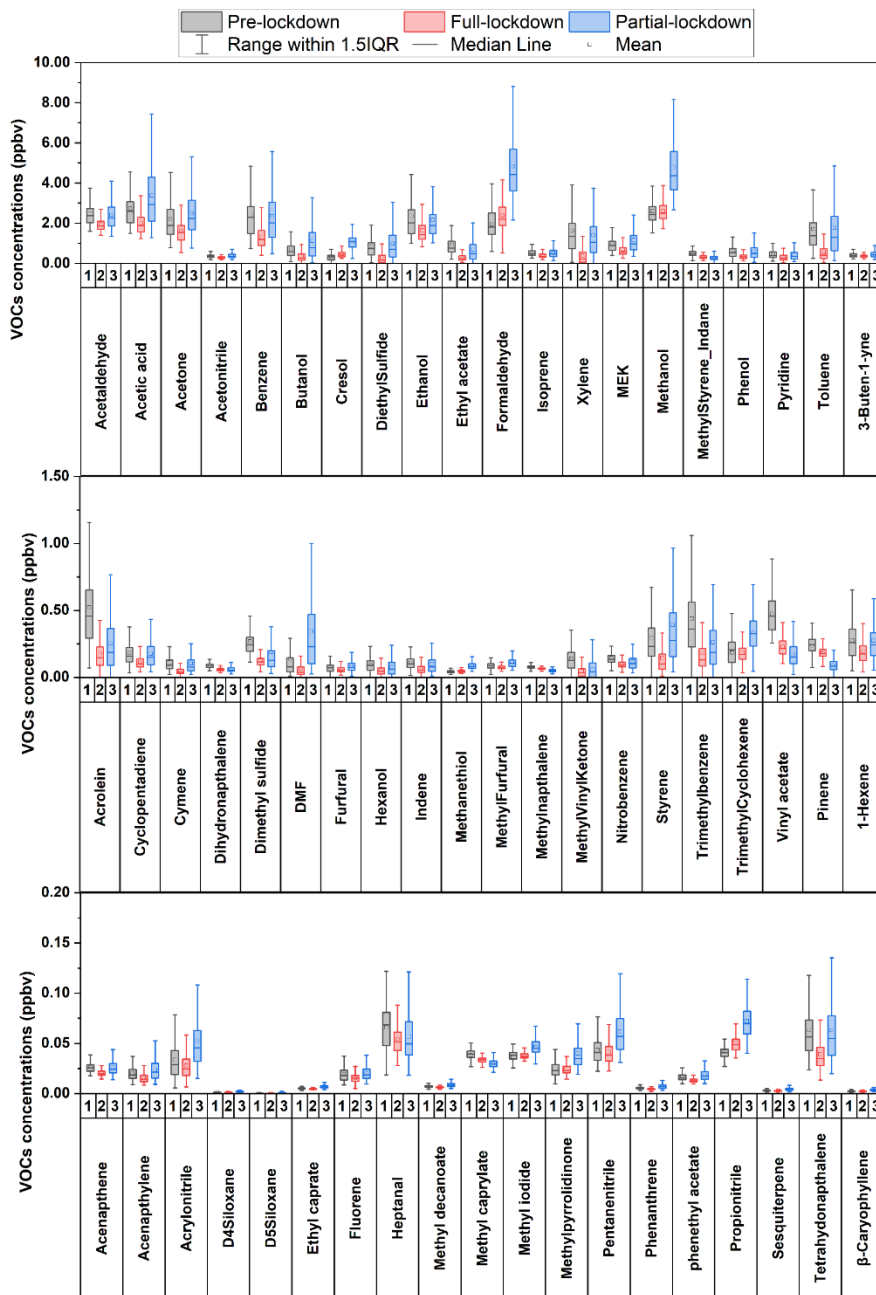


Figure 5. Concentrations of individual VOC species during different period.

*MEK, DMF, are abbreviation of Methyl ethyl ketone and dimethylformamide, respectively.

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Table 3. Top 10 VOCs with decreasing trend from Pre-lockdown to Full-lockdown

VOC	Z value	Q *10000 (ppbv h ⁻¹)	VOC	Z value	Q *10000 (ppbv h ⁻¹)
Toluene	-14.02	-7.73	Acetaldehyde	-10.31	-3.95
Benzene	-9.65	-7.36	Diethyl sulfide	-9.15	-3.16
xylene	-12.38	-7.20	Ethanol	-5.48	-3.09
Ethyl-acetate	-18.53	-5.20	Butanol	-10.42	-2.83
Acetic acid	-6.79	-4.12	Acrolein	-15.48	-2.76

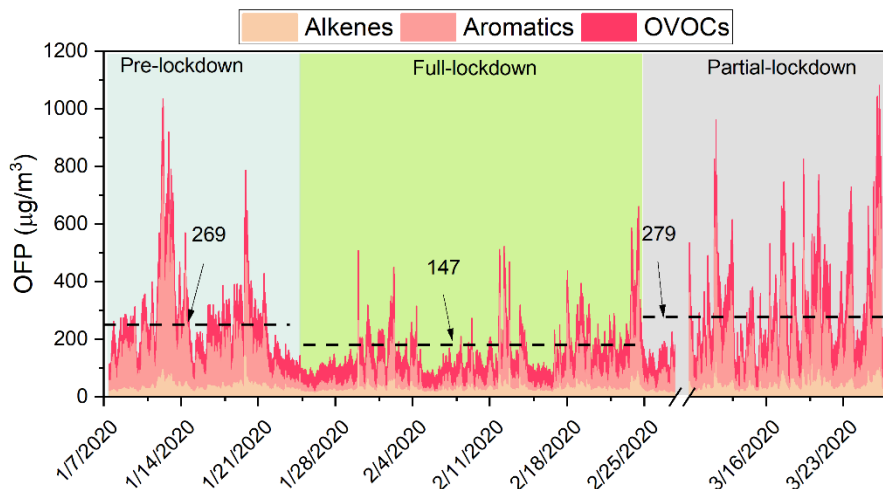
279 **3.2.3 Chemistry perspective**

280 The reactivities of different VOCs vary significantly, hence, ozone formation potential (OFP) is
 281 used in this study to assess the potential contribution of active VOCs (including alkenes, aromatics
 282 and OVOCs) to O₃ formation on the same basis, and it can be calculated by formula (5):

$$OFP_i = MIR_i \times [VOC_i] \quad (5)$$

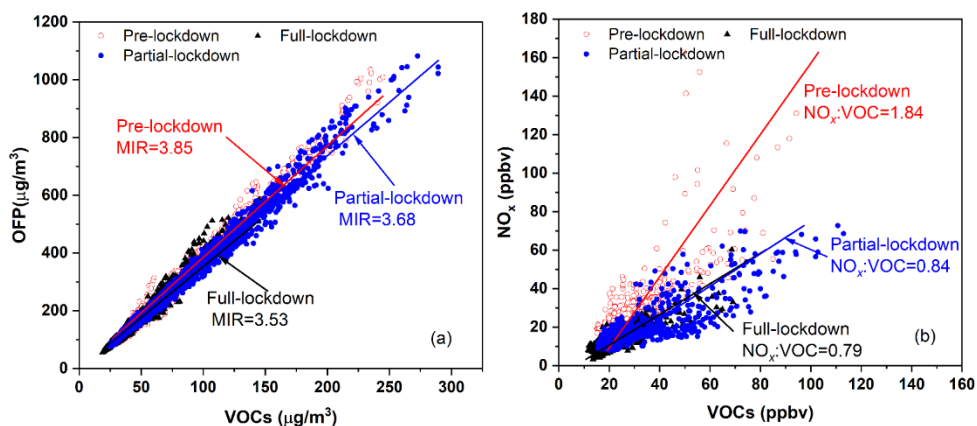
283 where MIR_i is the ozone formation potential coefficient for a given VOC species i in the maximum
 284 increment reaction of O₃, acquired from Carter (2009); $[VOC_i]$ is the concentration of VOC species i
 285 (in $\mu\text{g}/\text{m}^3$). It should be noted that OFP does not indicate O₃ concentration but only serves as a
 286 reference for the potential O₃ produced via the degradation of VOCs. The time series of total OFP is
 287 shown in Figure 6. The average OFP in Pre-lockdown, Full-lockdown, and Partial-lockdown period
 288 was 269.4 ± 146.0 , 147.2 ± 72.4 , $279.3 \pm 168.6 \mu\text{g}/\text{m}^3$, respectively. The trend of the total OFP
 289 indicates the drastic decrease of VOCs reactivities from Pre-lockdown to Full-lockdown period.
 290 During Pre-lockdown period, aromatics were the dominant OFP contributor (49%), followed by
 291 OVOCs (38%) and alkenes (13%) (Figure 4). Among VOCs, xylene exhibited the maximum OFP
 292 value ($68.6 \pm 59.3 \mu\text{g}/\text{m}^3$), followed by acetaldehyde ($28.8 \pm 6.4 \mu\text{g}/\text{m}^3$), toluene ($25.7 \pm 20.1 \mu\text{g}/\text{m}^3$)
 293 trimethylbenzene ($25.4 \pm 15.8 \mu\text{g}/\text{m}^3$), and formaldehyde ($22.7 \pm 9.1 \mu\text{g}/\text{m}^3$) (Figure S5). Compared to
 294 Pre-lockdown period, the OFP of aromatics decreased dramatically ($-91.2 \mu\text{g}/\text{m}^3$) during Full-
 295 lockdown period (Figure 4 (B)), which was mainly attributed to the rapid decline of human activities
 296 (e.g., transportation and industry). However, the OFP of alkenes and OVOCs only decreased by 8.9
 297 and $22.5 \mu\text{g}/\text{m}^3$, respectively. During the observation, the most abundant alkenes measured by

298 PTR-TOF-MS are 1-hexene and isoprene, with the k_{OH} of 37 and $100 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$
299 ¹ (Atkinson and Arey, 2003), respectively, which are much higher than that of the most
300 abundant aromatics (1.22 , 5.63 , and $17 \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ for benzene, toluene, and xylene,
301 respectively). The fast degradation of these alkenes could attribute to the small relatively
302 smaller change of OFP from alkenes. As for OVOCs, the secondary formation could compensate
303 the decrease in primary emissions. The OFP values of aromatics and alkenes during Pre-lockdown and
304 Partial-lockdown period are comparable, but OVOCs exhibited higher OFP contribution (~46%) in
305 Partial-lockdown period, which could be attributed to the higher AOC, enhanced solar radiation and
306 temperature during Partial-lockdown period. To compare the average reactivity of VOCs during
307 different periods, we calculated the mean MIR, derived by dividing the total OFP by total VOC
308 concentration, in each period. A higher MIR means stronger capability of VOCs to produce ozone. As
309 shown in Figure 7, the average MIR during Pre-lockdown, Full-lockdown, and Partial-lockdown
310 period was 3.85, 3.53 and 3.68 ($\text{g O}_3/\text{g VOC}$), respectively. This result suggests that VOC species
311 composition in Full-lockdown is more conducive to ozone formation than that in Pre-lockdown, and
312 Partial-lockdown period. However, the formation of O_3 was sensitive to the ratio of NO_x/VOCs and
313 meteorological conditions, which can be significantly different in each period. As shown in Figure 7,
314 the average NO_x/VOCs ratio in the three periods (shown in) was 1.84, 0.79, and 0.84, respectively,
315 suggesting more NO_x was reduced than VOCs during Full-lockdown period, which could further
316 influence the sensitivity of O_3 formation.



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Figure 6. Time series of OFP during the whole observation period (dash lines represent the average OFP value during each period)

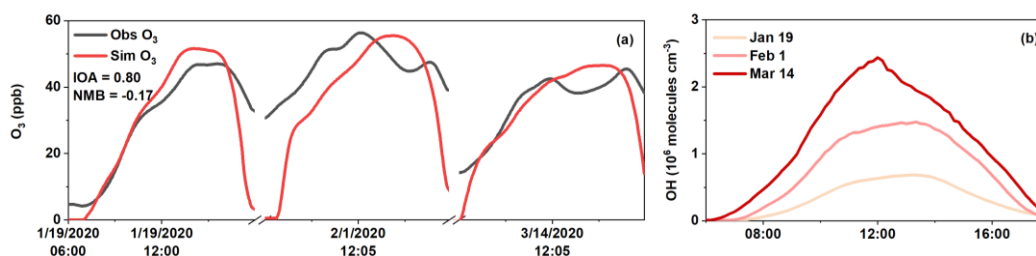


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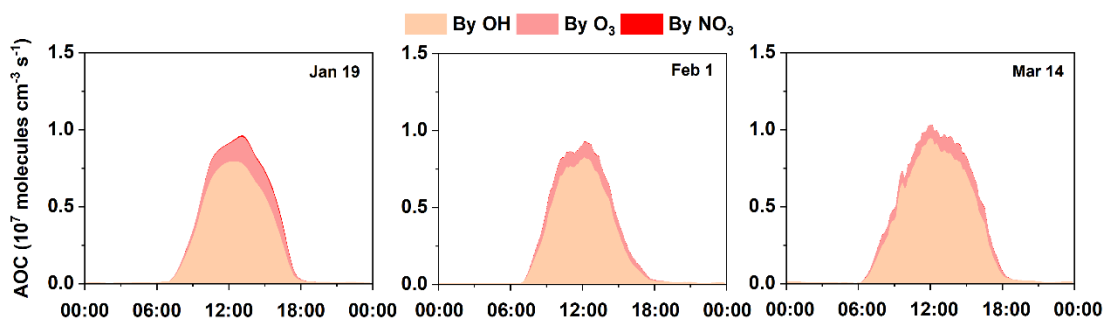
Figure 7. Plot of 1-hour averaged MIR and NO_x vs VOCs during three periods.

322 To investigate the detailed formation mechanism of O₃ in each period, three cases (January 19th,
323 February 1st, March 14th) with stagnant meteorological conditions were chosen. The index of
324 agreement (IOA) of O₃ is 0.80, indicating that the model can capture the daytime variation of O₃. The
325 simulated daytime OH concentrations exhibited an increasing trend from January 19th to March 14th,
326 with an average value of $0.36 \pm 0.27 \times 10^6$, $0.75 \pm 0.54 \times 10^6$ and $1.18 \pm 0.78 \times 10^6$ molecules cm⁻³,
327 respectively. This could be attributed to the increasing solar radiation and temperature from January to
328 March. To analyze the atmospheric oxidation, we calculated the AOC according to Eq(1). The average
329 daytime AOC on Jan 19th, Feb 1st, and Mar 14th was 0.26 ± 0.35 , 0.23 ± 0.33 , and 0.31 ± 0.38
330 molecules cm⁻³ s⁻¹, respectively (Figure 9). Comparatively, these values are much lower than those

331 simulated for Shanghai and Beijing (Liu et al., 2012; Zhu et al., 2020; Zhang et al., 2021) in summer,
 332 mainly due to the meteorological conditions in winter season. It is notable that the simulated OH on
 333 Jan 19th was significantly lower than that on Feb 1st, but the AOC on Jan 19th was comparable to that
 334 on Feb 1st. This should be ascribed to the abundant primary pollutants, which efficiently react with OH,
 335 during Pre-lockdown period.
 336



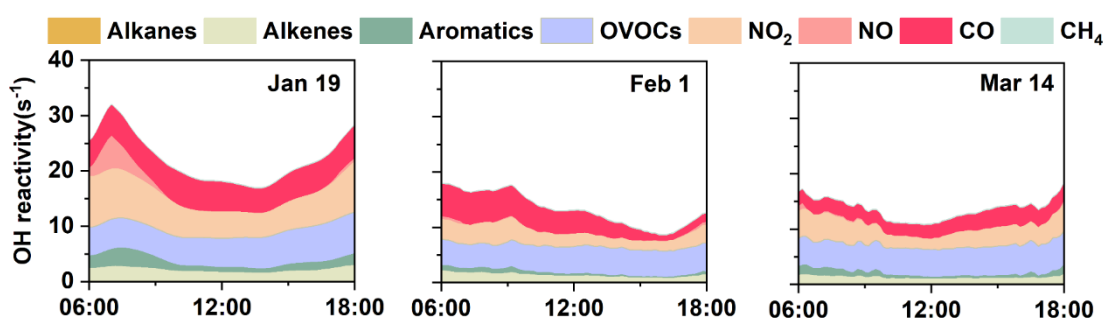
337
 338 **Figure 8. Comparison of simulated and observed O₃ (a) and simulated daytime OH concentrations (b) in three**
 339 **cases.**



340
 341 **Figure 9. Diurnal variation of AOC in three cases**

342 The daytime variations of OH reactivity calculated by OBM model are exhibited in Figure 10,
 343 including the contribution from measured pollutants (e.g., VOCs, NO_x, and CO) and model-simulated
 344 species (OVOCs). Generally, the k_{OH} assessed at Changzhou was in the range of 9~32 s⁻¹, which was
 345 comparable to that calculated for other cities in China (e.g., Shanghai 4.6~25 s⁻¹, Zhu et al., 2020,
 346 Chongqing 15~25 s⁻¹, Tan et al., 2019 and Beijing 15~25 s⁻¹, Tan et al., 2019). It is obvious that OH
 347 reactivity peaked in the morning, with maximum values of 31.76, 17.98, and 17.30 s⁻¹, respectively.
 348 The OH reactivity from NO₂ exhibited obvious daytime variation, especially during the morning rush

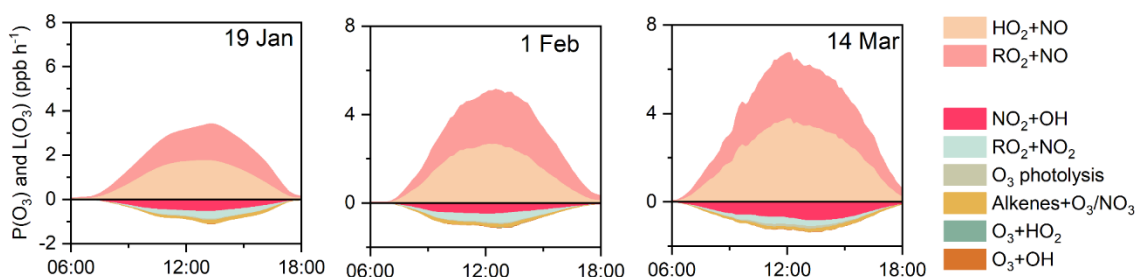
349 hour, which lead to the peak k_{OH} value during morning. The OH reactivity (k_{OH}) on Feb 1st was much
 350 lower than that in the other two cases, which was mainly due to the abundance of emissions during
 351 Pre-lockdown and Partial-lockdown period. Compared to Jan 19th, the k_{OH} from NO_2 on Feb 1st and
 352 Mar 14th showed lower levels, with an average value of 2.62 and 3.35 s^{-1} , respectively. This
 353 corresponds with the dramatic drop of traffic volume during lockdown periods. Similarly, compared to
 354 Jan 19th, the k_{OH} from alkenes and aromatics were lower on Feb 1st and Mar 14th. As k_{OH} from OVOC,
 355 it shared same trend as OVOC concentration, which reached the minimum value (5.56 s^{-1}) during the
 356 Full-lockdown period.



357
358 **Figure 10. Daytime variation of OH reactivity in three cases**

359 To investigate the variation of O_3 during different periods, the formation and loss pathways of O_3
 360 were calculated (Figure 11). The formation of O_3 ($P(O_3)$) was dominated by HO_2+NO and RO_2+NO
 361 pathways. Although the average MIR during Full-lockdown period was the minimum among the three
 362 periods, the $P(O_3)$ on Feb 1st was higher than that on Jan 19th. This could be attributed to the higher
 363 AOC and better photochemical conditions during Full-lockdown period. Similarly, much higher $P(O_3)$
 364 was found on March 14th. To avoid the influence of meteorological conditions and test the potential
 365 mean O_3 (Mean O_3) concentrations under different $NO_x/VOCs$ ratios, a series of scenario analyses
 366 were performed based on the average condition during the whole observation, and the isopleths of
 367 Mean O_3 concentrations are exhibited in Figure. 12. Note that the value of temperature and photolysis
 368 frequencies (J values) in the scenario analyses could be higher than the actual value during Pre-
 369 lockdown period and could further lead to overestimation of simulated Mean O_3 during Per-lockdown
 370 period. Additionally, the VOCs concentrations mentioned in this section only represent the VOC
 371 species in the MCM mechanism. By connecting the inflection points in each O_3 isopleth, we get the

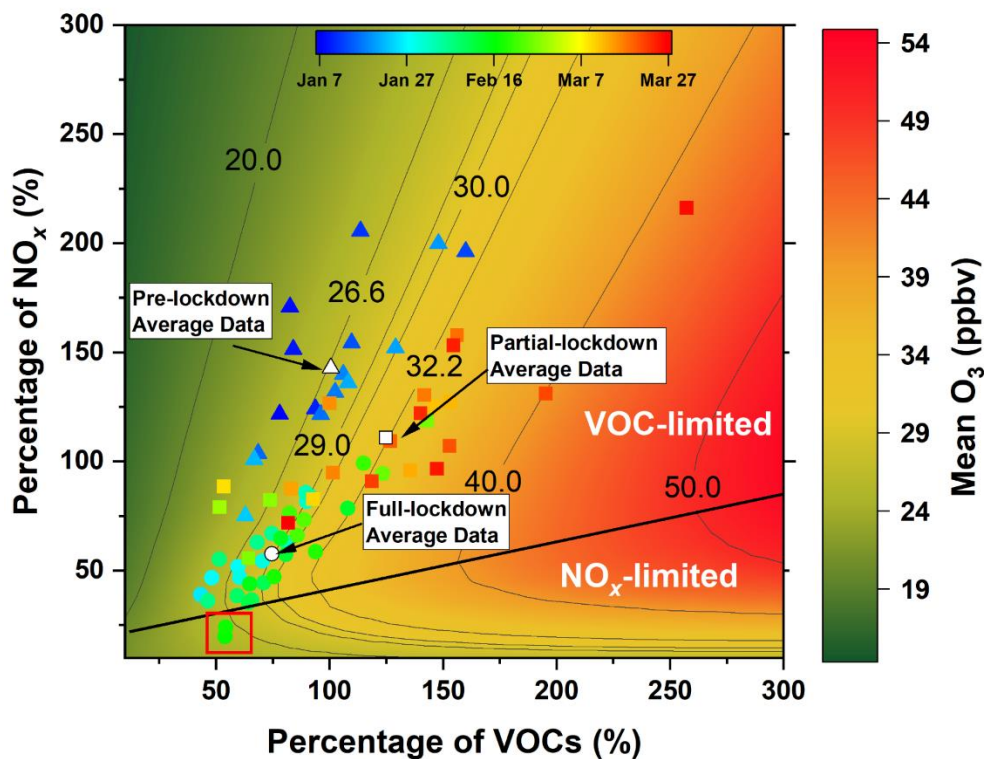
372 ridge line, which divides the whole regime into NO_x -sensitive and VOCs-sensitive regimes (Figure.
 373 12). During Pre-lockdown period, the O_3 formation was in VOC-limited regime (triangles in Figure.
 374 12), with an average NO_x/VOC ratio of 1.84. As for Full-lockdown period, significant decrease of
 375 NO_x and VOC emissions was observed, and the NO_x/VOCs ratio dropped to 0.79, which gradually
 376 switched the O_3 formation to the junction of VOCs-limited and NO_x -limited regimes, especially on
 377 Feb 16th and Feb 17th (circles in the red rectangle in Figure. 12), when the O_3 formation went into
 378 NO_x -limited regime. During Partial-lockdown period, increasing of VOCs and NO_x emission again
 379 dragged the formation of O_3 back into VOCs-limited regime (triangles in Figure. 12). Interestingly,
 380 although a great deal of NO_x and VOCs emissions were diminished during Full-lockdown period, the
 381 average Mean O_3 in Full-lockdown was supposed to be 2.4 ppbv higher than that in Pre-lockdown
 382 period. This result is consistent with the trend of the observed MDA8 O_3 and the results of the
 383 deweathered calculation. Therefore, expect for the influence of meteorology, the improper NO_x/VOCs
 384 reduction ratio and further influence on chemistry was the key reason for the obvious increase of O_3
 385 during Full-lockdown period in Changzhou in 2020.



386

387

Figure 11. Daytime variation of $\text{P}(\text{O}_3)$ and $\text{L}(\text{O}_3)$ in three cases



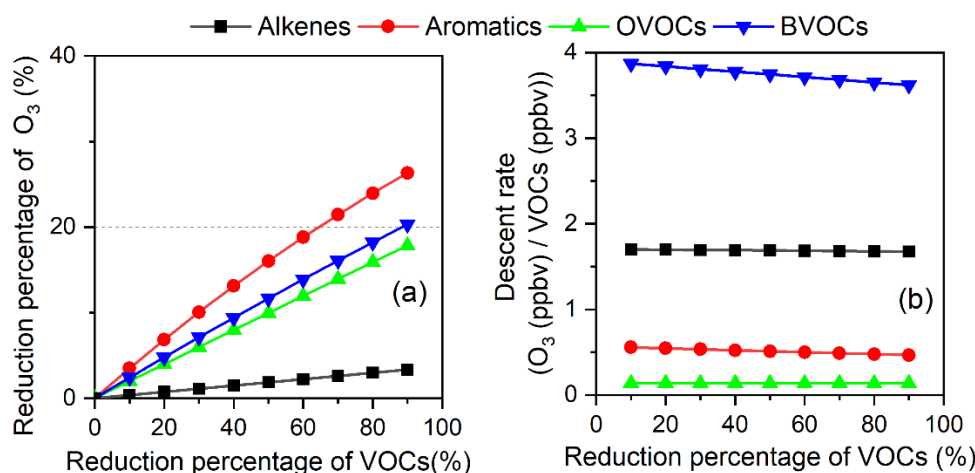
388

389 **Figure. 12 MeanO₃ isopleth.** The colored circles, triangles, and rectangles represent the daily average
 390 concentrations of NO_x and VOCs during Pre lockdown, Full-lockdown, and Partial-lockdown period,
 391 respectively. The white circle, triangle, and rectangle indicates the average NO_x and VOCs concentrations
 392 during Pre lockdown, Full-lockdown, and Partial-lockdown period, respectively.

393 The scenario analyses raise a question: how much O₃ would change as a function of reduction of
 394 NO_x and VOCs? Therefore, the reduction percentage of O₃ ($\Delta O_3/O_3$) during Pre-lockdown period as a
 395 function of reduction of VOCs and NO_x were calculated, and the result could be regarded as a
 396 potential to control O₃ pollution. Based on the VOCs species in MCM v3.3.1, we classified the
 397 measured VOCs into four groups: alkenes (n-butene); aromatics (including benzene, toluene, phenol,
 398 xylene, styrene, cresol, and trimethylbenzene); OVOCs (including methanol, ethanol, formaldehyde,
 399 aldehyde, acrolein, methyl vinyl ketone, methyl ethyl ketone, ethyl acetate, methyl isobutyl ketone,
 400 hexanol, and heptanal); and BVOCs (isoprene, pinene, and caryophyllene). The results in Figure 13(a)
 401 indicate that more reduction potential of O₃ could be achieved by diminishing aromatics, followed by
 402 BVOCs, OVOCs, and alkenes. It should be noted that many light alkanes and active alkenes, such as

403 ethene and propene, could not be measured by the PTR-TOF-MS and might further lead to the
 404 underestimation of ozone production from alkanes and alkenes. Additionally, this comparison has a
 405 drawback of being influenced by the concentrations of VOCs. To normalize the influence of
 406 concentrations of VOCs, the descent rate of O₃ (ΔO_3 (ppbv)/ $\Delta VOCs$ (ppbv)) as a function of
 407 reduction percentage of VOCs were calculated (Figure 13 (b)). O₃ exhibited the highest dependence
 408 on BVOCs, with an average descent rate of 3.74 ± 0.09 ppbv/ppbv. Differing from the result in Figure
 409 13 (a), diminishing alkenes could lead to decrease of O₃ by an average declining rate of 1.69 ± 0.01
 410 ppbv/ppbv. On the contrary, reduction of NO_x would lead to increase of O₃, with an average rate of
 411 1.29 ± 0.21 ppbv/ppbv (Figure S6). Although the descent rate of O₃ turned to decrease and the
 412 sensitivity of O₃ formation get into NO_x-limited regime when over 70% of NO_x were eliminated, it
 413 still causes net increase of O₃.

414 Although diminishing BVOCs seems to be the most efficient way to restrain O₃ pollution, most of
 415 BVOCs were emitted directly from plants and could not be easily controlled. Besides, huge number of
 416 OVOCs (such as formaldehyde, aldehyde, methanol, ethanol, methyl vinyl ketone, methyl ethyl
 417 ketone, etc.) could be directly emitted from anthropogenic processes or secondary generated from the
 418 oxidation of precursors (such as alkenes and aromatics), which complicates the control of OVOCs.
 419 Therefore, considering the reduction potential and descent rate of O₃, more efforts are needed on the
 420 control of alkenes and aromatics.



421
 422 **Figure 13. Reduction percentage of O₃ as a function of reduction percentage of VOCs (a); descent rate of O₃ as a**

423

424 **3.3 Uncertainty analysis**

425 Due to limitations in the observations, several issues should be noted in the application of the
426 OBM model to evaluate the local chemistry in the present study. Firstly, deficiency of the observation
427 of C2~C5 alkenes and alkanes could lead to underestimation of the simulated O₃. We can only obtain
428 the C2~C5 alkenes and alkanes concentrations from the observation during the autumn of 2018 at the
429 same site. To analyze the uncertainties from this disadvantage, we have done simulation by including
430 assumed diurnal variation of ethene, propene, butene, ethane, propane and butane which are key
431 C2~C5 alkenes and alkanes at this site, in the model. On average, adding 0.5~2 times alkenes or
432 alkanes could lead to 1.65%~9.49% or 1.37~5.36% increase of simulated daytime O₃, respectively
433 (Figure S7 and S8). In addition, the deficiency of C2~C5 has potential to cause uncertainty in O₃
434 formation potential. To quantify this impact, the EKMA analysis with the hypothetical diurnal
435 variation of C2~C5 was also performed. Generally, adding C2~C5 alkenes and alkanes in the model
436 would lead to increase of the simulated O₃, and could slightly shift the O₃ isopleth to the right without
437 changing the isopleth shape (Figure S9). Therefore, the deficiency of C2~C5 alkenes and alkanes
438 could result in additional uncertainties in O₃ simulation (both time series and EKMA). It should be
439 noted that, this sensitivity analysis is based on the “hypothetical” diurnal variation of C2~C5 alkenes
440 and alkanes, which would bring in uncertainty. We hope a wider range of VOCs would be monitored
441 simultaneously in future field campaign and avoid this deficiency. Secondly, the photolysis
442 frequencies (J values) were calculated as a function of solar zenith angle, altitude using lookup tables,
443 calculated using the Tropospheric Ultraviolet and Visible (TUV) model, which could lead to
444 uncertainty in the simulation of O₃. Hence, we analysis the influence of J values by increasing or
445 decreasing the photolysis rates by 10% and 20%. Results showed that the simulated O₃ could decrease
446 or increase by 25.14% or 21.73%, respectively, when photolysis rates were decreased or increased by
447 20% (Figure S10). In addition, the J values, which directly or indirectly influence the recycling of RO_x,
448 could lead to uncertainty in the calculation of AOC and *k*_{OH}. Based on above sensitivity analysis, we

449 found the relative changes in AOC and k_{OH} by 1% changes in J values was 1.07% and 0.14%,
450 respectively. Therefore, the J values is recommended to be measured during future observations.

451 **4. Conclusions**

452 After the outbreak of COVID-19, strict epidemic prevention measures have been adopted
453 throughout China, leading to dramatic decrease in traffic volume and industrial activities. Affected by
454 the decrease of number of vehicles on the road, non-essential industrial productivity, and associated
455 pollutant emissions, most of the air pollutants (e.g., PM_{2.5}, PM₁₀, NO, NO₂, SO₂, and VOCs) dropped
456 to a lower level during lockdown period (especially during Full-lockdown period). However, O₃
457 increased compared to that during the same period in 2019 in many urban areas of China. To figure
458 out the reasons for this obvious increase of O₃, the characteristics of O₃ precursors (NO_x, VOCs)
459 during Pre-lockdown, Full-lockdown, and Partial-lockdown periods in Changzhou were analyzed.
460 Although this study was conducted in single city of China, the representativeness of Changzhou
461 guaranteed the applicability of the results the YRD region. Results suggested that the decrease of
462 human activities during Full-lockdown period significantly suppressed the emissions of NO_x and
463 VOCs, which further lead to dramatic drop in the concentrations of most VOCs, especially aromatics.
464 As a result, the NO_x/VOCs ratios dropped from 1.84 at Pre-lockdown period to 0.79 during Full-
465 lockdown period. By deweathered calculation, we found that meteorology constrained O₃
466 concentration by 3.9 ppbv during Full-lockdown period in 2019, but exhibited negligible influence on
467 that during the same period in 2020. However, compared to Full-lockdown period in 2019, changes in
468 precursor emissions led to 1.46 ppbv increase in O₃ concentrations during the same period in 2020. To
469 verify this result, a box model was used to simulate the formation of O₃. Results show that the AOC
470 level during Full-lockdown was comparable to that during Pre-lockdown period, but the formation
471 rate of O₃ was much higher during Full-lockdown period. By scenario analysis, we found the decrease
472 of NO_x and VOCs in Full-lockdown period dragged the formation of O₃ from VOC-sensitive regime
473 to the junction of VOCs- and NO_x-limited regime, and the average simulated MeanO₃ in Full
474 lockdown period could be 2.4 ppbv higher than that in Pre-lockdown period. Although the

475 deweathered model and OBM model shows differences in the emission-derived change of O₃, the
476 results together point out that the improper reduction of NO_x and VOCs was the key reason for the
477 obvious increase of O₃ during Full-lockdown period in 2020. Overall, the outbreak of COVID-19 has
478 caused devastation over the world. However, it provided an extreme experiment to investigate the O₃
479 formation under strict emission control policies and provided insights into the policy formulation for
480 diminishing O₃ pollution in the YRD region. The data indicate that the concentrations of VOCs and
481 NO_x have changed dramatically during the pandemic, a common situation also found in other Chinese
482 cities, and led to the switch of O₃ formation sensitivity. These results have a clear indication that, in
483 the future, more efforts should be paid on the reduction ratio of anthropogenic VOCs and NO_x.

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487 **References**

- 488 Alhathloul, SH., Khan, AA., Mishra, AK.. Trend analysis and change point detection of annual and
489 seasonal horizontal visibility trends in Saudi Arabia. *Theoretical and Applied Climatology* 2021; 144:
490 127-146.
- 491 Atkinson, R. and Arey, J.: Atmospheric Degradation of Volatile Organic Compounds, *Chemical Reviews*
492 2003; 103, 4605–4638.
- 493 Jensen, A., Liu, ZQ., Tan, W., Dix, B., Chen, TS., Koss, A., Zhu, L., Li, Li., Gouw, J. Measurements of
494 Volatile Organic Compounds during the COVID-19 Lockdown in Changzhou, China. *Geophysical*
495 *Research Letters* 2021.
- 496 Carter, W. Updated maximum incremental reactivity scale and hydrocarbon bin reactivities for regulatory
497 applications. *California Air Resources Board Contract* 2009; 339.
- 498 Cheng, Z., Zhang, J., Zhou, J., Sun, J., Zhou, W., Chen, C., Zheng, J., Wang, TJ. Air pollutant emission
499 inventory and distribution characteristics in Changzhou (in Chinese). *The Administration and Technique*
500 *of Environmental Monitoring* 2016; 28: 24-28.
- 501 Fan, L., Fu, S., Wang, X., Fu, Q., Jia, H., Xu, H., Cheng, J. Spatiotemporal variations of ambient air

502 pollutants and meteorological influences over typical urban agglomerations in China during the COVID-
503 19 lockdown. *Journal of Environmental Sciences (China)* 2021; 106: 26-38.

504 Fu, X., Wang, S., Zhao, B., Xing, J., Cheng, Z., Liu, H., Hao, J. Emission inventory of primary pollutants
505 and chemical speciation in 2010 for the Yangtze River Delta region, China. *Atmospheric Environment*
506 2013; 70: 39-50.

507 Gao, C., Li, S., Liu, M., Zhang, F., Achal, V., Tu, Y., Zhang, S., Cai, C. Impact of the COVID-19 pandemic
508 on air pollution in Chinese megacities from the perspective of traffic volume and meteorological factors.
509 *Science of The Total Environment* 2021; 773: 145545.

510 Geyer, A., Alicke, B., Konrad, S., Schmitz, T., Stutz, J., and Platt, U. Chemistry and oxidation capacity of
511 the nitrate radical in the continental boundary layer near Berlin, *Journal of Geophysics Research* 2001;
512 106, 8013–8025.

513 Huang, L., Liu, Z., Li, H., Wang, Y., Li, Y., Zhu, Y., Ooi, M., An, J., Shang, Y., Zhang, D., Chan., A., Li, L.
514 The Silver Lining of COVID-19: Estimation of short-term health impacts due to lockdown in the Yangtze
515 River Delta Region, China. *GeoHealth* 2020; 4: e2020GH000272.

516 Inomata, S, Tanimoto, H, Kameyama, S., Tsunogai, U., Irie, H., Kanaya, Y., Wang, Z. J. A. C., and Physics:
517 Determination of formaldehyde mixing ratios in air with PTR-MS: laboratory experiments and field
518 measurements, 8, 273-284, 2008.

519 Li, L., An, J., Huang, L., Yan, R., Huang, C., and Yarwood, G. Ozone source apportionment over the
520 Yangtze River Delta region, China: Investigation of regional transport, sectoral contributions and
521 seasonal differences, *Atmospheric Environmental* 2019; 202, 269–280.

522 Li, L., Li, Q., Huang, L., Wang, Q., Zhu, A., Xu, J., et al. Air quality changes during the COVID-19
523 lockdown over the Yangtze River Delta Region: An insight into the impact of human activity pattern
524 changes on air pollution variation. *Science of the Total Environment* 2020; 732:139282.

525 Li, R., Zhao, Y., Fu, H., Chen, J., Peng, M., and Wang, C.: Substantial changes in gaseous pollutants and
526 chemical compositions in fine particles in the North China Plain during the COVID-19 lockdown period:
527 Anthropogenic vs. meteorological influences, 21, 8677–8692, <https://doi.org/10/gkgxw6>, 2021.

528 Liu, Z., Wang, Y., Gu, D., Zhao, C., Huey, LG., Stickel, R., et al. Summertime photochemistry during
529 CAREBeijing-2007: RO_x budgets and O₃ formation. *Atmospheric Chemistry and Physics* 2012; 12:

530 7737-7752.

531 Maji, S., Beig, G., Yadav, R. Winter VOCs and OVOCs measured with PTR-MS at an urban site of India:
532 Role of emissions, meteorology and photochemical sources. *Environmental Pollution* 2020; 258: 113651.

533 Pathakoti, M., Santhoshi, T., Aarathi, M., Mahalakshmi, DV., Kanchana, AL., Srinivasulu, J., et al.
534 Assessment of Spatio-temporal Climatological trends of ozone over the Indian region using Machine
535 Learning. *Spatial Statistics* 2021; 43: 100513.

536 Sen, PK. Estimates of the regression coefficient based on Kendall's tau. *Journal of the American statistical*
537 *association* 1968; 63: 1379-1389.

538 Shen, L., Zhao, T., Wang, H., Liu, J., Bai, Y., Kong, S., et al. Importance of meteorology in air pollution
539 events during the city lockdown for COVID-19 in Hubei Province, Central China. *Science of the Total*
540 *Environment* 2021; 754, 142227.

541 Shi, X., Ge, Y., Zheng, J., Ma, Y., Ren, X., and Zhang, Y. Budget of nitrous acid and its impacts on
542 atmospheric oxidative capacity at an urban site in the central Yangtze River Delta region of China,
543 *Atmospheric Environment* 2020; 238.

544 Sun, K., Zhou, J., Ding, H., Chen, X., Liu, Z., Xue, P. Anthropogenic source VOCs emission inventory of
545 Changzhou city (in Chinese). *Environmental Monitoring and Forewarning* 2019; 11: 57-62.

546 Tan, Z., Lu, K., Jiang, M., Su, R., Wang, H., Lou, SR., et al. Daytime atmospheric oxidation capacity in
547 four Chinese megacities during the photochemically polluted season: a case study based on box model
548 simulation. *Atmospheric Chemistry and Physics* 2019; 19: 3493-3513.

549 Valach, AC., Langford, B., Nemitz, E., Mackenzie, AR., Hewitt, CN. Seasonal and diurnal trends in
550 concentrations and fluxes of volatile organic compounds in central London. *Atmospheric Chemistry and*
551 *Physics* 2015; 15: 7777-7796.

552 Venter, ZS., Aunan, K., Chowdhury, S., Lelieveld, J. COVID-19 lockdowns cause global air pollution
553 declines. *Proceedings of the National Academy of Sciences of the United States of America* 2020; 117:
554 18984-18990.

555 Wang, W., Li, X., Shao, M., Hu, M., Tan, T. The impact of aerosols on photolysis frequencies and ozone
556 production in Beijing during the 4-year period 2012–2015. *Atmos. Chem. Phys.* 19, 9413-9429 (2019).

557 Wang, W., Parrish, D., Li, X., Shao, M., Zhang, Y. Exploring the drivers of the increased ozone production

558 in Beijing in summertime during 2005–2016. *Atmos. Chem. and Phys.* 20, 15617-15633 (2020).

559 Warneke, C., Veres, P., Holloway, J., Stutz, J., Tsai, C., Alvarez, S., Rappenglueck, B., Fehsenfeld, F., Graus,
560 M., and Gilman, J. J. A. M. T.: Airborne formaldehyde measurements using PTR-MS: calibration,
561 humidity dependence, inter-comparison and initial results, 4, 2345-2358, 2011.

562 Wolfe, GM., Marvin, MR., Roberts, SJ., Travis KR, Liao J. The Framework for 0-D Atmospheric Modeling
563 (F0AM) v3.1. *Geoscientific Model Development* 2016; 9: 3309-3319.

564 Xu, L., Zhang, J., Sun, X., Xu, S., Shan, M., Yuan, Q., et al. Variation in concentration and sources of black
565 carbon in a megacity of China during the COVID-19 pandemic. *Geophysical Research Letters* 2020; 47:
566 e2020GL090444.

567 Zhang, D., Cong, Z., Ni, G. Comparison of three Mann-Kendall methods based on the China's
568 meteorological data. *Advances in Water Science* 2013; 24: 490-496.

569 Zhang, K., Huang, L., Li, Q., Huo, J., Duan, Y., Wang, Y., Yaluk, E., Wang, Y., Fu, Q., and Li, L.: Explicit
570 modeling of isoprene chemical processing in polluted air masses in suburban areas of the Yangtze River
571 Delta region: radical cycling and formation of ozone and formaldehyde, *Atmos. Chem. Phys.*, 21, 5905-
572 5917, 10.5194/acp-21-5905-2021, 2021.

573 Zhang, K., Li, L., Huang, L., Wang, Y., Huo, J., Duan, Y., et al. The impact of volatile organic compounds
574 on ozone formation in the suburban area of Shanghai. *Atmospheric Environment* 2020a; 232: 117511.

575 Zhang, K., Xu, J., Huang, Q., Zhou, L., Fu, Q., Duan, Y., et al. Precursors and potential sources of ground-
576 level ozone in suburban Shanghai. *Frontiers of Environmental Science and Engineering* 2020b; 14: 1-12.

577 Zhang, P., Chen, T., Liu, J., Chu, B., Ma, Q., Ma, J., and He, H.: Impacts of Mixed Gaseous and Particulate
578 Pollutants on Secondary Particle Formation during Ozonolysis of Butyl Vinyl Ether, 54, 3909–3919,
579 <https://doi.org/10/gpd9p2>, 2020.

580 Zheng, H., Kong, S., Chen, N., Yan, Y., Liu, D., Zhu, B., et al. Significant changes in the chemical
581 compositions and sources of PM_{2.5} Wuhan since the city lockdown as COVID-19. *Science of the Total*
582 *Environment* 2020; 739: 140000.

583 Zhu, J., Wang, S., Wang, H., Jing, S., Lou, S., Saiz-Lopez, A., et al. Observationally constrained modeling
584 of atmospheric oxidation capacity and photochemical reactivity in Shanghai, China. *Atmospheric*
585 *Chemistry and Physics* 2020; 20: 1217-1232.

