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A retrospect of ozone formation mechanisms during the COVID-19 lockdown: The potential role of isoprene

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ABSTRACT
Wuhan took strict measures to prevent the spread of COVID-19 from January 26 to April 7 in 2020. The lockdown reduced the concentrations of atmospheric pollutants, except ozone (O₃). To investigate the increase in O₃ during the lockdown, trace gas pollutants were collected. The initial concentrations of volatile organic compounds (VOCs) were calculated based on a photochemical ratio method, and the ozone formation potential (OFP) was obtained using the initial and measured VOC concentrations. The O₃ formation regime was NOₓ-limited based on the VOCs/NOₓ diurnal ratios during the lockdown period. The reduced nitric oxide (NO) concentrations and lower wind speed (WS) could explain the night-time O₃ accumulation. The initial total VOCs (TVOCs) during the lockdown were 47.6 ± 2.9 ppbv, and alkenes contributed 48.1%. The photochemical loss amounts of alkenes were an order of magnitude higher than those of alkenes in the same period in 2019 and increased from 16.6 to 28.0 ppbv in the daytime. The higher initial alkene concentrations sustained higher OFP during the lockdown, reaching between 252.4 and 504.4 ppbv. The initial isoprene contributed approximately 35.0–55.0% to the total OFP and had a positive correlation with the increasing O₃ concentrations. Approximately 75.5% of the temperatures were concentrated in the range of 5 and 20 °C, which were higher than those in 2019. In addition to stronger solar radiation, the higher temperatures induced higher isoprene emission rates, partially accounting for the higher isoprene concentrations. Lower isoprene-emitting trees should be considered for future urban vegetation to control O₃ episodes.

1. Introduction
At the beginning of 2020, coronavirus disease 2019 (COVID-19) was first identified in Wuhan. To prevent the transmission of the virus, lockdown measures, including travel restrictions, factory shutdowns, and other measures, were developed to reduce industrial, transportation and commercial activities (Wang et al., 2020; Zheng et al., 2020). Atmospheric chemistry and air quality were also affected by the lockdown measures. During the lockdown period, the O₃ concentrations changed heterogeneously globally, with little change or small increase in Europe and 25.0% and 30.0% increases in East Asia and South America, respectively (Sokhi et al., 2021). Sicard et al. (2020) reported that O₃ increased by 2.4%–36.0% in Nice, Rome, Turin and Wuhan from January to April 2020. The unexpected increase in O₃ under stringent containment measures in urban areas could be ascribed to the following reasons: 1) O₃ formation is highly nonlinear, and the emission reduction of NOₓ (sum of NO₂ and NO) in a VOC-limited regime would induce O₃ formation (Le et al., 2020); 2) the influence of various meteorological conditions on the atmospheric chemistry and emissions of biogenic volatile organic compounds (BVOCs) (Liu et al., 2020; Liu et al., 2021; Ordóñez et al., 2020); and 3) lower aerosol concentrations would subsequently result in stronger UV radiation and higher photolysis rates (Wu et al., 2020). Additionally, the reduced PM2.5 concentrations supplied insufficient sinks for hydroperoxyl radicals (HO₂) during the lockdown, leading to the production of O₃ through the peroxy radical pathway (Adam et al., 2021; Le et al., 2020). The abovementioned
reasons focus on the emission reduction of anthropogenic pollutants, whereas the effect of biogenic emissions has received insufficient attention, and their roles in \( \text{O}_3 \) formation during the lockdown need further investigation.

In a world with reduced human activities, the impact of biogenic VOCs (BVOCs) on atmospheric chemistry and secondary pollutant formation may become crucial. Isoprene (2-methyl-1,3-butadiene, \( \text{C}_9\text{H}_{10} \)), monoterpenes, and sesquiterpenes are the most reactive BVOC species emitted by plants, and the released isoprene occupies approximately half of the total estimated BVOC emissions globally and has higher reactivity (Guenther et al., 1995; Lun et al., 2020). Isoprene is a significant contributor to surface-level \( \text{O}_3 \) production (Churkina et al., 2017; Hoffmann et al., 1997). The OPF for initial isoprene could account for 23.0% of the total OPF in urban areas in Beijing (Xie et al., 2008).

Although with lower concentrations than anthropogenic VOCs (AVOCs), BVOCs might be important precursors of regional \( \text{O}_3 \) and \( \text{MACR} \) and their role in secondary formation may become crucial. Isoprene (2-methyl-1,3-butadiene, \( \text{C}_9\text{H}_{10} \)) and its precursors (e.g., VOCs and \( \text{NO}_x \)) require further investigation. The lockdown offered an ideal period to investigate the role of BVOCs in \( \text{O}_3 \) formation during the lockdown.

Once emitted into the atmosphere, isoprene reacts quickly with OH radicals, forming methyl vinyl ketone (MVK), methacrolein (MACR), hydroxyhydroperoxides (ISOPOOH), and formaldehyde (HCHO). MVK and MACR can be further oxidized by OH radicals to produce additional peroxy radicals (Li et al., 2016; Spaulding et al., 2003). Within a certain range, the rate of isoprene emission is positively correlated with foliar temperature and photosynthetically active radiation (PAR) (Fitzky et al., 2019; Gu et al., 2021). During the lockdown, emissions of AVOCs evidently decreased (Li et al., 2020); however, the emission characteristics and atmospheric chemistry of BVOCs require further research. The lockdown offered an ideal period to investigate the role of BVOCs in \( \text{O}_3 \) formation during the lockdown.

In this study, we conducted field research to explore the unexpected increase in \( \text{O}_3 \) during the 2020 Wuhan lockdown. The relationships between \( \text{O}_3 \) and its precursors (e.g., VOCs and \( \text{NO}_x \)) during the lockdown and in the same period in 2019 were investigated. The OPF of the initial and measured VOCs were calculated. The contribution of initial and measured isoprene to OPF and the relationship between the OPF derived from isoprene and \( \text{O}_3 \) concentrations were studied. The effect of temperature on the emission rates of isoprene and concentrations was also discussed.

2. Methodology

2.1. Observation data

The sampling site was situated at Wuhan University (Fig. S1). Continuous observations were implemented from January 1 to April 30 in 2019 and 2020. Based on the control and management policy, the lockdown period was set between January 26 and April 7 in 2020, and the before-lockdown period and after-lockdown period were set between January 1 and January 25 and between April 8 and April 30 in 2020, respectively. The corresponding periods in 2019 were divided according to the period divisions in 2020.

In this study, \( \text{O}_3 \), \( \text{NO}_x \) and VOCs were monitored by the instruments listed in Table S1. A total of 91 VOC species, including 29 alkanes, 11 alkenes, 1 alkyn, 16 aromatics, 4 oxygenated VOCs (OVOCs) and 30 halohydrocarbons (XVOCs), were investigated (Table S2). In detail, a TH-300 B (Table S1) online gas chromatography–mass spectrometer/IR absorption spectrometer (GC–MS/FID) was used to determine the VOC samples. The whole procedure included sample collection, freeze trapping, thermal desorption, GC–FID/MS analysis, heating and anti–blow purification. Two channels, namely, the FID gas channel and MS channel, were incorporated into the system. Collected samples were split into two parts and then entered into the two separate channels. The samples in the FID channel were condensed and dewatered at \(-50^\circ\text{C}\); \( \text{CO}_2 \) was removed by \( \text{CO}_2 \) adsorption tubes. The \( C_2 - C_6 \) VOC species were gathered by a PLOT capillary column at \(-150^\circ\text{C}\). The samples in the MS channel were condensed and dewatered at \(-20^\circ\text{C}\). The \( C_6 - C_{12} \) species hydrocarbons, XVOCs, and OVOCs were gathered sequentially by a passivated empty capillary column at \(-150^\circ\text{C}\). The capture tubes were heated to 120 \( ^\circ\text{C} \) to remove VOCs. The thermally desorbed VOCs were separated by helium into two chromatographic columns. Meteorological data, e.g., relative humidity (RH), wind speed (WS), wind direction (WD), and temperature (T), were obtained simultaneously by an automatic meteorological station at the same temporal resolution.

2.2. Estimation of photochemical loss of VOCs

The photochemical loss of VOCs (VOCs reacted by photochemical oxidation) was obtained by the ratio method (Wiedinmyer et al., 2001; Yuan et al., 2013; Zhan et al., 2021). The following assumptions are made when using the method (de Gouw and Jimenez, 2009; Wiedinmyer et al., 2001; Yuan et al., 2013): 1) VOCs are mainly consumed by OH radicals; 2) VOCs are mainly consumed by OH radicals; 3) the speciation of VOC emissions is the same in the areas surrounding the site; and 4) the photochemical age can be obtained by the ratio of two measured VOC species. Due to the low reaction activity of XVOCs and the complex sources of OVOCs, the above two groups of VOCs were excluded when estimating the consumed VOC concentrations. Additionally, the photochemical reactions between VOCs and OH radicals occurred in the daytime; as a result, the initial concentrations were calculated only in the daytime (8:00 to 18:00 in this study, local time, LT). The initial concentrations of VOCs before photochemical reactions with OH radicals are described in Eq. (1):

\[
[\text{VOC}]_i = [\text{VOC}]_{i,\text{initial}} \times \exp(-k_{i,\text{OH}} \times [\text{OH}] \times \Delta t)
\]

where \([\text{VOC}]_i\) and \([\text{VOC}]_{i,\text{initial}}\) represent the determined and initial VOC concentrations, respectively; \(k_{i,\text{OH}}\) represents the reaction rate constant between VOC and OH radicals; and \([\text{OH}]\) and \(\Delta t\) represent the OH radical concentrations and time since emission, respectively. The \([\text{OH}]\) and \(\Delta t\) can be obtained by Eq. (2):

\[
[\text{OH}] \times \Delta t = \frac{1}{k_{\text{VOC,}a} - k_{\text{VOC,}b}} \times \left\{ \ln \left( \frac{b}{a} \right)_{t=0} - \ln \left( \frac{b}{a} \right)_{t=\Delta t} \right\}
\]

where \(k_{\text{VOC,}a}\) and \(k_{\text{VOC,}b}\) denote the reaction rate constants between VOC \( a \) or \( b \) with OH radicals, respectively. In this study, \( a \) is set as \( m,p\)-xylene, and \( b \) is set as ethylbenzene. Therefore, \(k_{\text{VOC,}a}\) is \( 18.9 \times 10^{-12} \) \( \text{cm} ^3 \text{molecule} ^{-1} \text{s} ^{-1} \), and \(k_{\text{VOC,}b}\) is \( 7.0 \times 10^{-12} \) \( \text{cm} ^3 \text{molecule} ^{-1} \text{s} ^{-1} \). The relationship between \( m,p\)-xylene and ethylbenzene is shown in Fig. S2. The two VOC species were well correlated during the lockdown (\( R^2 = 0.92 \)) and in the same period in 2019 (\( R^2 = 0.96 \)), implying that the two compounds were from the same origin (Ma et al., 2022).
The ratio method uses the same photochemical age for different VOC species. However, the emissions of isoprene by plants depend on solar radiation and leaf temperatures. In this study, the calculated initial isoprene concentrations and measured isoprene concentrations were both unimodal curves and showed similar variations during the lockdown (Fig. S4). Compared with the same period in 2019, the maximum initial and measured isoprene concentrations appeared at 14:00 LT and 15:00 LT during the lockdown, which was in line with the daily temperature variations, indicating the biogenic emissions of isoprene. These results suggest that the initial isoprene concentration calculated by the ratio method could reflect the real emission characteristics. Other oxidants (e.g., NO radicals and O₃) can react with VOCs in the atmospheric environment. As a result, the estimated initial VOC concentrations using the ratio method would be lower than the actual VOC concentrations. However, the ratio method has still been used in previous studies to estimate the initial isoprene concentrations (Gao et al., 2018; Zhan et al., 2021; Zheng et al., 2021).

2.3. Calculation of OFP

OFP estimation is based on the initial and determined VOC concentrations and maximum incremental reactivity (MIR). The OFP of each VOC species can be acquired by Eq. (3):

\[ \text{OFP} = [\text{VOC}]_i \times MIR_i \]  \hspace{1cm} (3)

where \([\text{VOC}]_i\) is the initial or determined concentration of VOC species \(i\), and \(MIR_i\) is the ozone formation factor of VOC species \(i\) (Carter, 2010).

2.4. Temperature dependence of isoprene emissions

Isoprene mainly comes from biogenic emissions. However, anthropogenic sources may also contribute to atmospheric isoprene concentrations, including traffic and industrial sources (Borbon et al., 2001; dos Santos et al., 2022; Ran et al., 2011). The weak correlations between isoprene and anthropogenic tracers (e.g., benzene, toluene and methyl tert-butyl ether) shown in Fig. S5 indicate nonsignificant contributions of anthropogenic sources to isoprene during the lockdown. Guenther et al. (1993) summarized that the influence of PAR and foliar temperature on isoprene emissions can be described as shown in Eq. (4):

\[ I = C_L \times C_T \]  \hspace{1cm} (4)

where \(I\) is the isoprene emission rate, and \(C_L\) and \(C_T\) are the solar radiation and foliar temperature dependence, respectively. In this study, the influence of foliar temperatures was investigated. The \(C_T\) can be obtained using Eq. (5):

\[ C_T = \frac{\exp \left( \frac{-C_{TP} - C_{T1}}{R_1 + R_6} \right)}{1 + \exp \left( \frac{-C_{TP} - C_{T1}}{R_1 + R_6} \right)} \]  \hspace{1cm} (5)

where \(C_{TP}\), \(C_{T1}\) and \(T_M\) are empirical parameters derived from experiments, and they were set as 95,000 J mol⁻¹, 230,000 J mol⁻¹ and 314 K, respectively; \(R\) equals 8.3 J mol⁻¹ K⁻¹; \(T_f\) is the foliar temperature under standard circumstances (e.g., 303 K); \(T\) is the foliar temperature (K), and the air temperature is used as the foliar temperature (Gu et al., 2022).

3. Results and discussion

3.1. Diurnal variations in ozone and its precursors

During the periods when emergency and control measures were strictly in effect, the \(O_3\) concentrations showed consistent abnormal increments. In this study, the average \(O_3\) concentrations during the lockdown were 53.8% higher than those during the same period in 2019 (41.4 ± 31.2 μg m⁻³), which was also reported in previous studies (Ansari et al., 2019; Huang et al., 2021; Ni et al., 2019; Zhang et al., 2020). The diurnal variations in \(O_3\) and its precursors during the lockdown and the same period in 2019 are shown in Fig. 1. The patterns in the two periods were similar, and \(O_3\) exhibited unimodal diurnal variations. The lowest and highest concentrations of \(O_3\) in the two periods occurred at 8:00 and 16:00 LT, respectively. The diurnal maximum concentrations of \(O_3\) at 16:00 LT were approximately 30.9 and 32.3 ppbv, respectively, for the lockdown and the corresponding period in 2019. However, the diurnal minimum concentration of \(O_3\) was approximately 17.2 ppbv, which was significantly higher than that in the same period in 2019 (9.9 ppbv). During the lockdown, the sunrise and sunset times were between 6:04 and 7:20 and 18:45 and 17:44, respectively. Therefore, 8:00 was set as the first hour of the daytime to ensure that the sun was already risen. In the afternoon, 18:00 was set as the beginning hour of night-time. The comparison of daytime (8:00 to 18:00, LT) and night-time (18:00 to 8:00, LT) \(O_3\) concentrations is depicted in Fig. S6. It can be clearly seen that the night-time difference in the \(O_3\) concentrations between the lockdown period and the same period in 2019 was much larger than the daytime difference. The average concentrations of \(O_3\) at night were 25.4% higher than those in the same period in 2019, whereas the value was only 6.0% in the daytime. The average wind speeds at night during the lockdown and in the same period in 2019 were 1.6 ± 0.2 and 1.6 ± 0.1 m s⁻¹, respectively (Fig. S7), and these wind speeds were beneficial to the accumulation of \(O_3\) (Caicedo et al., 2021; Lin et al., 2008; Tie et al., 2009; Tran and Mölders, 2011). Long-range transport from Guangdong and Guangxi Provinces could be another contributor for the increased \(O_3\) concentrations during the lockdown (Fig. S8). The decline in human activities also had a significant effect on the precursors of \(O_3\), as shown in Fig. 1. The concentrations of \(NO_x\) and VOCs in the lockdown period were much lower than those for the same period in 2019. In detail, the diurnal variations in \(NO_x\) were between 6.0 and 11.0 ppbv, and the VOC concentrations were between 20.0 and 40.0 ppbv during the lockdown. However, the diurnal variations in \(NO_x\) and VOCs were between 22.0 and 42.0 ppbv and 40.0 and 50.0 ppbv, respectively, in the same period in 2019. The change patterns of \(NO_x\) in the two periods were similar, decreasing between 0:00 and 6:00 LT, and with increasing transport, \(NO_x\) reached its peak at 8:00 LT. Then, the \(NO_x\) concentrations continued to decrease at 17:00 LT and increased gradually until 23:00 LT, which was opposite to the \(O_3\) diurnal variations. The changing patterns of VOCs were slightly different. During the lockdown, the VOC concentrations continued to decrease from 2:00 to 18:00 LT and then accumulated until 23:00 LT. The diurnal variations in the VOC groups are shown in Fig. S9. There were peaks of alkanes, aromatics and XVOCs at 2:00 LT. Alkanes mainly come from vehicular emissions (Huang and Hsieh, 2020; Liu et al., 2020), aromatics can come from vehicular emissions and industrial solvents (An et al., 2014), and XVOCs mainly come from industrial processes (Hui et al., 2019). However, the variations in VOCs for the same period in 2019 were not as obvious as those in the lockdown period, which might be due to the various sources of VOCs in 2019.

The production of \(O_3\) mainly occurs in the daytime. Atmospheric \(NO_2\) can undergo photolysis (\(λ ≤ 424\) nm) and generate atomic oxygen (\(O^+\)) and \(NO\) (R1). The resulting \(NO\) can react with \(O_3\) and regenerate \(NO_2\) (R2). Therefore, \(O_3\) will not accumulate when enough \(NO\) is available. However, ambient VOCs can be oxidized by OH radicals and generate peroxy radicals (RO₂) (R3), and RO₂ can be converted into \(HO_2\) radicals (R4 and R5). \(RO_2\) and \(HO_2\) are also effective oxidants that can oxidize \(NO\) into \(NO_2\) (R4 and R6), and sufficient \(O_3\) can accumulate.

\[ NO_2 + hv \rightarrow NO + O^+ \]  \hspace{1cm} (R1)

\[ NO + O_3 \rightarrow NO_2 + O_2 \]  \hspace{1cm} (R2)

\[ RH + OH + O_2 \rightarrow RO_2 + H_2O \]  \hspace{1cm} (R3)
RO₂ + NO → RO + NO₂ (R4)
RO₂ + O₂ → HO₂ + Carbonyls (R5)
HO₂ + NO → OH + NO₂ (R6)

The formation mechanisms were summarized by Seinfeld and Pandis (2016) and Wang et al. (2017). After sunset, the photochemical production of O₃ ceased due to the lack of light. Considering the much lower concentrations of NOₓ at night, the weakened effect of O₃ titration by NO might account for the accumulation of O₃ concentrations. Similar phenomena were also found in other cities in China and around the world (Qi et al., 2021; Zhang and Stevenson, 2022), and they lead to increasing concentrations of O₃ at night. Noting that the NOₓ concentrations in the daytime were also significantly lower during the lockdown than in the same period in 2019, the difference in the O₃ concentrations between daytime in the two periods was not as large as that at night.

The VOC/NOₓ (ppbC/ppbV) ratios were employed to investigate the O₃ formation sensitivity to NOₓ and VOCs. VOCs were expressed as the concentrations of carbon atoms (Seinfeld, 1989; Zou et al., 2015). In general, if the VOCs/NOₓ ratios were larger than 8, the O₃ formation regime was NOₓ-limited; if the ratios were less than 8 the O₃ formation regime was VOC-limited (Li et al., 2017; Seinfeld and Pandis, 2016; Zhang and Stevenson, 2022). The diurnal variations in VOCs/NOₓ are depicted in Fig. 2. The variations in VOCs/NOₓ during the lockdown were all above 8, indicating that the formation of O₃ was NOₓ-limited. In contrast, the VOCs/NOₓ ratio was generally below 8 in the same period in 2019, and O₃ formation was more sensitive to VOCs. During the lockdown period, the NOₓ-limited regime revealed that the O₃ concentrations would decrease with decreasing precursors (Fig. 1). However, the daytime average O₃ concentrations were still higher than those in the same period in 2019 (Fig. S6). Even with lower VOC concentrations, the reduction magnitude of VOCs during the lockdown period was more obvious than it was in the same period in 2019, indicating that more intense reactions might have occurred during the lockdown. The reaction of VOCs with OH radicals might generate considerable alternative radicals (e.g., RO₂ and HO₂) and in turn lead to the accumulation of O₃. Therefore, the photochemical losses of VOCs were further investigated.
3.2. Photochemical loss of VOCs

Once emitted into the atmosphere, reactions between VOCs and oxidants (e.g., OH, NO$_3$ and O$_3$) take place immediately, leading to the consumption of VOCs. As a result, the measured concentrations at the receptor site are lower than the initial concentrations. The diurnal variations (8:00 to 18:00, LT) in the initial and measured VOC concentrations during the two periods are shown in Fig. 3. The initial concentrations were calculated only for alkanes, alkenes, alkyne and aromatics, whereas the initial concentrations of OVOCs and XVOCs were substituted by the measured concentrations. During the lockdown, the measured diurnal concentrations of total VOCs (TVOCs) were much lower than those for the same period in 2019. The measured average concentrations in the daytime during the lockdown were 23.9 ± 2.2 ppbv, and these values were 40.9% lower than the concentrations in the same period in 2019 (40.4 ± 3.4 ppbv).

The diurnal variations in the initial VOC concentrations were significantly different from the measured concentrations. As shown in Fig. 3(a), the initial average TVOC concentrations in the daytime were much higher, reaching 47.6 ± 2.9 ppbv, and they were slightly lower than the initial TVOC concentrations in the same period in 2019 (48.3 ± 3.2 ppbv). During the lockdown, the daytime TVOC concentrations showed a gradual increasing pattern, whereas the TVOC concentrations in the same period in 2019 represented a unimodal pattern. The composition of TVOCs at each hour also changed evidently. Alkenes substituted alkanes and became the most abundant groups in the TVOCs, and the average alke concentration reached 22.9 ± 3.8 ppbv, which was higher than the initial average alke concentration (12.8 ± 1.1 ppbv). Alkenes were the only VOC group whose concentration was higher than that in the same period in 2019 (11.6 ± 0.8 ppbv) (Fig. 3(c)). The contribution of alkenes to TVOCs also increased by 24.7% and overwhelmed the contribution of alkanes (26.8%, Fig. S10(c)). The initial alke concentrations increased from 19.9 ppbv at 8:00 LT to 30.1 ppbv at 15:00 LT and then decreased to 24.4 ppbv at 18:00, which might account for the increasing TVOC concentrations in the daytime during the lockdown. However, the alke concentrations were between 12.4 and 11.5 ppbv during the daytime, showing an insignificant variation and a lower contribution to TVOCs.

The diurnal variations in the consumed VOC concentrations in the two periods are shown in Fig. 4. Alkenes were highly consumed by photochemical reactions compared with other VOC groups (right axis of Fig. 4(a) and (b)). During the study period in 2019, the photochemical loss concentrations of alkenes were approximately 7.0 ppbv at 8:00 LT,
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and then they increased to 7.6 ppbv at 17:00 LT. However, the consumed alkenes in the daytime continued to increase from 16.6 ppbv at 8:00–28.0 ppbv at 15:00 and then slightly decreased to 22.3 ppbv at 18:00. In this study, 11 alkenes were measured, and the reaction rate constants with OH radicals ranged from $9.9 \times 10^{-11}$ to $8.2 \times 10^{-12}$ cm$^3$ molecules$^{-1}$ s$^{-1}$. Therefore, compared with other VOC groups, alkenes always had higher reaction rate constants with OH radicals and were consumed quickly in the atmospheric environment. The average concentrations (8:00 to 18:00 LT) of the measured and initial alkenes in the two periods are summarized in Table 1. The initial average concentration of isoprene was 14.3 ± 2.8 ppbv, much higher than it was in the same period in 2019 (1.3 ± 0.2 ppbv), indicating the important potential role of isoprene in O$_3$ formation.

Isoprene is a significant contributor to ground-level O$_3$ production (Chameides et al., 1988; Churkina et al., 2017). Churkina et al. (2017) reported that BVOCs contributed to 17.0–20.0% of the daily maximum 8-h O$_3$ concentrations in Berlin in the temperature range of 22–24 °C. In the UK, during the lockdown, the contribution of isoprene to total OH reactivity increased to 25.0%, resulting from a 2 °C increase in temperature (Lee et al., 2020). Assuming that the AVOCs equalled zero and the emission rate of BVOCs was 30 kg km$^{-2}$ (Chameides et al. 1988) concluded that the simulated maximum O$_3$ concentrations reached 80 ppbv, suggesting that BVOCs could exert a profound influence on the production of O$_3$. Given that much more isoprene was produced in Wuhan during summer of Wuhan than in the rest of the seasons (Lyu et al., 2016; Zeng et al., 2018), temperatures might have a significant influence on the emissions of isoprene, which would contribute greatly to O$_3$ formation by photochemical reactions.

### 3.3. Changes in the OFP of VOCs

In this study, OFP was used to evaluate the reactivity activity of VOCs in ground-level O$_3$ production. The daytime diurnal variations in the abovementioned OFP values are illustrated in Fig. 5. The OFP calculated by the measured VOCs during the two periods mostly originated from alkanes, alkenes and aromatics. However, the total OFP during the lockdown was much lower than that during the same period in 2019 due to the reduction in AVOC emissions. During the lockdown, the highest OFP appeared in the morning (from 8:00 to 10:00 LT), reaching approximately 70.0 ppbv (Fig. 5(b)), which might be due to the relatively higher TVOC concentrations contributed by traffic and human activities. Then, the OFP decreased to approximately 55.0 ppbv in the afternoon. With decreasing OFP, the percentages of isoprene to the total OFP increased from 3.3% to 4.8% (14:00 LT) and then decreased slightly. The variations in the same period in 2019 were different (Fig. 5(d)). The OFP values were between 110.0 and 120.0 ppbv; however, the OFP reached approximately 150.0 ppbv at 12:00 and 13:00, which might be due to the strong reactions of VOCs. The contribution of isoprene to the total OFP was between 0.6% and 1.0% in this period, which might be due to two reasons: 1) the limited emissions of isoprene by plants in early spring and 2) the strong contribution of AVOCs under uninfluenced circumstances (e.g., without lockdown). The contributions of measured VOCs to the total OFP in the two periods are shown in Fig. S11. Aromatics contributed most to the OFP in the two periods, followed by alkenes and alkanes. Due to the considerable reduction in AVOCs, the contribution of aromatics decreased from 46.7% to 34.8% during the lockdown period compared with values of the same period in 2019, as did the contribution of XVOCs, which also resulted from industrial activities.

The OFP calculated by the initial concentrations were quite different in the two periods. During the lockdown, the OFP increased from 252.4 ppbv at 8:00–504.4 ppbv at 17:00, and the OFP was most contributed by alkenes and aromatics. Additionally, the contribution of isoprene to the total OFP also increased from approximately 35.0% at 8:00 to approximately 55.0% at 15:00. The percentage of alkenes was 76.5%, which was much higher than the contribution of aromatics (18.6%) (Fig. S11(a)). A similar phenomenon was observed in the OFP calculated by the initial concentrations in the same period in 2019, and the results also highlighted the contribution of alkenes to the total OFP (46.4%). In the daytime variations, the total OFP was between 231.0 ppbv and 290.0 ppbv (Fig. 5(c)). The contribution of isoprene (4.5–10.3%) was much lower than the OFP calculated by the initial isoprene concentrations during the lockdown, indicating the weakening effect of isoprene on O$_3$ formation in 2019.

The relationships between the O$_3$ concentrations and ΔOFP derived from isoprene (the difference between the initial isoprene OFP and the measured isoprene OFP) in the two periods are illustrated in Fig. 6. With increasing O$_3$ concentrations (from 10 to 40 ppbv), the median log (ΔOFP) values increased from 2.3 to 5.4, indicating a higher contribution of isoprene to the higher daytime O$_3$ concentrations during the lockdown. Nevertheless, there was an insignificant relationship between ΔOFP and O$_3$ in the same period in 2019. The ΔTOFP (derived from TVOCs) and O$_3$ concentrations showed similar variations as isoprene in the two periods (Fig. S12). However, OFP is not necessarily correlated with TVOCs or individual VOC species (Zulkifi et al., 2022). The OFP does not indicate the true O$_3$ concentrations, and it is used to indicate the potential O$_3$ production by photochemical reactions of VOCs and key VOC species in O$_3$ formation. Isoprene is a kind of highly reactive BVOC that is an important sink of atmospheric oxidants (e.g., OH, NO$_2$ and O$_3$) (Lee and Wang, 2006). The main products of reactions between VOCs and OH radicals are RO$_2$ and other products, including HO$_2$ and carbonyl compounds (mainly MVK and MACR) (Calfapietra et al., 2013). RO$_2$ and HO$_2$ radicals can react with NO and lead to the accumulation of O$_3$ (Fan and Zhang, 2004; Grosjean et al., 1993; Paulot et al., 2012). Previous studies have demonstrated the dominant role of biogenic isoprene in summer ozone formation. Pang et al. (2009) investigated the OFP of isoprene from April to October in Beijing, and the maximum OFP reached 56.0 ppbv in August. Xie et al. (2008) also reported that the mixing ratios of isoprene in urban and suburban areas could reach 3.3 ± 1.6 and 2.9 ± 1.5 ppbv, respectively, during the summer in Beijing. The contributions of initial isoprene to total OFP were 15.8% and 11.4% at urban and suburban sites, respectively. In Wuhan, the measured mixing ratios of isoprene reached 0.5 ppbv, indicating a strong contribution to O$_3$ formation (Lyu et al., 2016; Zeng et al., 2018). In this study, the initial isoprene was the top species contributing to the OFP during the lockdown (Table S3). The contribution of isoprene to O$_3$ formation during the lockdown in this study was similar to the situation in the summer seasons. Barlet et al. (2004) investigated the NO$_x$ dependence of isoprene in O$_3$ production at four North American sites. The results revealed that NO$_x$ concentrations

### Table 1

| Species | Measured conc. (ppbv) | Initial conc. (ppbv) |
|---------|-----------------------|---------------------|
|         | Lockdown period | Same period in 2019 | Lockdown period | Same period in 2019 |
| ethylene | 1.83 ± 0.38 | 3.04 ± 0.46 | 2.51 ± 0.40 | 3.76 ± 0.55 |
| propylene | 0.26 ± 0.08 | 0.60 ± 0.12 | 0.70 ± 0.08 | 1.24 ± 0.18 |
| 1-butene | 0.09 ± 0.03 | 0.16 ± 0.03 | 0.31 ± 0.03 | 0.40 ± 0.06 |
| 1,3-butadiene | 0.03 ± 0.03 | 0.11 ± 0.02 | 0.68 ± 0.27 | 0.76 ± 0.10 |
| trans-2-buten | 0.05 ± 0.01 | 0.09 ± 0.02 | 0.76 ± 0.21 | 0.51 ± 0.06 |
| cis-2-buten | 0.06 ± 0.01 | 0.08 ± 0.01 | 0.74 ± 0.20 | 0.40 ± 0.04 |
| 1-pentene | 0.03 ± 0.00 | 0.06 ± 0.01 | 0.10 ± 0.02 | 0.16 ± 0.03 |
| trans-2-pentene | 0.10 ± 0.01 | 0.09 ± 0.02 | 3.17 ± 1.74 | 0.61 ± 0.10 |
| cis-2-pentene | 0.02 ± 0.00 | 0.03 ± 0.00 | 0.45 ± 0.16 | 0.21 ± 0.02 |
| 1-hexene | 0.04 ± 0.00 | 0.07 ± 0.01 | 0.20 ± 0.04 | 0.20 ± 0.03 |
| isoprene | 0.16 ± 0.01 | 0.07 ± 0.01 | 14.31 ± 2.79 | 1.28 ± 0.22 |
| Total | 2.66 ± 0.51 | 4.85 ± 0.70 | 22.62 ± 3.40 | 11.57 ± 0.77 |
between 1.0 and 10.0 ppbv resulted in the largest O$_3$ production rates. The diurnal variations in NO$_X$ in the daytime during the lockdown were between 6.0 and 11.0 ppbv (Fig. 1), and these values were quite beneficial for the production of O$_3$.

3.4. Driving forces of increased BVOCs

The emissions of BVOCs (mainly isoprene in this study) are sensitive to environmental factors, such as relative humidity, ambient temperature, solar radiation, and stress factors, including damage, drought, CO$_2$ concentrations and ozone concentrations (Lun et al., 2020). Light intensity and temperature are the two key factors controlling the biogenic emissions of isoprene (Guenther et al., 1993; Niinemets et al., 2010; Peñuelas and Lušiá, 2001; Tani and Mochizuki, 2021). As shown in Fig. 7. The isoprene concentrations clearly increased with increasing temperature ranges during the lockdown, especially when temperatures were above 5 °C, suggesting that higher temperatures were beneficial for isoprene production. However, the variations in the same period were not as evident as they were in the lockdown period. In addition, the median and average isoprene concentrations within the same

![Fig. 5](image1.png)

Fig. 5. OFP calculated by the measured and initial daytime VOC concentrations during the lockdown period ((a) for measured concentrations and (b) for initial concentrations) and the same period in 2019 ((c) for measured concentrations and (d) for initial concentrations).

![Fig. 6](image2.png)

Fig. 6. Relationships between the ΔOFP derived from isoprene (the difference between initial isoprene OFP and measured isoprene OFP) and O$_3$ concentrations during the lockdown (a) and in the same period in 2019 (b).

between 1.0 and 10.0 ppbv resulted in the largest O$_3$ production rates. The diurnal variations in NO$_X$ in the daytime during the lockdown were between 6.0 and 11.0 ppbv (Fig. 1), and these values were quite beneficial for the production of O$_3$.

3.4. Driving forces of increased BVOCs

The emissions of BVOCs (mainly isoprene in this study) are sensitive

![Fig. 7](image3.png)

Fig. 7. Effect of temperature on the measured isoprene concentrations during the lockdown (a) and for the same period in 2019 (b).
temperature range during the lockdown were much higher than they were in the same period in 2019, especially at higher temperatures. For example, when the temperatures were between 5 and 10 °C, the median and average isoprene concentrations were 0.1 and 0.2 ± 0.1 ppbv, respectively; however, the corresponding values in the same period in 2019 were 0.1 and 0.1 ± 0.1, respectively. When the temperature continued to increase, the median isoprene concentrations were 114.3–280.0% higher than those in the same period in 2019, suggesting much higher measured isoprene concentrations during the lockdown, which might have been induced by higher temperatures. The percentages of temperature ranges in the two periods are shown in Table S4. The temperatures during the lockdown were mostly concentrated in the range of 5 and 20 °C (75.5%); however, the temperatures during the same period in 2019 were mainly concentrated in the range of 5 and 15 °C (77.7%). Higher temperatures might be an important reason for the higher isoprene concentrations. The diurnal variations in temperature, isoprene concentrations and temperature dependence (C_T) in the two periods are shown in Fig. 8. During the lockdown, the daytime temperatures were approximately 2–3 °C higher than those in the same period in 2019 (p < 0.05, except at 8:00 LT), accompanied by higher C_T values (Fig. 8(a)). Relatively higher daytime temperatures also resulted in higher isoprene concentrations (Fig. 7(b)). During the lockdown, the isoprene increased slightly from 0.16 at 8:00 LT to 0.17 at 14:00 LT with increasing C_T values. Eq. (5) suggests that the relationships between isoprene mixing ratios and temperatures were exponential. However, the exponential relationships were not remarkable in this study (Fig. S13), especially for the same 2019 period. This result might be due to the contradictory effects of abiotic factors (e.g., temperature, light, CO_2, relative humidity, O_3 and drought) on isoprene emissions (Holopainen et al., 2018). However, the higher temperatures during the lockdown led to higher enzymatic activity and better exponential relationships than those in 2019. The above results indicate that higher temperature was a key factor involved in increasing isoprene concentrations.

In the same temperature ranges, the higher isoprene concentrations during the lockdown indicated that other factors (e.g., solar radiation) might also be important in isoprene production. Due to the strict measures taken during the lockdown, anthropogenic emissions were greatly reduced, leading to cleaner atmospheric conditions. The improved air quality was believed to increase the atmospheric transparency and allow more solar radiation to reach the Earth’s surface (Song et al., 2021). During February and March in Wuhan, the columnar NO_2 and aerosol optical depth (AOD) decreased by 75.0% and 15.6% compared with those in the 2019 period, respectively, leading to a 19.3% increase in the average broadband direct normal irradiance (DNI) (Choi and Brindley, 2021). Increased solar radiation is expected to stimulate the biogenic emissions of isoprene (Wilton et al., 2011). In the future, the reduction of trace gas pollutants (e.g., SO_2, NO_x, NH_3, and AVOCs) will lead to a clear atmospheric environment, and the emissions of isoprene will be enhanced due to strong solar radiation and increased air temperatures. The role of BVOCs could be increasingly important in regional near-ground O_3 production. Therefore, low-BVOC-emitting tree species might be considered in future urban greening design and construction.

4. Conclusions

In this study, we collected trace gas pollutants during the 2020 Wuhan lockdown and for the same period in 2019. The average O_3 concentrations were 53.8% higher during the lockdown. The O_3 formation mechanisms shifted from being VOC-limited to NO_x-limited based on the VOC/NO_x ratios. The initial alkene concentrations contributed 48.1% to the TVOCs and sustained higher daytime TVOC concentrations during the lockdown. The photochemical loss of alkenes was between 16.6 and 28.0 ppbv, which was an order of magnitude higher than that in the same period in 2019. The OFP derived from the initial VOC groups was between 252.4 and 504.4 ppbv, and most was contributed by alkenes and aromatics during the lockdown. The contribution of isoprene to the total initial OFP increased from approximately 35.0%–55.0% during the daytime. The OFP calculated by the consumed isoprene showed a positive correlation with the O_3 concentrations during the lockdown. The significantly higher daytime temperatures induced relatively higher isoprene emission rates (C_T values) and elevated isoprene concentrations. The high emissions of isoprene could account for the increased daytime O_3 concentrations due to the strong reactivity activity of isoprene. A low isoprene emission regime, which could be achieved by selecting the respective tree species, would therefore be particularly beneficial in urban areas with reduced anthropogenic emissions.

![Fig. 8. Diurnal variations in temperature, C_T (a) and isoprene concentrations (b) during the lockdown period and for the same period in 2019.](image-url)
Author statement

Xiangang Liu: Conceptualization, Project administration, Funding acquisition. Kai Xu: Methodology, Writing – original draft. Yafei Liu and Huan Zhang: Writing – review & editing. Chenliu Li, Min Xiong and Chen Zhang: Software, Validation. Feng Li and Qiile Li: Resources, Data curation.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

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