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Characteristic changes of ozone and its precursors in London during COVID-19 lockdown and the ozone surge reason analysis

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HIGHLIGHTS

• Form 2001 to 2021, O₃ concentrations increase by 0.3 ppb-yr⁻¹, while other pollutants experience varying degrees of decline.
• During the COVID-19, NOx concentrations fall to 30% of the original levels, while O₃ concentrations increase exponentially.
• Urban London O₃ pollution is in the VOC-limited regime.
• The surge of O₃ concentrations during the COVID-19 is because NOx declined rapidly.

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ABSTRACT

The London COVID-19 lockdown reduced emissions from anthropogenic sources, providing unique conditions for air contamination research. This research uses tropospheric ozone (O₃), volatile organic compounds (VOCs) and NOx (NO + NO₂) hourly monitoring data at the London Marylebone Road station from 2001 to 2020 to investigate the effects of lockdown on (O₃) and its precursors. Both NOx and VOCs pollution showed a decreasing trend between 2001 and 2021, with a gradual increase in O₃ in contrast. During the COVID-19 lockdown period (from 23rd March to July 4, 2020), there was a surge in O₃ concentration, accompanied by a sharp reduction in NOx concentrations. Because all the monitoring VOCs/NOx results were less than eight during the lockdown, indicating that O₃ formation in urban London was in the VOC-limited regime. The rapid increase in O₃ concentrations caused by the lockdown was closely related to the rapid decrease in NOx emissions.

1. Introduction

Tropospheric ozone (O₃) can lead to serious respiratory diseases in the lungs and causes an estimated 0.7 ± 0.3 million deaths globally every year (Anenberg et al., 2010). In addition, high O₃ levels have a significant adverse effect on photosynthesis and respiration, cell membrane function, growth rate, quality of seeds produced, and gene expression in plants (Plessl et al., 2007; Mills et al., 2018; Gaudel et al., 2018).

O₃ is a product of photochemical reactions, which means that it has no direct source of emissions (Aqeg, 2009). It is a secondary pollutant produced by a complex reaction between volatile organic compounds (VOCs) and NOx (NO + NO₂) under light conditions (Eea, 2016; Sillman, 2003). NOx acts as a controlling factor and affects O₃ in three main stages (Fig. 1) (The Royal Society, 2008). At low NOx concentrations (1–60 ppt), O₃ production is in the net removal phase, and its generation rate is negative (Regime I). Ozone formation is in Regime II (NOx-limited regime) when NOx concentration is between 60 and 1000 ppt. As NOx reaches a higher concentration, the O₃ concentration also increases. As the NOx concentration increases above 1000 ppt, the VOCs concentration will directly determine the O₃ accumulation level (VOC-limited regime). When VOCs emission increases, the peak O₃ concentration shifts to the upper right (Regime III).

In 1988, O₃ concentrations increased due to human activity and urbanisation had already reached twice the level of 1950 (Volz and Kley, 1988). Due to the rise of the industrial revolution, in Europe and North America, peak O₃ concentrations often exceeding 200 μg m⁻³ in summer between 1970 and 1980 (Fowler et al., 2020). Following significant control measures of O₃ precursor emissions by local governments, O₃ contamination levels showed a decreasing trend in North America,
Western Europe and North Africa in the early 21st century (Simpson et al., 2014; Lin et al., 2017). Since 1990, when photochemical smog became a concern in East Asia region, most \( \text{O}_3 \) pollution studies in urban areas have shown a trend of increasing concentrations from year to year (Gaudel et al., 2018; Liu et al., 2020b). Similar to the East Asia region, annual mean \( \text{O}_3 \) concentrations in urban areas in the UK increase gradually over the period 1999–2019 and peak in 2020 (Aqeq, 2009; Defra, 2020).

The COVID-19 pandemic is the deadliest disease in human history. In response to the impact of the COVID-19, many countries around the world began to implement city lockdown from February 2020. For urban areas, the control of industrial, traffic and residential activities can have a significant impact on the emission of air pollutants (Zhang et al., 2020). Elevated \( \text{O}_3 \) concentrations were reported to varying degrees in many regions of the world. Compared to the same period in 2017–2019, average daily \( \text{O}_3 \) concentrations increased by 36%, 14%, 27% and 2.4% in Wuhan, Rome, Turin, and Valencia, respectively, during the 2020 lockdown (Sicard et al., 2020). In 20 urban areas in India, while the VOCs concentration decreased, \( \text{O}_3 \) concentrations increased over the same period (Pakkattil et al., 2021). Dantas et al. also reported a large increase in \( \text{O}_3 \) concentrations in Brazil after controlling VOCs and NOx emissions (Dantas et al., 2020). \( \text{O}_3 \) showed increases of about 59.5% (Liu et al., 2020b) and 25.1% (Le et al., 2020) in the Yangtze River Delta and Beijing of China. The National Statistics calculated annual averages of maximum eight-hourly \( \text{O}_3 \) concentrations for the period 1997–2020 for all sites in the UK. The results show a more pronounced upward trend in \( \text{O}_3 \) concentrations in urban areas and a 23-year peak during the 2020 COVID-19 lockdown (National Statistics, 2021). Much research reported that the increase in \( \text{O}_3 \) levels in Asian and European urban areas is partly due to a weakening of titration following a significant decrease in NO concentrations (Liu et al., 2020b; Ordóñez et al., 2020; Sicard et al., 2020; Grange et al., 2021). However, the effect of VOCs on \( \text{O}_3 \) production is not considered.

London is the largest European city and the second-largest economic centre globally, with dense road traffic and a large metropolitan area. Air quality research in London is of great relevance. As significant sources of the critical \( \text{O}_3 \) precursors are from mobile sources, this paper will use monitoring data from London’s urban transport areas to determine pollution levels of \( \text{O}_3 \), NOx, and VOCs and the relationship between \( \text{O}_3 \) and meteorological conditions. This information will help analyse the impact of lockdown on \( \text{O}_3 \) concentrations and identify the main precursors of \( \text{O}_3 \) in the area. These results may provide enough information to discuss why \( \text{O}_3 \) concentrations varied during the lockdown.

This research consists of three main sections: (1) analysis of pollutants’ long-term trends; (2) discuss the influence of meteorological conditions on \( \text{O}_3 \) production; (3) analysis of the impact extent of lockdown on \( \text{O}_3 \) pollution; (4) VOCs’ ozone formation potential (OPF) and \( \text{O}_3 \) precursors sensitivity analysis.

2. Methods

2.1. Monitoring stations and data

The Marylebone Road air quality monitoring station (51°31’12” N, 00°09’00” W) is a typical roadside site in London, only 1 m from the six-lane A501 (Fig. 2). This monitoring site provides a reliable indication of pollutants’ concentration emitted from mobile sources in London’s urban traffic area. It is bordered to the north by the Regent’s Park, and other directions are London main blocks. Because Marylebone Road is a trafficked street surrounded by various constructions with the heaviest traffic in London, it is a specific site that can represent the emission characteristics of the London urban area. Therefore, this study chose the Marylebone Road monitoring site as the primary research station for analysis.

This study used the pollutants’ concentrations and meteorological data at Marylebone Road from January 1, 2001 to May 17, 2021, obtained from the Department for Environment Food & Rural Affairs website (https://uk-air.defra.gov.uk). The running 8 h \( \text{O}_3 \), NOx concentrations and temperature, wind speed, wind direction are from the Automatic Urban and Rural Monitoring Network (AURN) (Defra, 2021b), and the VOCs data are from the Automatic Hydrocarbon Network (Defra, 2021a). The resolution of these data is hourly. According to the UK and EU air quality strategies for \( \text{O}_3 \) pollution, the indicator used to assess \( \text{O}_3 \) pollution levels is the running 8 h average concentration (Defra, 2007). The method used by the AURN to monitor \( \text{O}_3 \) concentration is UV absorption, while the NO and NOx concentrations are measured using chemiluminescence. Multiplying the NO concentration by the ratio of the relative molecular mass of NO to \( \text{N}_2 \) and summed with the \( \text{NO}_2 \) data to represent NOx concentration (\( \mu \text{g} \cdot \text{m}^{-3} \) expressed as \( \text{NO}_2 \)). Automatic Hydrocarbon Network using automatic PerkinElmer gas chromatograph monitor 29 VOCs (12 alkenes, ten olefins, one alkene, and six aromatic hydrocarbons), which significantly impact \( \text{O}_3 \) production.

2.2. The generalised additive model

The generalised additive model can calculate and do the long term trends for each pollutant (Carslaw, 2015, 2020) to determine the overall pollution change. The generalised additive model splits the data into multiple components, each matched with a separate segmental formula, ultimately finding the better equations that minimise the differences between simulated and actual monitored values (formula 1). This study calculated \( \text{O}_3 \) and its precursors’ (NOx and VOCs) different percentile smooth trend lines from 2001 to 2021 to assess the long-term trends and the development direction pollutants in recent years. It is worth noting that even though monthly average concentrations are useful for studying long-term trends in pollutant contamination degree, the results cannot be used to analyse specific concentration changes.

\[
y = \beta_0 + f_1(x_1) + f_2(x_2) + \cdots + f_d(x_d)
\]

2.3. De-seasonalisation

The daily average concentration of pollutants during the lockdown were compared with the intermediate pollution level for each month from 2001 to 2021 to obtain the normalised results. The normalised data represent the lockdown influences on pollutant emissions or production after balancing the various effects. Comparing the calculated results with one reflects a significant change in the pollutants’ concentration. When the calculated result is \( > 1 \), and \( < 1 \), the pollution level increased, remained the same and decreased during the lockdown,
respectively — the more significant the difference between the result and 1, the more remarkable pollutant concentration changes.

\[ \text{Des}_i = \frac{C_i}{\text{Longterm}C_i} \]  

(2)

Where:

- \( i \) indicates different types of pollutants (running 8 h \( \text{O}_3 \), \( \text{NOx} \), and VOCs).
- \( \text{Des}_i \) expresses de-seasonalised results.
- \( C_i \) represents the monitoring concentrations during the lockdown.
- \( \text{Longterm}C_i \) denotes the monthly average concentrations from 2001 to 2021.

2.4. Ozone formation potential

The ability and potential of different VOCs to generate \( \text{O}_3 \) vary from region to region, which is not only related to the atmospheric chemical reactivity of the VOCs but should also be considered in terms of volume fraction (Carter, 1994). This research uses the results of William P. L. Carter’s modelling of the \( \text{O}_3 \) generation capacity of different VOCs to calculate the Ozone Formation Potential (OFP), based on how changes in the volume fraction of the VOCs lead to changes in \( \text{O}_3 \).

\[ \text{OFP}_j = \phi_j/(\text{VOC}) \times \text{MIR}_j \]  

(3)

where:

- \( j \) denotes a different VOC species.
- \( \phi_j \) (VOC) means the volume fraction.
- \( \text{MIR}_j \) is the maximum incremental reactivity (Carter, 1994).

2.5. Sensitivity analysis

Sensitivity analysis by the photochemical ratio (VOCs/NOx) is a qualitative analytical method for determining \( \text{O}_3 \) generation precursors. A VOCs/NOx ratio of less than or higher than eight can be defined as a VOC-limited or NOx-limited regime, respectively (Nrc, 1992; Ren et al., 2021; Zou et al., 2014). In the NOx-limited regime, reducing the NOx concentration can effectively control \( \text{O}_3 \) pollution while the VOCs concentration remains constant. The VOC-limited regime suggests that \( \text{O}_3 \) pollution will mitigate as the VOCs concentration decreases. However, if both VOCs and NOx concentrations decline without a correct emission reduction ratio, a rise in \( \text{O}_3 \) may be brought about (Nrc, 1992).

3. Results and discussion

3.1. Rapid rise in ozone concentration from 2018 to 2020

Seven typical pollutants’ concentrations in the atmosphere from 2001 to 2020 were fitted using Theil-Sen trend analysis, and the results are shown in Table 1. Over the past 20 years, all pollutant concentrations except \( \text{O}_3 \) have experienced different decline degrees. In particular, \( \text{PM}_{10} \), \( \text{PM}_{2.5} \) and \( \text{SO}_2 \) have dropped gently, by 1.56 \( \mu \text{g m}^{-3} \), 0.49 \( \mu \text{g m}^{-3} \) and 0.34 \( \mu \text{g m}^{-3} \) per year respectively, while CO, NOx and VOCs have decreased from high levels to relatively low levels, changing 0.05 \( \text{mg m}^{-3} \), 5.86 \( \mu \text{g m}^{-3} \) and 3.72 \( \mu \text{g m}^{-3} \) per year respectively. Unlike other pollutants, \( \text{O}_3 \) pollution levels increased at 0.3 ppb per year from 2001 to 2020 based on hourly resolution concentration. This phenomenon is likely to be closely related to changes in the concentrations of its main precursors, NOx and VOCs.

Although Theil-Sen trend analysis can reflect the overall trend and direction of pollutant changes, it may hide some information on the changes in pollution conditions. The smoothed trend analysis method can make up for the shortcomings of the Theil-Sen trend by fitting a more apparent trend based on the monthly average concentration data at different percentile levels to determine the changes in other pollution conditions (Fig. 3). The high percentile (95%) indicates typical polluted weather, the middle percentile (75%, 50%, 25%) indicates standard pollution conditions in the area, and the low percentile (5%) indicates more stable background conditions (Li et al., 2014; Wang et al., 2021).

From 2001 to 2004, the 95% quartiles experienced a slight short-term decrease in NOx because the smoothed line showed a downward trend. So, at the turn of this century, only the heavily polluted weather improved to a minor extent, with overall pollution levels remaining high. Over the following decade, the overall pollution levels of NOx stabilised until 2017. The NOx concentrations at each percentile decreased rapidly between 2017 and 2020. The generally more stable NOx background concentration conditions (5% quantile) also showed a

| Pollutant | k (units/yr) | CI (units/yr) | P-value |
|-----------|--------------|---------------|---------|
| NOx       | -5.86        | [-7.67, -3.80] | <0.01   |
| \( \text{SO}_2 \) | -0.34        | [-0.39, -0.29] | <0.01   |
| CO        | -0.05        | [-0.06, -0.05] | <0.01   |
| VOCs      | -3.72        | [-4.34, -3.11] | <0.01   |
| \( \text{PM}_{10} \) | -1.56        | [-1.68, -1.44] | <0.01   |
| \( \text{PM}_{2.5} \) | -0.49        | [-0.58, -0.39] | <0.01   |
| \( \text{O}_3 \) | 0.3          | [0.14, 0.48] | <0.01   |

\( ^\circ \) CI indicates a 95% confidence interval for the k-value of the simulation results.
degree of decline, indicating a fundamental change in NOx pollution levels in the region. Since the primary source of NOx is the incomplete combustion of fossil fuels in road traffic (Amann, 2008). As a result, transport upgrades and a shift in fuel type to cleaner energy sources have led to a rapid reduction in NOx concentrations from incomplete combustion of fossil fuels. The UK government required the installation of three-phase catalytic converters in vehicles to catalytic oxide further CO and unburned hydrocarbons in the exhaust gases and reduce NOx compounds. In addition, the development and use of more biomass fuels and renewable energy sources will also contribute to the progressive reduction of NOx emissions from the transport sector (National Statistics, 2012). As the Marylebone Road station reflects pollution in built-up areas, particularly densely trafficked areas, the impact of motor vehicle upgrades and fuel transitions on their NOx monitoring values is evident.

VOCs have declined at a relatively rapid rate year on year between 2001 and 2010 at both the high (95%) and medium percentile concentrations (75%, 50%, 25%), with the rate of reduction slowing in the last decade, which is similar to Defra’s findings (Defra, 2021c). VOCs come from a wide range of sources, but road traffic emissions accounted for the largest share of VOCs in the UK from 1990 to 2010 (Lewis et al., 2020a, 2020b). However, from 2010 onwards, replacing older road traffic vehicles in London and the gradual stabilisation of petrol use has led to a more significant proportion of VOCs being emitted from solvent use than from road traffic (Lewis et al., 2020a). The replacement of vehicles and the gradual reduction in petrol use at the turn of the century has led to a rapid decline in VOC emissions. The UK government has not yet introduced controls on the use of solvents, which will stabilise pollution levels.

In addition to background O3 concentrations (5% quantile), typical pollution levels and characteristic pollution O3 concentrations showed only slight decreases until 2017, with a clear increasing trend after this year. There are two possible reasons for the extent of photochemical reactions to O3. The island heatwave event in the UK in 2018 made that year the hottest since 1884. Over the next three years, the UK experienced its highest and driest summer in terms of sunshine hours and radiation intensity for many years (Kendon et al., 2019). The strong photochemical reactions influence the production of O3 to some extent. In addition, O3 is one of the typical secondary pollutants. The changes of O3 has a significant association with precursors. Before 2017, the concentration of VOCs declined, while NOx remained almost unchanged, which made the decline in O3 insignificant. After 2017, the NOx concentration fell rapidly to a quarter of the 2001 level, while the VOCs also continued to decline, which affected the O3 generation process. This study will focus on the reasons for the rapid increase in O3 concentrations due to the continued decline in precursors.

3.2. COVID-19 causes a significant increase in ozone pollution

The first lockdown for London began on March 23, 2020, dividing the O3 concentration data from this monitoring station for 2001–2021 into two parts by that date. In Fig. 4, after the first lockdown, both hourly concentrations and average daily and monthly concentrations have experienced significant increases. Changes in concentrations of NOx and VOCs before and during the COVID-19 lockdown are provided.
in Supplementary Material 1 (S1 and S2). Contrary to the trend in O₃, the O₃ precursors’ concentrations both showed a significant decline during the lockdown.

Firstly, the O₃ pollution in London is not a typical single-peak curve but shows a double-peak during the day, suggesting that the photochemical reactions that generate O₃ during the midday, the weakened titration from reduced NOx emissions at night also allows for O₃ accumulation.

Fig. 4. Daily, weekly, and monthly change results of running 8 h O₃ concentration (ppb) at Marylebone Road divided by March 23, 2020. The red curve represents the average running 8 h O₃ concentration from January 1, 2001 to March 23, 2020, while the green line depicts the concentration during the first lockdown. The blue lines indicate the difference between the mean O₃ concentration and the post-lockdown concentration. The shaded area shows the 95% confidence interval. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

Fig. 5. Hot maps of O₃ versus temperature, wind speed, and wind direction during 2001 and 2021. From warm to cool colour of the hexagon indicates the density of the points from largest to smallest. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)
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Secondly, from April to June 2020, London’s most critical lockdown period, when NOx emissions decreased significantly, was accompanied by a sharp increase in O3 concentrations. In particular, O3 concentrations increased by approximately 26 ppb in April 2020 compared to the previous 20 years, a rise that was even higher than the average April emissions in a typical year, indicating that the contribution of lockdown to O3 pollution was significant. After the lockdown on 5th July, motor vehicle use quickly returned to 80% of pre-lockdown levels (National Statistics, 2020), and O3 concentrations fell for a short time after NOx emissions increased. The high temperatures and drought in August allowed the photochemical reactions met their conditions, bringing about a new increase in O3 concentrations.

Although the above changes are apparent, the impact of lockdown on O3 pollution cannot be directly determined from changes in concentrations, as meteorological factors are critical in the production and dispersion of O3. During 2018–2020, the UK experienced unprecedentedly high temperatures due to the Isles heatwave (Kendon et al., 2019; Met Office, 2020), which provided unique conditions for O3 production.

Heat maps of the relationship between O3 concentrations and temperature, wind speed and wind direction in urban London is provided in Fig. 5. O3 concentrations at London Marylebone Road are less than 20 ppb for most of the time during 2001 and 2021. Temperatures in the area generally range from 0 to 20 °C, with the most frequent temperature range occurring between 5 and 12 °C. It is not evident that O3 increases with rising temperature. However, it is worth acknowledging that the temperatures were higher when severe O3 pollution occurred. When O3 concentrations were more significant than 130 ppb, the ambient temperature must have been higher than 20 °C, suggesting that high-temperature conditions contribute to O3 pollution. One aspect of the positive correlation between temperature and O3 is because the critical factor affecting O3 concentrations is the intensity of solar radiation (Juraj et al., 2019). In weather with higher solar radiation, the ambient temperature also tends to be higher. In addition, high-pressure systems influence temperature and the accumulation of pollutants. The high-pressure systems cause warming and limit the mixed layer’s growth, which leads to the expansion of air pollutants in the troposphere.

When the O3 concentration is higher than 100 ppb, the wind speed is generally at a low rate (0–5 m/s). Therefore, when wind speeds are high, the likelihood of O3 pollution is also substantially reduced, as good dispersion conditions will favour the transport of O3 for dispersion to other regions. According to the relationship between wind direction and O3, the directions where more O3 polluted weather occurs are to the northeast and east. Based on the buildings surrounding the Marylebone Road monitoring site, Regent’s Park is in its northeast, suggesting that the number of mobile sources from the northeast would be much smaller than the other directions spread across the leading transport network. Therefore, lower fossil fuel combustion led to NOx emissions in the northeast, directly reducing titration and increasing O3 concentrations. The higher O3 concentrations in the east may be because this direction is the main London Road A404, where high concentrations of VOCs and NOx emissions from transport vehicles generate O3. In addition, heavy O3 pollution tends to occur downwind of areas with more intensive precursor emissions, and the effect of short-range transport is also an essential factor. Although the titration of NOx may remove some of the O3, when the concentrations of VOCs are high, the peak of O3 production will increase, resulting in more severe O3 pollution.

Any relationship between O3 and meteorological factors is difficult to quantify directly using mathematical models, this paper uses the relative ratio method to determine the extent to which lockdown affects O3 concentrations. According to Fig. 6, O3 concentrations exceeded the 20-year average pollution level on nearly 96% of the days during the 104-day lockdown period, and the O3 concentrations almost reached the 20-year peak. In contrast, the Met Office’s temperature statistics for 2020 show that only about 50% of days have temperatures above the 1981–2010 average, and the maximum temperatures are mainly within the normal range, suggesting that temperature’s influence on O3 concentrations is limited. In addition, the dispersion conditions for pollutants in the UK in 2020 are also worth considering. According to Madhumitha Jagannmohan’s statistics on the average wind speed in the UK from 2001 to 2020, it generally remains between 8 and 10 m/s (Jagannmohan, 2021). The average wind speed in 2020 is higher than in 2018 and 2019, which suggests that with better dispersion conditions in 2020, O3 pollution in London’s urban traffic areas is more severe. The VOCs and NOx concentrations have been almost lower than usual in the last 20 years. Therefore, it is practically certain that O3 concentrations increased during the lockdown period.

The reduction in NOx is very significant, being only about 30% of normal conditions. This result is highly correlated with the decrease in traffic sources because the decline in motor vehicle use during London’s lockdown was more than 65%, which affected NOx emissions. Fluctuations in VOCs were more considerable than NOx, and their reduction was less pronounced. Although traffic sources decrease rapidly, household VOCs emissions from lockdown may increase. The two compensating for each other may make it possible that VOCs do not reduce significantly. The precursors’ concentration may be the main reason linked to O3 generation.

3.3. Falling NOx is responsible for ozone surge

As the contribution of different VOCs to O3 production varies, VOCs are recalculated according to their oxidation capacity size before sensitivity analysis. The 29 VOCs belong to alkanes, olefins, alkenes and aromatic hydrocarbons. In Fig. 7, the seasonal variation of VOCs is pronounced, showing a trend of high emission in winter and low pollution in summer because the photochemical reactions generated by O3 can consume many VOCs in the summertime in high temperatures strong solar radiation. In May, the VOCs concentration is the lowest value of the year at about 43 μg m⁻³. The share of concentrations shows alkane (65%) > aromatic hydrocarbons (20%) > olefins (12%) > alkenes (3%). In terms of overall reactivity, olefins (48%) > aromatic hydrocarbons (28%) > alkane (23%). Whereas the composition of VOCs is greater than 60% alkane, the OFP of alkane is only about 24%.

The results of the OFP calculations by species are shown in Supplementary Materials 2. Table 2 summarises the comparison of the concentrations and reactivity of the ten most O3-generating VOCs. According to the analysis of the composition of VOCs, alkane account for more than 40.44% of the VOCs concentration, but their OFP total is only 13.97%. On the other hand, olefins are only 9.69% of the total.

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Fig. 6. De-seasonalised NOx, VOCs and O3 concentrations during the first lockdown. The x-axis is the lockdown period, while the y-axis is the ratio of monitored concentrations during lockdown to 20-year average concentrations by month. The red, green, and blue lines represent the NOx, O3 and VOCs. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)
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Concentration but contribute to half of the reactive substances in the O$_3$ generation reaction. According to the OFP calculation results, the most important species to form O$_3$ are ethene, propene, m+p-xylene, toluene, isopentane, n-butane, cis-2-pentene, o-xylene, iso-butane and ethane. Although their concentration only occupies 64.84% of the total concentration, their summation OFP holds nearly 80% OFP. Therefore, the analysis of emission sources and concentration control of the above ten VOCs will be crucial.

This study uses the characteristic ratio method to determine whether VOCs or NOx controls O$_3$ production in the London urban area. VOCs concentrations are the result of weighting the top ten species in terms of the percentage of OFP. Fig. 8 shows the smoothed VOCs/NOx ratios for 2001–2021, and the daily VOCs/NOx profiles for each year are provided in S3. The VOCs/NOx ratio results are lower than 3, well below the NOx control regime boundary (VOC/NOx = 8). The ratio is unaffected mainly by seasonal variations. Based on these results, O$_3$ generation in the London urban area is in the VOC-limited regime. The VOCs/NOx ratio also declined rapidly during this period. After 2018, as NOx falls quickly, the VOCs/NOx ratio rises quickly, leading to a surge in O$_3$ concentrations. Notably, the VOCs/NOx and O$_3$ concentrations from March to June 2020 were significantly higher than the trend line fit. Therefore, O$_3$ production in the London area is controlled by VOCs. However, reducing VOCs concentrations in the room while keeping NOx constant does not significantly affect O$_3$ concentrations. In contrast, preventing constant VOCs concentrations and significantly reducing NOx concentrations resulted in a significant spike in O$_3$ concentrations.

This research plots a three-dimensional scatter plot of NOx-VOCs-O$_3$ from 23rd March to July 4, 2020 to determine O$_3$ precursors during lockdown (Fig. 9). During the lockdown, NOx concentrations ranged from 0 to 100 $\mu$g m$^{-3}$, and VOCs concentration lower than 40 $\mu$g m$^{-3}$. O$_3$ concentrations were influenced by both VOCs and NOx, with most O$_3$ concentrations below 30 ppb.

The VOCs-NOx-O$_3$ scatter plots during the lockdown are located where VOCs/NOx < 8. Therefore, O$_3$ pollution in the London City traffic area is likely controlled by VOCs. Besides, there is a gradual decrease in O$_3$ concentrations as NOx concentrations increase, suggesting that NOx may have reached saturation and insufficient OH in the atmosphere to compensate for NO$_2$ consumed. At the same time, when the VOCs concentration increase, O$_3$ pollution is also reduced, which means that the mechanism of O$_3$ generation in London’s urban traffic zones is in regime III. The VOC concentration level only affects the magnitude of the peak O$_3$ age and the time to reach it. As VOCs increase, the fuel for the

Table 2

| VOCs          | Pollutants | Conc (μg m$^{-3}$) | Conc proportion | OFP | OFP proportion | Total OFP proportion |
|---------------|------------|-------------------|-----------------|-----|----------------|---------------------|
| Alkanes       | ethane     | 7.99              | 14.03%          | 6.21| 2.65%          | 13.97%              |
|               | iso-butane | 3.35              | 5.88%           | 6.51| 2.78%          |                     |
|               | n-butane   | 5.92              | 10.39%          | 9.72| 4.14%          |                     |
|               | iso-pentane| 5.78              | 10.14%          | 10.33| 4.40%          |                     |
| Olefins       | ethene     | 3.10              | 5.44%           | 76.44| 32.59%          | 49.34%              |
|               | propene    | 1.52              | 2.67%           | 31.72| 13.53%          |                     |
|               | cis-2-pentene| 0.90             | 1.58%           | 7.55 | 3.22%          |                     |
| Aromatic      | toluene    | 4.87              | 8.55%           | 13.35| 5.69%          | 15.67%              |
|               | m+p-xylene | 2.20              | 3.86%           | 15.90| 6.78%          |                     |
|               | o-xylene   | 1.31              | 2.30%           | 7.51 | 3.20%          |                     |
| Total         | –          | 36.94             | 64.84%          | 185.24| 78.98%          |                     |

Fig. 7. Stacked graphs of the concentrations of the four VOC components with seasonal variations from 2001 to 2021. Figure A shows the monthly concentration changes for the various classes of VOCs. Figure B shows a stacked graph of the monthly concentration ratios of different VOCs. The x-axis is the month, and the y-axis is the concentration (μg m$^{-3}$) and contribution percentage (%), respectively. Yellow, green, purple, and orange indicate alkanes, olefins, alkynes, and aromatic hydrocarbons. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

Fig. 8. Interannual variation in the monthly average VOCs/NOx ratio from 2001 to 2021.
photochemical reaction increases, and the peak concentration of \( \text{O}_3 \) generated and the amount of NOx required to achieve the peak increases. However, when the amount of NOx exceeds the amount of reactive material that the VOCs can supply, the reaction to generate \( \text{O}_3 \) will not proceed smoothly. The process of depletion of \( \text{O}_3 \) concentration will take its place. Therefore, VOCs will become the controlling condition in the whole reaction process.

Based on the above analysis, the \( \text{O}_3 \) generation process in London Marylebone Road is in the VOCs-limited regime, both in terms of the qualitative ratio analysis process and the mechanism of \( \text{O}_3 \) generation. The results are consistent with the conclusions obtained for the relationship between \( \text{O}_3 \) and NOx in the UK during COVID-19 and in European urban areas (Lee et al., 2020; Beck et al., 1998).

\( \text{O}_3 \) is a typical representative of secondary pollutants, and the concentration of NOx and VOCs in the atmosphere determines the level of \( \text{O}_3 \) pollution. VOCs mainly provide the reactive group for photochemical reactions, while NOx plays a more critical role in controlling \( \text{O}_3 \) pollution. Because when NOx concentrations reach a certain level, there will have NO titration, leading to the gradual depletion of \( \text{O}_3 \). Therefore, NOx is the critical factor in determining the production or consumption of \( \text{O}_3 \) (The Royal Society, 2008). Because the VOC-limited regime controls \( \text{O}_3 \) formation in London’s urban areas, \( \text{O}_3 \) pollution increases rapidly as the NOx concentration decreases. As mentioned earlier, the titration of NOx has a very significant effect on eliminating \( \text{O}_3 \) in the area, which is the dominant reason \( \text{O}_3 \) shows a significant negative correlation with NOx.

4. Conclusion and suggestions

This research uses NOx, VOCs, and running 8 h \( \text{O}_3 \) concentrations data from the London Marylebone Road monitoring station (2001–2021) to analyse the COVID-19 lockdown’s impact on the \( \text{O}_3 \) and do sensitivity analysis to judge the dominant precursor of the \( \text{O}_3 \) formation.

\( \text{O}_3 \) concentrations increased from 2018 onwards, while NOx and VOCs experienced varying degrees of decline between 2000 and 2021. Pollution levels of \( \text{O}_3 \) are rising rapidly because of the heat island enhanced photochemical reactions and the NOx decline after 2017 reduced titration.

After removing the meteorological factors on pollution levels during the COVID-19 lockdown, NOx experienced a more pronounced cliff-like fall, while \( \text{O}_3 \) concentrations increased explosively. And the results of the sensitivity analysis show that VOCs are a critical factor in controlling the photochemical reaction of \( \text{O}_3 \) in the area (VOC-limited regime). This result indicates that urban London is saturated with NOx in the photochemical reaction. As the NOx concentration decreases, the \( \text{O}_3 \) concentration increases instead, resulting in more severe \( \text{O}_3 \) pollution. Therefore, the main reason for the \( \text{O}_3 \) surge during COVID-19 was the significant drop in NOx concentrations.

To control \( \text{O}_3 \) pollution in urban London, a decrease in NOx concentrations will not help solve \( \text{O}_3 \) production but will instead cause its concentration to increase. Therefore, it would be wiser to start with VOCs to control summer \( \text{O}_3 \) pollution. The top ten OFP VOC species are ethene, propene, m-xylene, toluene, isopentane, n-butane, cis-pentane, o-xylene, iso-butane and ethene. Their combined share of the OFP contribution is almost 80%. At the same time, olefins provide about 49.34% of the reactive material to \( \text{O}_3 \) production, although their concentration shares are only 9.69%. Therefore, controlling emissions of olefinic substances is more cost-effective than several other VOCs in London’s urban traffic zones. At the same time, analysing the sources of the top ten species of OFP, such as through source analysis, so that their emissions can be targeted and controlled will positively affect the control of \( \text{O}_3 \) pollution.

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Data access

All monitoring data can be obtained from the Department for Environment Food & Rural Affairs website (https://uk-air.defra.gov.uk/data/data_selector) under the UK AIR topic, Air Information Resource.

CRediT authorship contribution statement

Chenyue Zhang: Conceptualization, Methodology, Software, Formal analysis, Data curation, Writing – original draft, Visualization.

David Stevenson: Validation, Supervision, Writing – review & editing.

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.

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Appendix A. Supplementary data

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