Changes in ambient air quality and atmospheric composition and reactivity in the South East of the UK as a result of the COVID-19 lockdown

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HIGHLIGHTS
• Boundary layer trace composition changed during the COVID-19 pandemic.
• NO2 concentrations across measurement sites were down by ~14–38%.
• PM10/PM2.5 concentrations were influenced by interregional pollution episodes.
• O3 concentrations were up by as much as 15% and total O3 levels were preserved.
• Under HC limited regime, increased O3 led to increased radicals and reactivity.

ABSTRACT
The COVID-19 pandemic forced governments around the world to impose restrictions on daily life to prevent the spread of the virus. This resulted in unprecedented reductions in anthropogenic activity, and reduced emissions of certain air pollutants, namely oxides of nitrogen. The UK ‘lockdown’ was enforced on 23/03/2020, which led to restrictions on movement, social interaction, and ‘non-essential’ businesses and services. This study employed an ensemble of measurement and modelling techniques to investigate changes in air quality, atmospheric composition and boundary layer reactivity in the South East of the UK post-lockdown. The techniques employed included in-situ gas- and particle-phase monitoring within central and local authority air quality monitoring networks, remote sensing by long path Differential Optical Absorption Spectroscopy and Sentinel-5P’s TROPOMI, and detailed 0-D chemical box modelling. Findings showed that de-trended NO2 concentrations decreased by an average of 14–38% when compared to the mean of the same period over the preceding 5-years. We found that de-trended particulate matter concentrations had been influenced by interregional pollution episodes, and de-trended ozone concentrations had increased across most sites, by up to 15%, such that total O3 levels were preserved. 0-D chemical box model simulations showed the observed increases in ozone concentrations during lockdown under the hydrocarbon-limited ozone production regime, where total NOx decreased proportionally greater than total non-methane hydrocarbons, which led to an increase in total hydroxyl, peroxy and organic peroxy radicals. These findings suggest a more complex scenario in terms of changes in air quality.
1. Introduction

By the 1st July 2020 there were in excess of 10 million confirmed cases of COVID-19 worldwide. Of these cases, it was reported that the virus had claimed an estimated 511,037 lives (ECDC, 2020). In an effort to halt the spread of the disease, governments across the globe put into place a range of measures based on ‘social distancing’ and ‘self-isolation’, which resulted in many industries suspending operations and most citizens (i.e. non ‘key-workers’) staying in their homes (PHE, 2020a). As such, anthropogenic activity around the globe decreased rapidly, to such an extent that emissions of air pollutants began to decline dramatically, with this period now being referred to as an ‘anthropause’ (Rutz et al., 2020). In the early stages of the pandemic, remote sensing data from satellites indicated that nitrogen dioxide (NO₂) concentrations had fallen by as much as 30% across China and by as much as 50% across areas of central Europe (NASA, 2020). Early work using in-situ measurements confirmed these findings, with studies from China (Chen et al., 2020), Korea (Ju et al., 2020), India (Sharma et al., 2020), USA (Zangari et al., 2020) and Europe (Tobias et al., 2020; Sicard et al., 2020) all reporting decreases in ambient NO₂ concentrations. The UK government advised that the general population should avoid ‘non-essential’ travel and social contact, on 16th March 2020. At this point, the total number of confirmed cases in the UK had surpassed 1500. Subsequently, on 23rd March 2020, the government announced a UK-wide partial lockdown, to contain the spread of the virus. The Health Protection (Coronavirus, Restrictions) (England) Regulations 2020 (SI 350) (PHE, 2020b), the statutory instrument to enforce the lockdown, was enacted shortly after. The total number of confirmed COVID-19 cases and deaths in the UK from 1st January 2020 to 6th July 2020, is shown in the Supplementary material (Fig. S1), for reference.

Air pollution is one of the single biggest on-going threats facing global public health today (WHO, 2016). It is estimated that ~90% of the world’s population live in areas where levels of air pollution are above limits deemed safe for human health (WHO, 2018), and that this results in ~7-million deaths per year (i.e. ~13% of all global deaths) and a reduction in average life expectancy by ~2-years (Greenstone and Fan, 2018). Consequently, it follows that such a significant and widespread reduction in air pollutant emissions as has been experienced across the globe during the COVID-19 pandemic, should result in a decrease in air pollution related morbidity and mortality. According to recent research by the Centre for Research on Energy and Clean Air, the reductions in NO₂ and particulate matter (PM) experienced across Europe after government restrictions were put into place was likely to have reduced the number of air pollution associated deaths by 11,000 over just 30 days (Myllyvirta and Thieriot, 2020). However, such estimates do not take into account changes in the abundance of secondary pollutants, which can often be proportionally more harmful to human health than some primary species (e.g. Mustafa et al., 1984).

Such a dramatic reduction in certain air pollutants across the species emissions spectrum, over such a relatively short time interval and across so many different countries, is unprecedented. As such, the resultant impacts on tropospheric chemical processes and composition need to be investigated. For instance, with reductions in ambient NOₓ (i.e. NO + NO₂) concentrations there will be a shift in the balance of chemistry, and levels of secondary pollutants such as ozone (O₃) are likely to be perturbed from the expected norm (Monks et al., 2015). Also, we are likely to experience a shift in the size distribution of particulate numbers; as PM₁₅ and PM₂₅ act to suppress the formation and abundance of ultrafine particles (UFP; Guo et al., 2020). A reduction in the abundance of larger particles could result in a burst in the number concentration of the finest, more harmful fractions (e.g. Harrison and Yin, 2000; Araujo and Nel, 2009; Rückerl et al., 2011; Hofman et al., 2016; Rychlik et al., 2019).

Therefore, it is vital that we act rapidly to quantify and understand the changes occurring within our atmosphere, particularly with respect to major respiratory air pollutants which can exacerbate the effects of respiratory diseases such as COVID-19, and pollutants which could act as vectors for these viruses (Comunian et al., 2020). One major tool available to assist in this regard is the network of automated air pollution monitors installed by central governments to make the necessary measurements of air pollution parameters to check air quality levels and ensure regulatory compliance (Munn, 1981). In the UK, the national Automatic Urban and Rural Network (AURN) is run by the Environment Agency on behalf of the UK Government Department for Food and Rural Affairs (DEFRA). It currently comprises 150 monitoring stations deployed in a range of different receptor environments (DEFRA, 2020a), supported by various local authority networks, including in the South East of the UK, the Sussex-Air Network (SUSSEX-AIR, 2020).

In this work, we combine findings from the AURN and Sussex-Air Network with data from the University of Brighton JOAQUIN Advanced Air Quality reSearch (JAAQS) laboratory and ESA’s Sentinel-SP satellite, to investigate changes in tropospheric composition and reactivity in the South East of the UK during the COVID-19 pandemic. The South East of the UK is an interesting region for studying air quality, having the largest regional population of the country, with an estimated 9.13 million people living in the area according to the latest available census data published by the Office for National Statistics (ONS, 2020), and being geographically located between two major air pollution hotspots, i.e. the mega-city of London and the industrial and urbanised North West Europe. The results presented show a more complex scenario with respect to atmospheric reactivity than has been initially reported, with falling NO₂ concentrations, interregional particulate matter episodes and rising O₃ levels (particularly under urban conditions). Unlike other studies conducted thus far, we integrate comprehensive air quality measurements made both in-situ and by remote sensing with non-methane hydrocarbon (NMHC) data and near-explicit 0D chemical box modelling to investigate perturbations to chemical processes. Our findings show that the abundance of NMHCs in the suburban boundary layer (of outer London in the South East of the UK) decreased proportionally less than total NOₓ species, such that there was an increase in the NHMC:NOₓ ratio and a resultant shift within the NMHC sensitive regime toward greater net O₃ production. Model simulations indicate that these perturbations to local boundary layer air led to an increase in hydroxyl radical (OH) concentrations and a potential change in oxidative capacity/capability.

2. Methodology

2.1. The Automatic Urban and Rural Network and Sussex-Air Network

Twenty-five automatic monitoring stations, including six Automatic Urban and Rural Network (AURN) stations, seventeen Sussex-Air and two monitoring stations managed by the Transport Research Laboratory (TRL), with appropriate data coverage, were available in the study area. The locations of these sites are shown in Fig. S2 in the Supplementary material and further information, including environment type and
pollutants monitored, are listed in Table 1. Each monitoring station was variably equipped with chemiluminescence NOx analyser, UV absorption O3 analyser, and Fidas-200, Beta Attenuation Monitor (BAM), or Tapered Element Oscillating Microbalance with Filter Dynamics Measurement System (TEOM-FDMS) gravimetric PM analysers. All AURN and Sussex-Air Network data were screened for service periods and anomalies prior to analysis.

2.2. The JOAQUIN Advanced Air Quality reSearch Laboratory

The JOAQUIN Advanced Air Quality reSearch Laboratory (JAAQS) was established in Brighton in 2015. It comprises a climate controlled, clean laboratory instrumented with a suite of state-of-the-art analytical instruments for making detailed, real-time measurements of tropospheric composition. It is equipped with long-path Differential Optical Absorption Spectroscopy (DOAS; Opsi AB) for remote sensing of trace gas parameters (path length ~ 300 m), including NOx, O3, SO2, formaldehyde (HCHO), nitrous acid (HONO) and benzene (C6H6; indicative data only); total and size-resolved particle counters (7 μm ≤ r ≤ 1000 nm; TSI 3031 and TSI 3783); a black carbon monitor (Thermo MAAP 5012); a PM2.5 monitor (Met One ES-642); and a meteorology station (Campbell Scientific; data from 01/01/2019). JAAQS is situated in a suburban background environment, roughly 5 km from Brighton city centre. JAAQS data were recorded at 5-minute averaging intervals and were screened for service periods and anomalies prior to analysis.

2.3. Meteorology data

Regional meteorology data were obtained from Shoreham Airport, Gatwick Airport, Herstmonceux and Lydd, and local meteorology data were obtained from the JAAQS Laboratory in Brighton and Hove. Parameters employed, included wind speed (m s⁻¹), wind direction (°), atmospheric pressure (Pa), relative humidity (%), air temperature (°C) and solar radiation (Wm⁻²). South East regional meteorological data for Shoreham Airport, Gatwick Airport, Herstmonceux and Lydd were extracted from NOAA’s Integrated Surface Database using the R Package ‘worldmet’ (Carslaw, 2020). Regional meteorology data were recorded at hourly averaging intervals, and local meteorology data were recorded at 10-minute averaging intervals; both data sets were screened for service periods and anomalies prior to analysis. Back trajectory analyses were conducted for key periods using the NOAA Hybrid Single Particle Lagrangian Integrated Trajectory (HYSPLIT) transport and dispersion model (http://ready.arl.noaa.gov/HYSPLIT.php).

2.4. Data analysis procedure

After all data sets were screened for errors, anomalies, instrument downtime and maintenance intervals, they were analysed using the open-source Openair tools (Carslaw, 2015) in the statistical computing software, R (R Development Core Team, 2015). Data capture percentage for 2015–2020, for each monitoring site used for analysis is provided in the Supplementary material (Table S1). As part of the analysis procedure, the ‘de-weather’ package within Openair was used to ‘de-trend’ the data and remove the influence of meteorology in order to help assess the extent to which changes in ambient pollutant concentrations were attributed to sudden changes in emissions following government-imposed lockdown restrictions (Grange and Carslaw, 2019). Each ‘de-weather’ analysis was conducted using historic 5-year air pollutant monitoring and regional meteorological data.

Further analytical methods were then applied to the de-weathered data, namely relative change analysis, and normalisation; key summary statistics are given in Table 2. To produce the data in Table 2, period mean data for March to May, inclusive, were calculated for all assessment years (i.e. 2015–2020). This enabled comparison of average de-weathered pollutant concentrations during lockdown with the preceding 5-year mean (i.e. 2015–2019) for the same period, both in terms of absolute and relative percentage changes. In addition, de-weathered data were normalised to the 2020 average to produce Fig. 1(a–d), and to the 2015–2019 annual averages to produce Fig. S3(a–d) to show
the deviation in average pollutant concentrations during 2020 from the preceding 5-year mean.

2.5. Sentinel-5P TROPOMI observations

Level-2 (L2) TROPOMI NO2 products were sourced from the Sentinel-5P Pre-Operations Data Hub for dates between 23rd March and 22nd April of both 2019 and 2020 (Copernicus, 2020). The pixels covering the South East quadrant of the UK were extracted from each dataset and filtered to remove problematic and cloud influenced observations, i.e. where pixel values were negative or associated with a Quality Assurance flag <0.75 (Eskes et al., 2019). The filtered data were appropriately averaged, and units converted to molec cm\(^{-2}\). Percentage changes in tropospheric column NO2 values were determined by expressing the concentration difference between 2020 and 2019 as a fraction of the 2019 value before multiplying by one hundred.

2.6. Model construction

The average diurnal evolution of local boundary layer gas-phase composition in the spring before (i.e. March, April and May over the period 2015–2019, inclusive) and after initiation of lockdown restrictions (i.e. from 24th March to 31st May 2020), was simulated using a 0-D photochemical box model incorporating appropriate inorganic and organic atmospheric oxidation schemes extracted from the Master Chemical Mechanism (v3.3.1; Jenkin et al., 1997; Jenkin et al., 2002; Saunders et al., 2003; http://mcm.leeds.ac.uk/MCM). With no comprehensive non–methane hydrocarbon (NMHC) data available in the monitoring networks of the South East of the UK, the data required to initialise

<table>
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<th>Site</th>
<th>NO2 Absolute / µg m(^{-3})</th>
<th>NO2 Relative / %</th>
<th>O3 Absolute / µg m(^{-3})</th>
<th>O3 Relative / %</th>
<th>PM(_{2.5}) Absolute / µg m(^{-3})</th>
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</table>

Cell colour scale represents the level of change in concentration. The darker the shade of blue, the larger the reduction in concentration for that particular pollutant; lighter shades/white represent the middle of the change scale; the darker reds represent the opposite end of the scale, where concentrations have decreased the least or increased.
and constrain the model were obtained from the suburban AURN facility in Eltham, south London. In order to reduce the complexity of the box model, it was constructed around oxidation mechanisms for the 27 NMHCs measured by Gas Chromatography coupled to Flame Ionisation Detection (GC-FID) in Eltham over the study period, these were: ethane, propane, n-butane, isobutane, isopentane, n-pentane, methyl-2-pentane, n-heptane, n-octane, ethene, propene, 1-butene, cis-2-butene, trans-2-butene, 1-pentene, trans-2-pentene, 1,3-butadiene, isoprene, ethyne, benzene, toluene, m- and p-xylene, o-xylene, ethylbenzene, 1,2,4-trimethylbenzene and 1,3,5-trimethylbenzene. Simulations were conducted for periods of 24 h, starting at midnight, and were constrained using appropriate hourly averaged measured data for NOx, O3, NMHCs, CO, temperature and relative humidity and an average background level of 1275 μgm⁻³ methane. In total, the MCM subset employed comprised 2316 different species and over 7000 reactions.

3. Results

3.1. Changes observed by ambient monitoring networks

Fig. 1(a–d) shows the relative changes in the abundance of common ambient air pollutants NO2, PM2.5, PM10 and O3 with respect to the 2020 average (i.e. January–May, inclusive). A companion plot, showing the relative changes in air pollutant abundance relative to the 2015–2019 mean can be found in the Supplementary material (Fig. S3).

Fig. 1(a) shows that reductions in de-weathered NO2 relative to the 2020 mean, occurred at eighteen Sussex-Air and AURN monitoring stations which monitored NO2 during the lockdown period. Significant reductions can be seen at all kerbside sites, although with some variation. As shown in Table 2, NO2 concentrations at kerbside sites were reduced to ~62% of the 2015–2019 average for March to May, inclusive. This represents an average 38% reduction in de-weathered NO2 concentrations.

Fig. 2(a) shows the absolute changes in de-weathered NO2 concentrations at kerbside monitoring stations in μgm⁻³ since 1st January 2020. It shows that de-weathered concentrations at all sites in the network declined following the enforced lockdown period from 24th March 2020. However, there is a pattern of larger reductions adjacent to busier roads, likely reflecting the relative importance of road traffic emissions at these locations. For example, the greatest reductions were seen at RG7, CI1 and HOT (HO5), of which RG7 and CI1 are located adjacent to the A23 and A27, respectively, which are major A-roads in the South East region of the UK.

During the lockdown period, de-weathered NO2 concentrations fluctuated, with intermittent peaks evident in the time series data, however overall, de-weathered concentrations were generally below those of the preceding period (1st January to 23rd March 2020, inclusive) at all locations. In addition, the data in Table 2 show that the mean reduction across the study area was 10.7 μgm⁻³, relative to the 2015–2019 period mean for March to May, inclusive. For comparison, the equivalent mean reduction in NO2 concentrations prior to de-weather analysis (i.e. simply the ambient values) was 11.7 μgm⁻³, which corresponds to a reduction of ~38% relative to the 2015–2019 period mean for March to May, inclusive.

Figs. 1(a) and 2(b) show the de-weathered NO2 concentrations at background sites across the networks (urban, suburban and rural). Mean de-weathered concentrations declined at suburban background...
sites (FAL, RG1, RG5 and RG6) to values ~63% of the 2015–2019 period mean for March to May, inclusive (Table 2). However, notably, de-weathered concentrations of NO\textsubscript{2} at EB1 and EB3 (urban background) and LL1 (rural background) (located on the south coast within ~7 km of each other) increased relative to the 2020 average, and the 2015–2019 baseline average for EB1 and EB3. For LL1, this is consistent with the findings of Marner et al. (2020), who showed that NO\textsubscript{2} concentrations at many rural sites across the UK were higher during the lockdown period. It should be noted that the temporal profile of the

Fig. 2. Absolute changes in air pollutant abundance by monitoring site type in the southeast of the UK during the pandemic lockdown period (starting 24/03/2020); all data ‘de-weathered’ using concomitant meteorology parameters (see Methodology). (a) NO\textsubscript{2} kerbside, (b) NO\textsubscript{2} urban, suburban and rural background, (c) PM\textsubscript{2.5} suburban and rural background, (d) PM\textsubscript{10} kerbside, (e) PM\textsubscript{10} urban and suburban background. (f) O\textsubscript{3} suburban and rural background. See Table 1 for site codes.

increases in de-weathered NO\textsubscript{2} concentrations at EB1, EB3 and LL1 were well correlated, as shown in the time-series in Fig. 2(b). The increase is visible in the trendlines from approximately 28th March to 15th April 2020. The 7-day HYSPLIT back trajectory analysis in Fig. 3 highlights that anticyclonic easterly mass air movements over North West Europe correlate with the increase in de-weathered NO\textsubscript{2} values at EB1, EB3 and LL1 and that air masses originating from the Atlantic and North Sea correlate with periods of background NO\textsubscript{2} values. Accordingly, despite the relatively short boundary layer lifetime of NO\textsubscript{x} (ca.
hours – 1 day; e.g. Wenig et al., 2003; Liu et al., 2016), owing to the proximity of these particular receptor sites on the south coast of the UK to mainland Europe, it is possible that transboundary dispersion and transport of emissions from the heavily polluted regions of the North West of the continent (e.g. Hofman et al., 2016; Cordell et al., 2016; Wyche et al., 2020) had some degree of influence on the de-weathered NO2 concentrations at these sites, despite a reduction in local emissions sources as a result of the UK lockdown.

Three monitoring stations, BH0, CA2 and EF1, monitor PM2.5 concentrations at urban background locations in the AURN and Sussex-Air Network. There was a marginal increase in de-weathered PM2.5 concentrations at these sites after the lockdown started, from 24th March 2020, relative to the 2020 mean, as shown in Fig. 1(b). In addition, de-weathered concentrations were ~106% of the 2015–2019 baseline mean for the same period, as shown in Table 2.

The time series of de-weathered PM2.5 concentrations shown in Fig. 2(c) across all three monitoring stations were in good agreement. This is an important finding owing to the separation distance between the sites, which are located at Brighton Preston Park (BH0), Gatwick East (CA2) and Eastbourne Holly Place (EF1), and is indicative of regional, rather than isolated/local changes. There are three clearly defined peaks in the trendlines, first at the beginning of the lockdown period, secondly around the 8th April 2020, and again at the beginning of May 2020. These peaks correlate with regional pollution episodes detailed above and again, can be explained from inspection of the HYSPLIT 7-day back trajectory analysis of mass air movements shown in Fig. 3. As discussed, during this period, anticyclonic easterly mass air movements caused transboundary transportation of pollutants such as NH3, O3, O3 precursors and particulate matter (likely emanating from building emissions, fires, and industrial processes) from North West Europe to the UK, elevating local pollutant concentrations, as is a common occurrence in the South East region (AQEG, 2012).

Thirteen stations monitor PM10 concentrations in the AURN and Sussex-Air Network (eight at kerbside, three at urban background and two at suburban background locations). As shown in Fig. 1(c), relative to the 2020 average, de-weathered PM10 concentrations increased during the lockdown period, most notably during April. Fig. 2(e) and (f) show similar trends in de-weathered PM10 concentrations to those of PM2.5, whereby there is good agreement in the data at all sites, and there are clearly defined peaks in de-weathered concentrations which correspond with the timing of regional pollution episodes, as shown in the back trajectory analysis in Fig. 3. As such, there is little evidence of an impact from traffic reductions owing to lockdown restrictions on ambient PM10, as de-weathered concentrations were higher than the preceding months in 2020. However, both kerbside and background (urban and suburban) de-weathered concentrations of PM10 were ~86% of the 2015–2019 period mean for March to May inclusive, overall, as shown in Table 2. This equates to an average reduction of 3.1 μg m⁻³.
across the network when compared to the same time period during the preceding 5 years.

Finally, there are nine monitoring stations within the networks employed which monitor ambient concentrations of O₃, one at kerbside, two in urban background, one in suburban background and five in rural background locations. As shown in Fig. 1(d), de-weathered daily O₃ concentrations increased at all of these sites, relative to the 2020 mean. Fig. 2(f) shows the equivalent timeseries plot of absolute de-weathered O₃ concentrations since 1st January 2020, which again illustrates the increase in ambient O₃ concentrations experienced during the lockdown period. In addition, the data in Table 2 show that de-weathered mean daily O₃ concentrations were on average ~105% of the 2015–2019 period mean for March to May, inclusive; this increase relative to the 2015–2019 mean for the same period equates to 2.9 μg m⁻³. The largest increases in de-weathered O₃ concentrations were observed in urban locations, where mean values increased in the range 5–15%. Of the five rural background locations investigated, two sites (LL1, ARZ) showed a small decrease in de-weathered O₃ concentrations relative to the 2015–2019 mean. This decrease was only observed for ARZ in the ambient O₃ data before de-trend analysis, while LL1 exhibited a small increase in O₃ concentrations relative to the same period of the 5-year baseline, by ~4%. Looking further at the ambient O₃ data prior to de-trend analysis, it is noteworthy that the mean increase across the sites relative to the 2015–2019 baseline is somewhat larger than the de-weathered equivalent, being 4.9 μg m⁻³, i.e. an average increase across the region of ~8% (which breaks down to an average increase of 11% across urban locations and 5% across rural backgrounds).

Direct comparisons can be made between Fig. 2(b) and (f) where both NO₂ and O₃ concentrations are monitored at background sites LL1, BH0, RC3 and E1B. There is a negative correlation between NO₂ and O₃ at all of these locations. At BH0 and RC3, the coefficient of determination (R²) is 0.56 and 0.60, respectively, which suggests that NO₂ reductions had a moderate effect on O₃ increases at these sites. The R² value at LL1 and E1B showed a very weak effect however, which could be due to increases in NOₓ/NO₂ at these locations during the lockdown period.

The changes observed in O₃ concentrations likely result from perturbations to boundary layer NOₓ-NHMC-O₃ chemistry (see Section 4), and to some extent to transport of O₃ and O₃ precursor species from mainland Europe. While it remains difficult, without complex chemical transport modelling, to separate the respective contributions of local factors and regional transport to local ambient O₃ levels (Monsk et al., 2015), it is possible to infer the potential influence of regional O₃ and O₃ precursor species at the monitoring sites, by comparing the daily average concentrations of O₃ and PM₂.₅ (using the latter as a marker for transported pollution) with results from back trajectory modelling. In order to make this comparison, data were taken from the Brighton and Hove site (BH0; which monitors both PM₂.₅ and O₃), and the Lullingthorpe Heath (LL1; which monitors O₃) and Eastbourne (EF1; which monitors PM₂.₅) sites, located within close proximity of one another (~7 km). To assist with analysis of the NOₓ-NHMC-O₃ chemistry during the lockdown period, this comparison was also made for the suburban AURN site in Eltham (see Section 4).

Fig. S4 in the Supplementary material shows the daily average O₃ and PM₂.₅ data for BH0, LL1/EF1 and Eltham, alongside further results from HYSPLIT back trajectory modelling for key periods. As shown in Fig. S4 (and as discussed above), during periods of high PM₂.₅ concentrations at receptor sites, air masses originated from/passaged over the air pollution ‘hotspot’ of North West Europe. As can also be seen in Fig. S4, there is some degree of correlation between O₃ and PM₂.₅ concentrations at these sites during certain time frames (e.g. 22/04/2020–25/04/2020), and occasionally with a time lag (e.g. 25/03/2020–30/03/2020). However, the overall correlation between daily PM₂.₅ and O₃ concentrations at the three sites over the period of 10/03/2020–05/05/2020 was relatively weak (i.e. R² for BH0 = 0.01, LL1/EF1 = 0.11 and Eltham = 0.04). Collectively, this suggests that there was likely to have been some contribution to local O₃ concentrations in the South East from transportation of O₃ and O₃ precursors from mainland Europe, however, the time lags in the trendline, plus the presence of non-correlated peaks in O₃ (with respect to PM₂.₅) suggest that increases in O₃ concentrations cannot solely be explained by interregional transport; see Section 4 for further details.

3.2. Changes observed by satellite remote sensing

Fig. 4 shows regional daily average NO₂ concentrations as recorded by TROPOMI over (a) the period 25/03/2019–22/04/2019 (i.e. the pre-pandemic baseline) and (b) 23/03/2020–20/04/2020 (i.e. post-implementation of lockdown restrictions). The percentage change between the two periods is also shown (c), as are the locally integrated values over the city of Brighton and Hove, plot alongside long-path DOAS measurements made on the ground (over a total path length 300 m) for the same time period (d).

The data shown in Fig. 4 confirms findings presented in Section 3.1 from analysis of the in-situ monitor observations made by the Sussex Air Network and AURN, extending the reach of the data capture to the entire South East of the UK on a 7 × 7 km resolution scale. In-line with the in-situ monitors, TROPOMI measured a decrease in the concentrations of NO₂ across the entire region during the lockdown, with the regional average value falling by ~33%, from 4.9 × 10¹⁶ to 3.3 × 10¹⁶ molecule m⁻². Fig. 4(c) shows that the largest changes in NO₂ were observed in the centre of the region, in the areas surrounding London and at certain coastal locations.

As seen in Fig. 4(d), when integrated across the city scale (Brighton and Hove in this instance), TROPOMI is relatively successful in capturing local daily variations when compared to remote sensing conducted on the ground, in this case by long-path DOAS. Here, TROPOMI measured NO₂ values across the city during the 2020 lockdown period to be 59% of those measured over roughly the same time period the previous year (with mean values falling from 4.4 × 10¹⁶ to 2.9 × 10¹⁶ molecule m⁻²), comparing favourably with DOAS, which recorded NO₂ values that were ~64% of those measured during the previous two years over roughly the same time period (see Section 3.3).

3.3. Changes observed in high time resolution

Average diurnal profiles of pollutants measured by DOAS for March and April before (2018–2019) and after (2020) initiation of lockdown restrictions are shown in Fig. 5. As observed by the wider monitoring networks, ambient NO₂ throughout the average day was measured to decrease significantly during the lockdown period, by ~7 μg m⁻³, to values ~62% of those seen over the same time period during previous years. Although the average daily NO₂ value during the lockdown period was measured to be significantly lower, the typical bi-modal diurnal profile was maintained, with early morning (~05:00–09:00) and late afternoon/evening (~16:00–23:00) peaks in concentration. As is clear in Fig. 5, the morning peak, usually associated with commuter and transport activity (e.g. Mellkonyan and Kuttler, 2012; Roberts-Semple et al., 2012; Hofman et al., 2016), did not reduce in magnitude after restrictions were imposed, although its duration did decrease by ~1 h; this is most likely indicative of the UK transport and delivery fleet maintaining operations on major UK road networks, such as the nearby A27, and citizens staying at home rather than commuting to their places of work. The high-time resolution NO₂ data shows therefore, that besides during the morning period (~05:00–07:00), anthropogenic activity responsible for NO₂ emissions (primarily transport related in the UK: AQEG, 2004; DEFRA, 2020b), did decrease significantly throughout the day, by as much as ~13 μg m⁻³ later in the evening (~19:00), suggesting that citizens were conforming to mobility and distancing restrictions during hours typically associated with social activities. The peak in concentration during the morning period noted above,
was likely influenced by Freight and Heavy Goods Vehicle movements, which continued during lockdown. Similar to ambient NO₂ concentrations, HONO were observed to decrease; with daily averages going down by almost 1 μg m⁻³ during lockdown to values ~74% of those seen over the same time period during previous years. With NOₓ being a source of HONO (reactions (3.1)–(3.3); e.g. Harris et al., 1982; Alicke et al., 2002; Finlayson-Pitts et al., 2003), decreases in HONO are to be expected, in-line with falling (primary) vehicle emissions and ambient NO₂ values (Calvert et al., 1994; Harrison et al., 1996; Kirchstetter et al., 1996).

\[
\begin{align*}
\text{OH} + \text{NO} + \text{M} & \rightarrow \text{HONO} + \text{M} & (3.1) \\
2\text{NO}_2 + \text{H}_2\text{O} & \rightarrow \text{HONO} + \text{HNO}_3 & (3.2) \\
\text{NO} + \text{NO}_2 + \text{H}_2\text{O} & \rightarrow 2\text{HONO} & (3.3)
\end{align*}
\]

Comparable to other monitoring sites in the AURN and Sussex-Air Network, ambient daily O₃ concentrations measured by DOAS in the suburbs of Brighton and Hove were higher during the lockdown period, by an average of ~11 μg m⁻³, reaching values ~115% of those seen over the same time period during previous years, presenting with roughly the same diurnal profile (Fig. 5; i.e. with higher levels persisting slightly longer into the evening). As is well known, NOₓ, O₃ and hydrocarbons exist in a complex photochemically induced balance within the troposphere (Monks, 2005), where depending on relative concentrations, a decrease in NOₓ and an increase in solar radiation (as was observed during the lockdown period relative to previous years, see Fig. 5) can lead to an increase in the ambient O₃ concentration. O₃ production during the pandemic period is discussed in more detail in Section 4.

Average daily levels of formaldehyde (both a primary and secondary pollutant in sub/urban air; e.g. Parrish et al., 2012; Franco et al., 2016; Fu et al., 2019) did not differ significantly during the lockdown period compared to previous years, i.e. the average daily formaldehyde concentration after lockdown increased by only ~0.2 μg m⁻³, to values 102% of those observed across the same time period during previous years. Interestingly, however, the formaldehyde diurnal profile did differ somewhat after the lockdown date. As can be seen in Fig. 5, hourly HCHO averages were higher between ca. 07:00 and 12:00 (by as much 20%) and lower between solar noon, ca. 13:00, and 18:00, presumably as photolysis (reactions (3.2) and (3.3)) and photochemical (reaction (3.4)) losses (Calvert et al., 1972; Fried et al., 1997; Pope et al., 2005; Parrish et al., 2012) were greater during the 2020 pandemic period when levels of solar radiation were significantly higher (by ~27% compared to the same period during 2019; Fig. 5).

\[
\begin{align*}
\text{HCHO} + \text{hv} & \rightarrow \text{H} + \text{HCO} & (3.4) \\
\text{HCHO} + \text{hv} & \rightarrow \text{H}_2 + \text{CO} & (3.5) \\
\text{OH} + \text{HCHO} & \rightarrow \text{CHO} + \text{H}_2\text{O} & (3.6)
\end{align*}
\]

Primary pollutants SO₂ and C₆H₆ were observed to increase in concentration during the average day after lockdown restrictions were imposed, with SO₂ increasing by 0.5 μg m⁻³ to values 125% those observed during previous years, and C₆H₆ increasing by ~1 μg m⁻³, to values ~147% of previous years. As is evident in Fig. 5, SO₂ and C₆H₆ diurnal profiles were largely similar before and after lockdown, with the exception of SO₂ between 19:00 and 23:00 h, where the evening peak was enhanced with restrictions in place, presumably owing to local activity. As noted in Section 2.2, C₆H₆ data reported here should be treated with caution and used as an indicative guide only, as measurements were typically on or below the DOAS sensitivity limit for this species during the measurement periods before and after lockdown. Absolute C₆H₆...
values at the Falmer site in Brighton and Hove are likely to be significantly lower than those reported here.

4. Discussion

4.1. Boundary layer composition

It is now clear that changes in tropospheric trace composition occurred as a direct result of dramatically decreased anthropogenic activity during the anthropause of 2020, triggered by lockdowns imposed by governments in response to the COVID-19 global pandemic (e.g. Siciliano et al., 2020; Kerimray et al., 2020; AQEG, 2020a). As discussed in Section 3, data from across the AURN and Sussex-Air monitoring networks show that there was a clear overall decline in average ambient NO₂ across a range of environment types (urban – rural, kerbside – background) in the South East of the UK during the lockdown period, relative to the 2020 mean and the preceding 5-year baseline. It is now clear that these changes were principally owing to fewer vehicle movements during the UK during the lockdown period, by up to 70% by mid-April (AQEG, 2020a).

The impact of the lockdown on ambient PM concentrations is less clear. Overall, the data show a decrease in de-weathered PM₁₀ concentrations across the environment range (by ~14%), and an increase in PM₂.₅ (by ~6%), relative to the preceding 5-year mean. As was noted in Section 3.1, there were clearly defined peaks in de-weathered PM₁₀ and PM₂.₅ concentrations across the South East of the UK during the lockdown period, which corresponded with regional pollution episodes, where interregional transport brought the continental plume across to the UK. As a result, there is limited evidence of a decline in particulate matter concentrations during the UK lockdown which can be attributed directly to reductions in local traffic volumes in the South East. Accordingly, more research is needed to understand the impact of lockdown measures on PM chemical composition and the abundance of PM precursors (AQEG, 2020a) in order to investigate any potential shifts in PM abundance and size distribution, such as increases in concentrations of UFPs. Such an investigation would require complex coupled emissions, physio-chemical and transport modelling, and is beyond the scope of this work.

The data also show that with the decrease in NO₂, there was a concomitant increase in average ambient daily O₃ concentrations at kerbside, urban background, suburban background and rural background sites, relative to both the 2020 mean and the preceding 2015–2015 baseline, with the biggest increases observed under urban conditions. This trend is consistent with the findings of other authors and is not limited to the UK (e.g. Siciliano et al., 2020; Kerimray et al., 2020; AQEG, 2020a).

As shown in Fig. 2(f), absolute de-weathered concentrations of O₃ at urban sites were largely comparable to several rural locations during

Fig. 5. Average diurnal evolution of trace gases measured by DOAS (μg m⁻³), temperature (°C) and solar radiation (Wm⁻²) during the pandemic lockdown period (starting 24/03/2020; blue line), compared to their average diurnal pattern for the same time period during the preceding 2-years (i.e. March and April 2018–2019, inclusive; red line). The difference between the two datasets (i.e. the 2020 lockdown period and the March and April 2018–2019 baseline) is also shown (green line), along with the O₃/solar radiation ratio (bottom right), coloured by NO₂ concentration (μg m⁻³). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)
the lockdown period. Indeed, this urban rise toward concentrations typical of rural sites is expected owing to the reduction in titration of $O_3$ by nitric oxide (NO) as NOx emissions reduced (e.g. Monks, 2005).

Owing to a larger production footprint and interregional transport at certain times during lockdown, there was likely some contribution to local $O_3$ levels in the South East of the UK from the transport of $O_3$ and $O_3$ precursors from polluted regions of North West Europe (Monks et al., 2015; AQEG, 2009). However, as shown in Fig. S4, the time lag between the $O_3$ and PM$_{2.5}$ trends and the presence of isolated peaks in $O_3$, suggest there were significant contributions to local $O_3$ concentrations derived from changes in UK emissions. Importantly, these findings are not limited to the UK, with other studies from a range of countries also showing that tropospheric $O_3$ concentrations increased owing to changes in emissions profiles during lockdown, including in Spain (Tobías et al., 2020), Brazil (Siciliano et al., 2020), Italy, (Sicard et al., 2020), China (Chen et al., 2020; Le et al., 2020; Zhang et al., 2020), Korea (Ju et al., 2020) and India (Sharma et al., 2020).

If the $\Sigma(NO_2 + O_3)$, i.e. ‘$O_3$', is observed over the 2020 period, it becomes clear that the overall abundance of total $O_3$ species did not change significantly as a result of the UK lockdown, as can be seen for example in Fig. 6, which shows daily mean NO$_2$ and $O_3$ concentrations measured by DOAS during 2020 in Brighton and Hove. The anti-correlation observed between NO$_2$ and $O_3$, as NOx emissions reduced during the COVID-19 anthropopause, can also be seen in higher time resolution during the typical diurnal cycle, as shown in Fig. 5. The preservation of total $O_3$ species witnessed here is the result of well known tropospheric NOx-$O_3$ photochemistry in polluted air (Monks, 2005), principally:

$$\text{NO}_2 + h\nu (\lambda < 420 \text{ nm}) \rightarrow \text{NO} + \text{O}_3$$

$$\text{O}_3(\text{P}) + \text{O}_2 + \text{M} \rightarrow \text{O}_4 + \text{M}$$

where M is a reaction third body. Fig. 5 clearly shows that over the average diurnal cycle in the spring of 2020, more solar radiation (hence actinic flux) was available at ground level to initiate tropospheric photochemistry (e.g. Madronich, 1993; Kleinman, 1994; Monks, 2005). As seen from the $O_3$:Solar Radiation ($O_3$:SR) ratio (Fig. 5, bottom right), the increase in both solar radiation and $O_3$ were well correlated, with $O_3$:SR ratios being roughly the same throughout daylight hours (i.e. ca. 07:00-17:00) during the lockdown period as during the baseline year (i.e. 2019 in this instance for local meteorology data in Brighton and Hove). The major differences noted in $O_3$:SR ratios between 2020 and 2019 occurred during the early morning and late afternoon, i.e. periods marked by higher ambient NOx concentrations. Further to this, it is clear from Fig. 5 that during the UK lockdown period, where NOx emissions were reduced, $O_3$ persisted longer, at higher relative concentrations, during nocturnal hours, owing to lower ambient concentrations of NO, and a decrease in $O_3$ scavenging via:

$$\text{NO} + \text{O}_3 \rightarrow \text{NO}_2 + \text{O}_2$$

However, NOx-$O_3$ photochemistry is highly non-linear and also involves the oxidation of hydrocarbons and the production and cycling of hydro ($H_2O$) and organic ($RO_2$) peroxy radical species (e.g. Haagen-Smit and Fox, 1954; Sillman, 1999; Salisbury et al., 2002; Monks, 2005). Thus, to fully understand the changes observed in tropospheric composition (and reactivity) during the UK lockdown period, hydrocarbon and radical species must also be considered.

It should be noted that at certain stations, where NOx spikes were noted, e.g. at Eastbourne/Lullington Heath (see Figs. 1 and 2), total $O_3$ levels increased transiently during the aforementioned transboundary pollution episodes (e.g. 09/04/20 and 24/04/20) owing to transported pollution from mainland Europe (see Figs. 3 and S4). This is most likely a result of short-lived, continental NOx persisting long enough to influence local $O_3$ concentrations in the UK during transport and before titration from the boundary layer (i.e. typical NOx lifetime in interregional plumes is <1 day).

As discussed in Section 2.4, there were no comprehensive NMHC monitoring sites available in the Sussex-Air Network or AURN in the South East of the UK from which to acquire hydrocarbon data for this study. As such, data were acquired from the nearest available facility, i.e. the suburban AURN site in Eltham, south London. Changes in the NOx and $O_3$ data obtained from Eltham were largely consistent with those observed across the South East UK AURN and Sussex-Air Network, and thus the site offers a valid reference point for this study. More specifically, at Eltham, average ambient 2020 NOx values were down by -6 $\mu$g m$^{-3}$, to values -65% of those seen over the same time period over the baseline years of 2015–2019 (c.f. non-de-weathered data from the suburban FAL site in Brighton and Hove: -7 $\mu$g m$^{-3}$ and 64%), total NOx values were down by -8 $\mu$g m$^{-3}$, to values -66% of the baseline, and 2020 $O_3$ values were up by -11 $\mu$g m$^{-3}$, to values -122% of those seen previously over baseline years (c.f. non-de-weathered data from the suburban FAL site: -8.4 $\mu$g m$^{-3}$ and 112%).

From the Eltham GC-FID measurements, it was determined that over the spring of 2020, during the UK lockdown period, total ambient NMHC concentrations were -3 $\mu$g m$^{-3}$ lower than the average of the same period between 2015 and 2019, i.e. 2020 total NMHC concentrations had reduced to values -83% of those typically expected over the spring months. Of the hydrocarbon fractions, aromatics were found to have proportionally decreased the most, i.e. to levels -66% of previous years (an absolute change of ~0.7 $\mu$g m$^{-3}$), followed by alkanes (~84%, ~2 $\mu$g m$^{-3}$) and then alkenes (~94%, ~0.1 $\mu$g m$^{-3}$). This finding is somewhat expected, with road transport comprising a major source of aromatic hydrocarbons (e.g. Brocco et al., 1997; Kerbach et al., 2006;
Correa and Arbilla, 2006) and road transport activities having reduced significantly during the UK lockdown (total motor vehicle use dropping to a low of 23% of typical values on 13/04/2020; DfT, 2020).

The NOx-NMHC-O3 relationship is best visualised using a surface plot, where NOx and NMHC are plotted with their corresponding O3 contours, or ‘isopleths’ (Sillman, 1999); such a plot for the atmosphere of Eltham is shown in Fig. 7(a), constructed using monthly averaged measurements between 1st January 2015 and 1st June 2020.

Fig. 7(a) shows a regime where the boundary layer air over Eltham is generally characterised by a total NOx load that is greater than the total (measured) NMHC load, and where higher O3 concentrations typically result from lower absolute values of both species. Fig. 7(b) shows the same data presented as a scatter plot of O3 vs. NMHC: NOx ratio, which presents a roughly increasing O3 concentration profile with NMHC: NOx ratio, as is typically seen under urban conditions (e.g. Finlayson-Pitts and Pitts, 1993; Wolff and Korsog, 1992; Monks, 2005; Tobias et al., 2020). Both plots also show the relative positions of atmospheres in the NOx-NMHC-O3 space before (labelled: ‘Baseline Years’) and during the lockdown period (labelled: ‘Pandemic Year’), using data averaged appropriately over March, April and May for 2015–2019 and 2020, respectively.

The Eltham springtime boundary layer (for the baseline years and the pandemic year) sits within a NMHC (sensitive) limited regime (Sillman, 1999), as is common with many urban atmospheres (e.g. Finlayson-Pitts and Pitts, 1993; Monks, 2005), where an increase in ambient NMHCs (at constant NOx concentration) would cause an increase in O3 concentration, and where an increase in ambient NOx (at constant NMHC concentration) would cause a decrease in O3 concentrations, and vice versa. As shown in Fig. 7(a) and (b), a greater decrease in concentrations of ambient NOx species occurred during the UK lockdown period, relative to the 2015–2019 baseline, than total ambient NMHCs, i.e. the former seasonal (i.e. March, April, May) average decreasing by 33% and the latter only by 17%, such that the NMHC: NOx ratio increased from 0.70 to 0.87. In a NMHC limited regime under sufficient actinic flux, this led to an increase in ambient O3 concentrations during lockdown, which is clearly shown in Fig. 7(a) and (b), with the atmosphere transitioning to a higher O3 concentration isopleth and higher O3 concentration point, respectively. This change in atmospheric composition is most likely rooted in the non-linear reductions that occurred during lockdown, in emissions of pollutant trace gases across a ranges of sources, with road traffic (the principle source of UK NOx emissions; NAEI, 2019a, 2019b) reducing significantly after restrictions were imposed, as many citizens remained in their homes, while other ‘key’ industries (which are known to emit NMHCs) continued to operate (AQEG, 2020b). To illustrate, National Atmospheric Emissions Inventory data (NAEI, 2019b) shows that the largest sources of NMVOC (NMHC) emissions in the UK are industrial processes and product use (53% of the UK total), extraction of fossil fuels (19%) and agriculture (13%).

As noted in Section 3.1, mean de-weathered O3 concentrations were found to have increased a greater amount across the various urban environments than in rural backgrounds (i.e. 10% vs. 1%), and that mean de-weathered O3 values had decreased slightly relative to the 5-year baseline at rural background sites LL1 and AR2 (Table 2). With no NMHC data available at the AURN and Sussex-Air sites in the South East of the UK, it is not possible to conclusively comment on potential underlying chemistry at these locations, however as noted above, it is common for urban locations to reside within the NMHC limited regime and for rural background environments to reside within the NOx limited regime. Despite observed potential influences from interregional transport, the mean de-weathered NO2 concentrations across the three urban location types was ~33% lower during the lockdown period than over the 2015–2019 baseline, and across rural background sites, was ~22% lower. Such a decrease in ambient NO2 within the NHMC limited O3 production regime of urban locations will have resulted in an increase in net O3 production, whereas reducing NOx under rural, NOx sensitive conditions, is likely to have resulted in a decrease in net O3 production (presuming in both cases a roughly constant NMHC loading) (Finlayson-Pitts and Pitts, 1993; Sillman, 1999; Monks, 2005).

4.2. Boundary layer reactivity

As is well known, the OH radical and the O3 molecule are the primary oxidants of the sunlit troposphere, and their abundance will control tropospheric ‘oxidative capacity’, i.e. “the diurnal mean ability of the [troposphere] to oxidise trace compounds” (Monks, 2005). In essence, the abundance of OH and O3 will control how ‘reactive’ the troposphere is.

O3 photolysis in the presence of water vapour is the primary daytime source of the tropospheric OH radical (Levy, 1971):

![Image](98x85 to 497x299)

Fig. 7. Ozone isopleth plot for the AURN suburban Eltham site in outer London (a) and corresponding ozone versus hydrocarbon:NOx ratio relationship (b) using monthly averaged data between 01.01.2015 and 01.06.2020. The respective atmospheric positions for averages taken over March, April and May over the ‘baseline years’ (2015–2019) and for the corresponding average taken during the ‘pandemic year’ (2020) are shown.
\[
\text{O}_3 + h\nu (\lambda < 335 \text{ nm}) \rightarrow \text{O}_2 + \text{O}^\text{(I D)} \quad (4.4)
\]
\[
\text{O}^\text{(I D)} + \text{H}_2\text{O} \rightarrow 2\text{OH} \quad (4.5)
\]

It follows then, that a suitably humid, daylit troposphere with increased \(\text{O}_3\) loading would generate more \(\text{OH}\) and (depending on loss routes) have a higher overall oxidative capacity, or `reactivity' (Lelieveld and Dentener, 2000; Monks, 2005; Yang et al., 2016), and be characterised by a greater production rate of secondary trace species (e.g. Atkinson, 2000; Calvert et al., 2002; Calvert et al., 2008).

In order to investigate the change in radical species, and hence atmospheric oxidative capacity/reactivity experienced during the lockdown period, a 0-D box model was constructed using inorganic and organic oxidation mechanisms extracted from the Master Chemical Mechanism website (http://mcm.leeds.ac.uk/MCM/). In order to create an approximation of local boundary layer air for the average springtime diurnal cycle before and after lockdown, models were run constrained with average measured \(\text{NO}_x\), \(\text{O}_3\), NMHC, CO, \(\text{CH}_4\), temperature and relative humidity data (see Section 2.4 for details); the results are given in Fig. 8.

Fig. 8 shows the diurnal profile data for \(\text{NO}_x\), \(\text{O}_3\), and the sum of NMHCs before and during lockdown, as employed to constrain the 0-D box model. Fig. 8 also shows simulated end-stage organic reaction products, formaldehyde (\(\text{HCHO}\)) and methyl glyoxal (\(\text{Me Gly}\)), which derive from the atmospheric oxidation of a range of organic primary pollutants (e.g. Atkinson, 2000; Calvert et al., 2002; Calvert et al., 2008 and references therein). Despite the 2020 model being constrained to a daily average NMHC loading 17\% lower than the 2015–2019 baseline simulation, the daily average modelled secondary formaldehyde and methyl glyoxal values were 87\% and 117\% higher, respectively, in lockdown air compared to their respective baselines, indicating a more reactive atmospheric environment in 2020. The modelled concentrations of such secondary species represent an estimate in this instance; as shown in the measured data obtained from the DOAS system in Brighton and Hove (Fig. 5), HCHO values where higher before midday and lower around, and after, solar noon during lockdown. This is likely due to a combined result of a different NMHC loading in the local atmosphere of Brighton, and the higher levels of solar radiation experienced in the UK during the 2020 lockdown period, hence increased branching toward photolytic destruction of such photolabile species as \(\text{HCHO}\) (e.g. Calvert et al., 1972; Fried et al., 1997; Pope et al., 2005), which is not directly accounted for in the MCM model employed here.

The results obtained from the 0-D box model also indicate that after the 2020 lockdown was imposed, \(\text{OH}\), \(\text{HO}_2\), and \(\text{RO}_2\) radical levels were significantly higher than average modelled values calculated over the same period time during baseline years, by 109, 245 and 259\%, respectively. As well as an increased radical loading, the MCM model also suggests that there was a shift in partitioning between atmospheric \(\text{HO}_x/\text{RO}_x\) species after government restrictions were imposed, where both \(\text{OH}:\text{HO}_2\) and \(\text{OH}:\text{RO}_2\) 2020 ratios were lower than the 2015–2019 baseline. This is indicative of an increase in forward cycling of \(\text{OH}\) to \(\text{HO}_2\) and \(\text{RO}_2\) via reaction with CO and organic species (\(\text{RH}\)), and a concomitant decrease in recycling of \(\text{HO}_2\) and \(\text{RO}_2\) back to \(\text{OH}\) via reaction with (reduced) \(\text{NO}\) (Monks, 2005), via:

\[
\text{OH} + \text{CO} \rightarrow \text{H} + \text{CO}_2 \quad (4.6)
\]
\[
\text{H} + \text{O}_2 + \text{M} \rightarrow \text{HO}_2 + \text{M} \quad (4.7)
\]
\[
\text{OH} \rightarrow \text{RH} + \text{H}_2\text{O} \quad (4.8)
\]
\[
\text{R} + \text{O}_2 + \text{M} \rightarrow \text{RO}_2 + \text{M} \quad (4.9)
\]
\[
\text{HO}_2 + \text{O}_2 \rightarrow \text{OH} + \text{O}_2 \quad (4.10)
\]

Fig. 8 also gives the daily modelled temporal profiles of reservoir species, hydrogen peroxide (\(\text{H}_2\text{O}_2\)) and nitrous acid (\(\text{HNO}_3\)), before and after lockdown. Owing to their propensity to partition out of the gas phase, both \(\text{H}_2\text{O}_2\) and \(\text{HNO}_3\) are able to terminate the chain cycling of tropospheric radical species (Lee et al., 2000):

\[
\text{HO}_2 + \text{HO}_2 \rightarrow \text{H}_2\text{O}_2 + \text{O}_2 \quad (4.11)
\]
\[
\text{OH} + \text{NO}_2 + \text{M} \rightarrow \text{HNO}_3 + \text{M} \quad (4.10)
\]

As expected in a NMHC sensitive regime, formation of \(\text{HNO}_3\) comprises the dominant chain termination route and radical sink (Monks, 2005), with modelled \(\text{H}_2\text{O}_2:\text{HNO}_3\) ratios of \(-0.01\) in both cases.

It is clear from Fig. 8 that the modelled concentrations of both \(\text{H}_2\text{O}_2\) and \(\text{HNO}_3\) were slightly larger in 2020, with their daily averages being \(-112\%\) of their 2015–2019 baseline values. By comparing the modelled radical recycling to chain termination routes and the modelled \(\text{HO}_2:\text{NO}_2\) ratios, the simulation suggests that during the lockdown period, branching shifted toward more radical chain cycling/propagation and away from termination via loss routes, with the daily average modelled \(\text{HO}_2:\text{H}_2\text{O}_2\), \(\text{RO}_2:\text{HNO}_3\) and \(\text{OH}:\text{HNO}_3\) ratios being larger within the 2020 simulation than that of the 2015–2019 baseline, and the \(\text{OH}:\text{NO}_2\), \(\text{HO}_2:\text{NO}_2\), and \(\text{H}_2\text{O}_2:\text{NO}_2\) ratios all increasing by roughly a factor of five in the 2020 simulation. Collectively these results suggest that the dominance of radical cycling over termination routes increased after government restrictions were imposed.

In addition, with reduced ambient HONO concentrations (see Section 3.3), and HONO being widely recognised as an important radical source in the early part of the day in the sub/urban atmosphere (e.g. Harris et al., 1982; Calvert et al., 1994; Harrison et al., 1996; Finlayson-Pitts et al., 2003), it is likely that the daily temporal profile of atmospheric reactivity would also have changed during lockdown, as would the overall contribution of typical \(\text{OH}\) sources to the \(\text{OH}\) budget. The combined measured and modelled data presented here point toward a relative decrease in \(\text{OH}\) production (and hence tropospheric reactivity) during early hours of the day, and a relative increase in \(\text{OH}\) production (and hence tropospheric reactivity) around and after solar noon. Such a perturbation to the reactivity profile of the boundary layer would clearly have a knock-on effect on a range of atmospheric phenomena in both the gas- and particle-phases.

Here, the MCM model simulations comprise only an aid to interpret measured data and a guide to relative changes in atmospheric composition (and hence oxidative capacity/reactivity), which resulted from the rapid changes in air pollutant emissions during the spring of 2020 after lockdown restrictions came into force. Simplifications made in the construction of MCM oxidation schemes have been discussed in detail elsewhere ( Jenkin et al., 1997; Saunders et al., 2003), but in brief, include (i) exclusion of routes to “low-probability reaction channels”; (ii) abridged oxidation schemes for “minor” species and those not well characterised; and (iii) peroxy radical parameterisation to reduce complexity.

4.3 Future implications

The COVID-19 pandemic has provided a unique opportunity to test the atmospheric response to rapid, widespread anthropogenic emissions reductions. It has enabled the ‘real-world’ simulation of the potential impact of policy interventions to reduce certain pollutant emissions in the long-term and move society toward a low carbon future (Monks, 2020).

It is clear that significant \(\text{NO}_x\) reductions have resulted from governments around the world imposing lockdown restrictions on everyday life (e.g. Sicard et al., 2020). However, as presented here, owing to the complex, non-linear nature of tropospheric chemistry, mass reductions in individual pollutants can cause an increase in others, and can trigger changes in wider tropospheric trace composition and reactivity. In this study, the data show that total \(\text{O}_3\) species were preserved during the UK lockdown, with an increase in tropospheric \(\text{O}_3\) concentrations...
under the NMHC limited O3 production regime (where total NOx decreased proportionally greater than total NMHCs), and an increase in overall boundary layer reactivity.

The adverse health effects of acute and chronic exposure to both O3 and NO2 are well documented, with links to significantly exacerbated cardiovascular morbidity, diabetes, airway oxidative stress and asthma (e.g. Zhang et al., 2019; Travaglio et al., 2020). While there is limited recent comparative evidence which explores the health effects of the two pollutants in isolation, owing to their synergy in atmospheric composition, there is evidence that O3 exposure can cause greater lung damage than NO2 at the same concentration, and that NO2 concentrations up to 20 times higher than O3 could lead to comparable health effects; such findings suggest that O3 is a more harmful pollutant to human health (e.g. Crapo et al., 1984; Mustafa et al., 1984). As such, we urge caution in the statement that there were comprehensive improvements in air quality as a result of the UK lockdown during the COVID-19 pandemic, owing to potential health effects from exposure to increased concentrations of O3, particularly in urban environments. Indeed, AQEG (2009) have previously predicted that long-term reductions of NHMC and NOx emissions, by 60% or more, would be necessary to reduce O3 by NO. As noted by Zhang et al. (2019), substantial reductions in fossil fuel consumption are needed to reduce NOx and NHMCs (VOCs), as well as greenhouse gas emissions, in order to reduce the impact of O3 on human health.

Fig. 8. Average diurnal evolution of trace gases (NO, NO2, O3 and the 15 most abundant NHMC’s; molecules cm$^{-3}$), temperature (K) and relative humidity (%), with modelled formaldehyde (HCHO; molecules cm$^{-3}$) and methyl glyoxal (MeGly; molecules cm$^{-3}$) and radical species (OH, HO2 and RO2; molecules cm$^{-3}$) during the pandemic lockdown period (starting 24/03/2020; blue line), compared to their average diurnal pattern for the same time period during the preceding 5-years (i.e. March and April 2018–2019, inclusive; red line). Measurement site: Eltham, south London. Note: in the NOx panel, NO2 is given by solid lines and NO by dashed lines; also, in the HCHO/MeGly panel, HCHO is given by solid lines and MeGly by dashed lines. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

There is also an emerging body of evidence which seeks to link long-term exposure to poor air quality with susceptibility to, and severity of, COVID-19 symptoms. Alipio (2020) found that the number of cases of the virus was positively related to higher O3 concentrations based on analyses from 34 different countries, while Travaglio et al. (2020) found that O3 concentrations were significantly associated with COVID-19-related deaths, together with population density.

Studies have also started to look at linkages between COVID-19 and exposure to particulate matter (e.g. Cole et al., 2020; Wu et al., 2020), where Cole et al. investigated this linkage in the Netherlands, while Wu et al. investigated the linkage in the United States. In both studies, an increase in PM$_{2.5}$ concentrations by just 1 μg m$^{-3}$ was positively associated with an increase in COVID-19 cases. There is also emerging evidence of a role for particular matter in the airborne transmission of COVID-19, in particular PM$_{10}$, with some early results indicating that the virus could be present on PM in ambient air (e.g. Setti et al., 2020; Tung et al., 2020; Comunian et al., 2020; Manoj et al., 2020). With further research needed to support these early studies, the issue of PM air pollution is likely to be central to future discourse surrounding respiratory diseases.

While recent action at the policy level has been focused on reducing the adverse health effects of human exposure to NO2 (DEFRA, 2017) and particulate matter, impacts of the lockdown (as presented herein) highlight that targeted emissions reductions must be applied across the species range. As shown from evidence in the United States and in China (Zhang et al., 2019), non-compliance with health-based O3 standards
has been attributed to regulatory regimes seeking only to reduce anthropogenic emissions of NOx and PM, while NMHC/VOC emissions remained constant (Finlayson-Pitts and Pitts, 1993; Pun et al., 2003). Furthermore, Le et al. (2020) argue that regulatory protocols aimed at reducing NOx from road traffic serve only to limit progress in reducing concentrations of PM and O3, where simultaneous regulatory controls to reduce emissions from power plants and industrial processes are not also implemented. Accordingly, it is vital that future policies to control and reduce emissions and ambient concentrations of air pollutants fully consider the complex trace composition and reactivity of the atmosphere, and that such findings as discussed herein should guide the implementation of strategies based on intelligent reduction mechanisms which consider a range of pollutant species and environmental conditions.

In order to ensure both health and air quality policy is effectively informed, there is now a pressing need for further studies (including simulation chamber experiments and model development and implementation) across a range of scenarios (e.g. NHMC/NOx regimes and emission spectra) and long-term, detailed atmospheric measurements of baseline and event conditions.

5. Conclusion

The COVID-19 pandemic led governments around the globe to place restrictions on anthropogenic activity to halt the spread of the disease. Such restrictions caused a rapid decline in primary emissions, and in turn, a decline in ambient concentrations of certain air pollutants, most notably reductions in NOx from road traffic sources. Such reductions over a relatively short time interval is entirely unprecedented and has provided the research community with an opportunity to investigate the atmospheric response to potential policy interventions which seek to reduce pollutant emissions in the long-term.

In this work, we have combined air quality monitoring data from the UK’s AURN and Sussex-Air monitoring network with data from the University of Brighton JOAQUIN Advanced Air Quality reSearch laboratory and ESA’s Sentinel-5P satellite, and findings from detailed chemical modelling, to investigate changes in tropospheric composition and reactivity in the South East of the UK during the 2020 COVID-19 pandemic.

The results presented have shown that there was a clear decline in average ambient NO2 during the UK lockdown period, effective from 24th March 2020, owing to a reduction in vehicle traffic by as much as 70%. However, there was also a concomitant increase in average ambient O3 concentrations (most noticeably under urban, hydrocarbon limited ozone production conditions), and the overall abundance of total O3 species did not change significantly at chosen study locations as a result of the UK lockdown. Our model simulations indicate that in environments that experienced a significant increase in O3 loading during lockdown, the average daily abundance of OH would also have significantly increased (by 10% for the Eltham example investigated here). Combined with higher ambient O3 concentrations, this would have led to an increase in boundary layer oxidative capacity/reactivity. As such the scenario is somewhat complex, and attention must also be given to the wider altered trace composition and reactivity of the atmosphere that occurred during lockdown, as well as the significant reductions in emissions of NOx species, as have widely been publicised.

It has also been shown that there were clearly defined peaks in PM10 and PM2.5 concentrations with respect to the 2020 average, which corresponded with the timing of regional pollution episodes. As a result, there is limited evidence of a decline in particulate matter concentrations which can be attributed to lockdown restrictions. As such, more research is needed to investigate potential shifts in particle size distribution, PM chemical composition and the abundance of PM precursors as a result of a decline in anthropogenic activity, which have the potential to lead to increasing concentrations of UFP fractions.

It is vital that future policies to control and reduce emissions fully consider the complex trace composition and reactivity of the atmosphere. As pandemics are predicted to become more regular, there is now both a global need for pollutant emissions reductions to combat poor air quality and climate change, and for a better understanding of atmospheric effects and interactions with such diseases.

Credit authorship contribution statement

K.P. Wyche: Conceptualization, Data curation, Formal analysis, Funding acquisition, Investigation, Methodology, Project administration, Resources, Software, Supervision, Validation, Visualization, Writing - original draft, Writing - review & editing. M. Nichols: Conceptualization, Data curation, Formal analysis, Investigation, Methodology, Project administration, Resources, Validation, Visualization, Writing - original draft, Writing - review & editing. H. Parfitt: Conceptualization, Data curation, Formal analysis, Investigation, Methodology, Resources, Software, Validation, Visualization, Writing - review & editing. P. Beckett: Funding acquisition, Investigation, Supervision, Validation, Writing - review & editing. D.J. Gregg: Data curation, Formal analysis, Investigation, Methodology, Software, Validation, Visualization, Writing - review & editing. K.L. Smallbone: Funding acquisition, Investigation, Supervision, Validation, Writing - review & editing. P.S. Monks: Funding acquisition, Investigation, Supervision, Validation, 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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References


