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Impact of the COVID-19 on the vertical distributions of major pollutants from a tower in the Pearl River Delta

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**HIGHLIGHTS**

- The vertical profile of NO\textsubscript{x}, PM\textsubscript{2.5} and O\textsubscript{3} before and during COVID19 lockdown were observed from a tower in PRD, China.
- Significant reductions in surface NO\textsubscript{x}, PM\textsubscript{2.5} and MDA8O\textsubscript{3} during the lockdown by 76.8%, 49.4%, and 18.6%.
- Compared with the pre-lockdown, the vertical profiles of NO\textsubscript{x} and O\textsubscript{3} changed but PM\textsubscript{2.5} remain the same during the lockdown.

**ABSTRACT**

The outbreak of the 2019 novel coronavirus (COVID-19) had a large impact on human health and socio-economics worldwide. The lockdown implemented in China beginning from January 23, 2020 led to sharp reductions in human activities and associated emissions. The declines in primary pollution provided a unique opportunity to examine the relationship between anthropogenic emissions and air quality. This study reports on air pollutant and meteorological measurements at different heights from a tall tower in the Pearl River Delta. These measurements were used to investigate the vertical scale response of pollutants to understand reductions in human activities. Compared to that in the pre-lockdown period (from December 16, 2019), the concentrations of surface layer nitric oxide (NO\textsubscript{x}), fine particulate matter (PM\textsubscript{2.5}), and daily maximum 8 h average ozone (MDA8O\textsubscript{3}) declined significantly during the lockdown by 76.8%, 49.4%, and 18.6%, respectively. Although the vertical profiles of NO\textsubscript{x} and O\textsubscript{3} changed during the lockdown period, those of PM\textsubscript{2.5} remained the same. During the lockdown period, there were statistically significant correlations between PM\textsubscript{2.5} and O\textsubscript{3} but not between PM\textsubscript{2.5} and NO\textsubscript{x} at four heights, indicating that the main composition of PM\textsubscript{2.5} have dramatically changed, during which the impact of NO\textsubscript{x} on PM\textsubscript{2.5} became insignificant. Additionally, O\textsubscript{3} concentrations were also insensitive to NO\textsubscript{x} concentrations during the lockdown, implying that O\textsubscript{3} levels were more of a representative of regional
1. Introduction

The novel coronavirus 2019 (COVID-19) pandemic has completely changed the world and caused the considerable loss of life around the world. At present, over 200 countries and regions have been affected by the pandemic, and the number of infections and deaths from severe acute respiratory syndrome coronavirus 2 (SARS-CoV-2) and its variants continue to rise (Wang et al., 2020). Many countries have opted to implement lockdowns to curb the spread of the pandemic; this has meant reducing gatherings and instigating social distancing among individuals. Generally, these measures have reduced human activity, and either decreased or completely halted manufacturing work and the movement of people. Although lockdowns have had devastating socio-economic impacts, recent studies have demonstrated that they have been beneficial for the natural environment (Chakraborty and Maity, 2020).

The reduction in human activities due to the pandemic has greatly decreased primary pollutant emissions, with significant impacts on regional air quality (Xing et al., 2020; Salma et al., 2020; Wang et al., 2021; Kim et al., 2021) and climate (Gettelman et al., 2021), despite differences between regions. In South East Asia, the lockdown led to a notable decrease in aerosol optical depth over the region and in pollution outflow over oceanic areas. A significant decrease (27%–30%) in tropospheric nitrogen dioxide (NO2) was observed over territories unaffected by seasonal biomass burning (Kanniah et al., 2020). Srivastava (2021) noted that the aerosol optical depth had reduced by up to 50% over the Indo-Gangetic Plain during lockdown. In Italy, urban road traffic decreased by 48%–60% on average during the implemented lockdowns, greatly decreasing concentrations of NO2 and particulate matter with an aerodynamic diameter <10 μm (PM10) and <2.5 μm (PM2.5) (Gualtieri et al., 2020). Rodríguez-Urrego and Rodríguez-Urrego (2020) found that the average PM2.5 concentration of the 50 most polluted capital cities in the world had decreased by 12% on average. The analysis of the emissions data of 28 cities in the United States of America (USA) during its first round of lockdowns (March 15, 2020 to April 25, 2020) showed that two of three cities experienced substantial reductions in NOx and carbon monoxide (CO) concentrations (with decreases up to 49% and 37%, respectively), compared with the 2017–2019 historical baseline and pre-lockdown levels. The extent of decreases in NOx and CO concentrations were in proportion to local population density; however, the PM2.5 and PM10 concentrations only decreased significantly in north-eastern USA, California, and Nevada, which also experienced the largest decreases in NOx concentrations (Rodríguez-Urrego and Rodríguez-Urrego, 2020).

Shenzhen is a highly developed city experiencing intense human activities, facing air quality problems (Li et al., 2015; Yang et al., 2020). Li et al. (2020) analysed the vertical distribution of pollutants, including PM2.5, NOx, and O3, in the PRD during peak pollution season, based on air quality and meteorological datasets obtained at the Shenzhen Meteorological Gradient Tower (SZMGT) from December 2017. This analysis provided useful insights on the vertical structure of air pollutant distribution in the PRD. As the beginning of the COVID-19 pandemic coincided with peak pollution season in the PRD, the vertical distribution of pollutants recorded by the SZMGT during this period was invaluable in terms of demonstrating how reductions in human activity may affect the vertical distribution of pollutant concentrations. This study characterises changes in the vertical distribution of atmospheric pollutants induced by the extreme emissions reduction caused by human activities and explores possible mechanisms. The results provide scientific support for air pollution mitigation, particularly regarding the coordinated control of PM2.5 and O3 concentrations.

2. Data and methods

Observational data used in this study were sourced from a meteorological observation base on the east side of the Pearl River estuary, spanning from December 16, 2019 to February 15, 2020; namely, the Shiyuan Meteorological Observation Base (hereafter Shiyuan Base), managed by the Shenzhen National Climate Observatory (Fig. 1a). The SZMGT is the most important observational platform in Shiyuan base. The base lies approximately 10 km from the coastline, and is located is a woodland area surrounding a reservoir. As the reservoir is an important source of drinking water for residents of Shenzhen, the environment within 1 km around the SZMGT is protected and rarely disturbed by human activity, ensuring that the underlying surface will remain natural for a long time.

The entire Shenzhen area is located within a subtropical monsoon climate zone. The dominant wind direction in summer is southerly, and airflow introduces clean air from the ocean to the base. In winter, the dominant wind direction becomes northerly, and airflow carries pollutants from the inland PRD to the base; this favours the accumulation and formation of air pollutants (Li et al., 2020). The peak of the COVID-19 pandemic largely occurred during winter, when meteorological conditions are generally favourable to pollutant formation and accumulation in Shenzhen.

The SZMGT is 365 m tall (Fig. 1b), contains 13 layers of meteorological observation platforms that begin from 10 to 350 m (Fig. 1c). Four
of these layers (i.e., at 60–70, 110–120, 210–220, and 325–335 m, respectively), are atmospheric observation platforms (Fig. 1c). The distance from the SZMGT to the nearest built-up area is approximately 1 km. Approximately 800 m north-east of the Shiyan Base, there is a busy highway from which vehicular pollutant emissions may influence the measurements on the tower. There is also an airport located approximately 10 km west of the base which serves an estimated 356000 flights in a normal year. As such, the departure and arrival of airplanes at the airport may also potentially influence pollutant concentration measurements by the SZMGT (Li et al., 2020). An additional atmospheric environmental observation station has been installed at the bottom of the SZMGT. As this station is located on the ground, the height of its sampling port is lower than the surrounding forest top.

The meteorological data used in this study were collected at all 13 platform heights, as shown in Fig. 1c, whereas the environmental data were collected at heights of 110–120, 210–220, and 325–335 m. The data at 60–70 m height was not included in the analysis as equipment failure had occurred at this point during the pandemic. Data obtained by the atmospheric environmental observation station at the bottom of the SZMGT were also used.

The equipment used at the SZMGT to measure wind, temperature and humidity, and visibility included the Vaisala WMT700 Ultrasonic Wind Sensor, Vaisala HMP155 Humidity and Temperature Probe, and Vaisala PWD Present Weather Visibility Sensor, respectively. PM$_{2.5}$, NO$_x$, and O$_3$ concentration data were collected using the Thermo Scientific™ 5030i Sharp Particulate Monitoring equipment, Thermo Scientific™ 42i Gas Analyser, and the Thermo Scientific™ 49i Gas Analyser; data from these instruments were downloaded once every 5 min. Arithmetic averaging of the data was carried out for all measured parameters, with the exception of wind direction; this averaging was undertaken to obtain hourly average data. The daily average data by arithmetic averaging were obtained using the hourly average data over 24 h. To determine the wind direction, representative values were obtained by calculating the maximum wind frequency for the hour and for the day. The instruments on the tower were maintained by professional service providers; meteorological observation instruments were routinely exchanged for calibration once every three months, and air quality observation instruments were maintained once every month.

3. Results and discussion

3.1. Changes of pollutant concentrations and meteorological parameters

Fig. 2 shows the daily mean concentrations of PM$_{2.5}$, O$_3$, and NO$_x$ observed at Shiyan Base in Shenzhen, alongside the daily mean relative humidity (RH), daily mean temperature, daily mean wind speed, and daily dominant wind direction from December 16, 2019 to February 15, 2020. Two key dates were marked with blue dotted lines on the PM$_{2.5}$, O$_3$, and NO$_x$ graphs: 15th–23rd January 2020. The first case of COVID-19 in Shenzhen was reported by local news outlets on January 15, 2020. Then, Guangdong Province (where Shenzhen is located), activated its top-level emergency response on January 23, 2020; all residents in Shenzhen were stay at home unless necessary. Therefore, the intensity of human activity in Shenzhen in terms of manufacturing and traffic, had begun to decrease on January 15, 2020. By January 23, 2020, Shenzhen had been virtually shut down due to the strengthening of activity restrictions. Aside from the most vital logistics chains, very little traffic remained on the streets. Although it has not been possible to quantitatively estimate the degree to which human activity decreased in Shenzhen during this period due to a lack of data, air traffic from the airport to the west of Shiyan Base may provide some indication of the reduction extent. News reports mentioned that the number of passengers at the airport had decreased by as much as 79.5% in February 2020. In addition, a nationally popular navigation service provider announced that during lockdown, the daily traffic flow was ~14.1% compared to that in the pre-lockdown period. This means there were approximately 282000 vehicles on the road in all of Shenzhen (spanning 2000 km$^2$) every day during the lockdown; by contrast, the average number of vehicles under pre-lockdown levels is usually ~2 million vehicles. As the Spring Festival (Chinese New Year) is usually in February, this decrease in passenger volume and road traffic is a testament to the magnitude by which human activity decreased in this region.

Fig. 2a and c shows that the daily mean concentrations of PM$_{2.5}$ and NO$_x$ closely tracked the lockdown-mediated change in human activity.
As there were no cases of COVID-19 in Shenzhen prior to January 15, 2020, the local government did not impose any restrictions between December 16, 2019 and 15th January 2020; maintaining relative high pollutant concentrations. Following the first report of COVID-19 on January 15, 2020, many residents began to reduce the frequency of their outdoor activities due to their awareness of the pandemic. As these reductions in human activity were voluntary and not universal, pollutant concentrations had only gradually decreased. The widespread implementation of high-level restrictions on January 23, 2020 led to drastic and sustained reductions in pollutant concentrations. In general, the daily mean concentrations of PM$_{2.5}$ and NO$_x$ remained low after this date, whereby their range of variation had become significantly restricted. Although all three pollutant emissions had been reduced by the lockdown, the change in NO$_x$ concentrations was the most significant. This is because NO$_x$ is primarily derived from traffic emissions; as the decrease in human activity also prompted a decline in traffic emissions, the concentration of NO$_x$ in the atmosphere decreased instantaneously upon the cessation of vehicular traffic. Although the daily mean concentration of O$_3$ did not change significantly after 23rd January 2020 (Fig. 2b), the daily range of variation in its concentration (i.e., difference between the minimum and maximum concentration within a day), did decrease significantly after this date.

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The large scale surface weather maps (figures not provided here) showed that during the period of study, Shenzhen was primarily controlled by uniform pressure or a weak high pressure ridge with sparse ground isobaric lines for most of the time; this is typical for this area in winter. During the study period, three cold fronts occurred on 26th-27th December 2019, January 12, 2020, and 27th–30th January 2020. When a cold front passes over Shenzhen, there were more dense ground isobaric lines than those in normal conditions. Fig. 2d and e presents the variations in daily mean temperature, daily mean RH, daily mean wind speed, and daily dominant wind direction during the study period. As evident in Fig. 2d, the RH and temperature were strongly correlated, indicating that the dry air in the PRD predominantly comes from cold air masses. Whenever a cold front passes over the Shiyan Base, the daily mean temperature and RH will decrease. Fig. 2e shows that the daily mean ground wind speeds during the study period were usually below 2 m/s, even when cold fronts had passed. Although there was no dramatic change in the daily mean ground wind speed during the entire study period, the most polluted periods were related to weak wind speed $< 1.5$ m/s. During the pre-lockdown period, the peak PM$_{2.5}$ and NO$_x$ concentrations occurred on December 22, 2019, and the daily mean wind speed recorded that day was $\sim 0.9$ m/s. During the lockdown, relatively high concentrations of PM$_{2.5}$ and NO$_x$ occurred during from 11th–13th February 11–13, 2020, when the daily mean wind speed was between 1.0 m/s to 1.3 m/s. Additionally, the daily dominant wind direction was northerly for approximately 75% of the time. Generally, the weather during the study period was relatively typical of winters in Shenzhen, indicating that no meteorological abnormalities had occurred during this time.

Table 1 illustrates the decrease in PM$_{2.5}$ and NO$_x$ concentrations during the lockdown, where the decrease in the latter was much more drastic than that in the former. The change in O$_3$ was more complex than PM$_{2.5}$ or NO$_x$; the daily average O$_3$ concentration had slightly increased during the lockdown, consistent with the findings from other studies.

![Daily variations in pollutant concentrations and related meteorological factors in the surface layer from 16th December 2019 to February 15, 2020: (a) PM$_{2.5}$; (b) O$_3$; and (c) NO$_x$ concentrations averaged using data from the four different levels of the SZMGT; (d) air temperature and relative humidity observed at the Shiyan Meteorological Observation Base; and (e) wind speed and direction observed by the automatic weather station at the Shiyan Meteorological Observation Base.](image-url)
Comparison of pollutants and meteorological elements during the COVID-19 lockdown and prior to the lockdown.

| Time period       | Before 23rd Jan. | After 23rd Jan. | Relative changes |
|-------------------|------------------|-----------------|------------------|
| PM$_{2.5}$ (μg/m$^3$) | 38.5             | 19.5            | -49.4%           |
| O$_3$ (ppbv)      | 26.8             | 29.4            | +9.7%            |
| MDA$_8$O$_3$ (ppbv) | 51.4            | 42.1            | -18.6%           |
| NO$_x$ (μg/m$^3$) | 50.9             | 11.8            | -76.8%           |
| Temperature (°C)  | 18.9             | 16.5            | -12.7%           |
| RH (%)            | 75.3             | 77.0            | +2.3%            |
| Wind speed (m/s)  | 1.6              | 1.8             | +12.5%           |
| Wind direction    | NNE              | NNE             | –                |

* NNE: north-north-east. All pollutant concentrations in the table are averages for the whole surface layer recorded by the tower.

However, the mean daily maximum 8 h average O$_3$ (MDA$_8$O$_3$) concentration had significantly decreased during the lockdown. As the daily O$_3$ concentration and MDA$_8$O$_3$ exhibited different types of changes indicates the relatively different chemical environments related to O$_3$ prior to and during lockdown.

The changes in meteorological factors during the lockdown compared with those in the pre-lockdown period may largely be attributed to the intense cold air front that developed on 27th–30th January 2020; this event decreased the mean temperature during the lockdown period. By contrast, there was little change in the RH following the implementation of the lockdown. The meteorological factors most closely related to pollutant dispersal in the Shenzhen region were wind speed and direction. Although the average wind speed increased during the lockdown, it was still weak and rarely exceeded 2.0 m/s, limiting improvement in pollutant dispersion. The dominant wind direction during the pre-lockdown and lockdown periods was north-north-east, indicating that the winds in Shenzhen largely travel from the inland regions of China. In a normal year, these winds transport large amount of air pollution from the inland parts of the PRD, causing a spike in pollutant concentrations (Li et al., 2020). The changes in meteorological factors during the lockdown, with the exception of the strong cold front that had begun on January 27, 2020. The weathers during both periods may be generally considered poor meteorological conditions for air quality in Shenzhen. Although an intense cold spell occurred after 27th January 2020 and the average wind speed had slightly increased, this change was not sufficient to cause dramatic decreases in average PM$_{2.5}$ and NO$_x$ concentrations recorded during the entire lockdown period. Overall, the drastic changes in pollutant concentrations over the study period were unlikely to be caused by changes in meteorological factors.

### 3.2. Diurnal variations at different heights

Fig. 5 shows the diurnal variations in PM$_{2.5}$, NO$_x$, and O$_3$ concentrations on the surface (2 m) and at three different heights (120, 220, and 335 m) of the SZMGT, before and during the lockdown. The PM$_{2.5}$ time series curves in Fig. 5a are characterised by two trends: (1) a bimodal distribution for the ground level (2 m) and 120 m curves; and (2) a unimodal distribution for the 220 and 335 m curves. The peaks of the bimodal curves occurred at 09:00 Local Sidereal Time (LST) and 20:00 LST; these peaks roughly correspond to the morning and evening rush hours. The difference between the PM$_{2.5}$ curves at 0/120 m and that of 220/335 m is likely to reflect the uplift process of the top mixing layer in this area. During winter nights and early mornings, the height of the top mixing layer is frequently between 110 and 220 m (Fig. 6); therefore, the diurnal curves of pollutants in the upper and lower layers are relatively disparate. Following noon, the rise of the top mixing layer causes the pollutants curves of all layers to become similar. Although the PM$_{2.5}$ concentrations at 2 and 120 m followed the same qualitative trend, the ground values were generally lower than those at 120 m. There was no direct pollution source within 100 m around the Shiyan Base, as it is located in a water source protection area and surrounded by a litchi forest. Pollutants affecting the base are typically sourced from the surrounding highways, airports, and built-up urban areas. The litchi forest surrounding the SZMGT is 10 m high on average, and thus, is able to obstruct pollutants beyond the base from reaching the sensors on the ground of the base; however, it cannot prevent these pollutants from reaching the measurement point located at 110–120 m height. The peaks of the unimodal 220 and 335 m curves occurred at 17:00–19:00 LST. Therefore, diurnal variations in PM$_{2.5}$ concentration differed at lower and higher heights. This is consistent with Li et al. (2020) who...
implied that high and low-height PM$_{2.5}$ may have different sources or formation mechanisms. High-height PM$_{2.5}$ is formed predominantly by secondary chemical reactions, whereas low-height PM$_{2.5}$ may be derived from multiple sources, including surface-level primary emissions and secondary chemical reactions.

Fig. 5b presents the diurnal variations in PM$_{2.5}$ concentrations at 2, 120, 220, and 335 m during the COVID-19 lockdown. It was obvious that PM$_{2.5}$ concentrations had decreased significantly at all heights following January 23, 2020. The highest PM$_{2.5}$ concentration still occur at 110–120 m and retained the bimodal structure of its pre-lockdown counterpart. The PM$_{2.5}$ concentrations at 220 and 335 m were still unimodal, where the peak occurred at a similar time. The largest lockdown-mediated change in PM$_{2.5}$ concentration occurred at 2 m, where the diurnal profile did not have a morning peak.

In terms of O$_3$, it was evident that the diurnal variation in its concentration was unimodal and peaked at approximately 15:00–16:00 LST, when photochemical O$_3$ formation is most active, before and during the lockdown (Fig. 5c and d, respectively). These diurnal variations were also qualitatively invariant with altitude; this means only the average concentration varied from one altitude to the other. However, the shape of the O$_3$ diurnal profile did become significantly flatter during the lockdown, indicating a narrower range in the diurnal variations. The flattening of the peaks and valleys of the O$_3$ curve implies that chemical reactions related to anthropogenic emissions (e.g., NOx, VOCs) generating O$_3$ during the day and consuming O$_3$ at night-time became more inactive during lockdown (Liu et al., 2021; Qi et al., 2021). Despite this, biological volatile organic compound (VOC) emissions may contribute to the generation of a very weak peak during the afternoon. Under these conditions, the O$_3$ concentration appeared to be primarily determined by the background O$_3$ concentration (Xu et al., 2020). Notably, a flatter O$_3$ curve means a decrease in MDA8O$_3$, implying that the mitigation of O$_3$ and PM$_{2.5}$ pollution may theoretically be realized concurrently.

The diurnal variations of NO$_x$ concentrations were bimodal before the lockdown (Fig. 5e); the 2 and 120 m curves showed a peak at 09:00 LST, coinciding with the morning rush hour. The second peak, beginning at 18:00 LST and continuing until 21:00 LST, was likely caused by the evening rush hour and night-time decreases in the altitude of the mixed layer. The first peak in the 220 and 335 m curves showed a 1 h lag from the first peak of the lower altitude curves; however, the second peak occurred at roughly the same time in both sets of curves. Although the mean NO$_x$ concentrations had decreased significantly during lockdown, its diurnal variations were still bimodal (Fig. 5f). The inter-altitude differences in NO$_x$ concentrations did become much lower during the lockdown and the timings of NO$_x$ peaks at each altitude were also closer to each other. During the lockdown, the first peak was delayed by 1 h, whereas the second peak occurred at 17:00–19:00 LST. The other significant way in which NO$_x$ concentrations had changed was that they were lower at 2 and 120 m than that at 220 and 335 m. The absolute decrease in the NO$_x$ concentration at the surface layer was much larger than that at 220 and 335 m, demonstrating that NO$_x$ in the surface layer
was much more easily affected by emissions change.

To further analyse changes in pollutants during the lockdown, the concentration ratios of pollutants before and during the lockdown were calculated; this diurnal variation of the ratios is illustrated in Fig. 7. The diurnal variation curves of different pollutants exhibited various characteristics. For NO\textsubscript{x}, curves at different heights were relatively consistent being roughly flat and maintained around 0.3; this indicates that there was an even and significant decrease in NO\textsubscript{x} concentration decreased in the boundary layer. The curves for PM\textsubscript{2.5} differed from NO\textsubscript{x}; ratio curves were relatively flat and maintained at ~0.5 all day at heights >110 m, although there were relatively large ground level fluctuations. The ratio on the ground increased significantly between 7:00 and 18:00 LST as opposed to maintaining a relatively flat pattern. This indicates that the decrease in ground level PM\textsubscript{2.5} concentrations (~−30%) during the day over the lockdown period was not as drastic as that of the average data of the whole boundary layer (~−50%). However, it was still difficult for PM\textsubscript{2.5} generated on the ground to affect the air mass at >100 m height. The fluctuations in the ratio diurnal curves for O\textsubscript{3} were clearer than those in the ratio diurnal curves for other two pollutants. The ratios were generally greater than 1.0 at night, clearly demonstrating less effective NO\textsubscript{x} titration at this time leading to relatively higher ozone concentrations at night than those observed in the pre-lockdown period. The ratios were <1.0 in the afternoon, which suggests that during lockdown, the O\textsubscript{3} concentration decreased in the afternoon.

### 3.3. Vertical distribution of pollutants

Fig. 8 presents changes in the vertical distribution of the three pollutants and O\textsubscript{3} (= O\textsubscript{3} + NO\textsubscript{2}), measured at 2, 120, 220, and 335 m of the SZMGT before and during the lockdown. In terms of the all-day averages (Fig. 8a–d), it was apparent that the PM\textsubscript{2.5}, NO\textsubscript{x} concentrations were lower across all altitudes during the lockdown; the differences passed the significance test at \( p < 0.01 \). By contrast, O\textsubscript{3} concentrations did not decrease significantly, although their vertical gradations were less pronounced; as such, O\textsubscript{3} concentrations became more uniform in the vertical direction during the lockdown. The daytime and night time average Ox concentrations (Fig. 8h–i) were generally lower during the lockdown period than during the pre-lockdown period, where the difference also passed the significance test at \( p < 0.01 \), indicating a weakened oxidation capacity for the whole boundary layer during the lockdown. The nitrate radical production rate (\( - k_{NO2+O3}[NO2][O3] \)) was also examined during the nighttime as it is an indicator of nighttime oxidation reactions. This rate experienced a large decline, averaging ~70%, suggesting a weakened NO\textsubscript{x} oxidation capacity. The decrease in nighttime oxidation is mainly attributed to the dramatic reductions in NO\textsubscript{x} levels. Overall, the vertical observations showed that atmospheric oxidation processes, including photochemistry and nighttime chemistry, had largely been reduced due to the lockdown.

Fig. 8a shows that the PM\textsubscript{2.5} concentrations initially decreased with increasing altitude from 120 m, before increasing slightly with further
altitude increases; this occurred before and during the lockdown period. The PM$_{2.5}$ concentration was the highest at 120 m, whereas the concentration at 335 m was between those recorded at 120 and 220 m. This is an interesting result as it contradicts the expectation that PM$_{2.5}$ concentrations should decrease monotonically with increasing altitude (Sun et al., 2010). This is understandable when considering the results of previous studies on possible PM$_{2.5}$ sources at each altitude. At the lowest height (120 m), PM$_{2.5}$ may have been sourced from ground photochemical reactions and primary pollution sources. At mid- and higher altitudes, PM$_{2.5}$ is mainly formed by photochemical reactions; as such, the efficiency of PM$_{2.5}$ generation at these heights may be affected by the oxidative potential of the atmosphere. Based on the observations from the SZMGT, the O$_3$ concentration generally increased with height, and the Ox was higher at 335 m than at 220 m. As such, it is likely that the oxidation capacity of the atmosphere increased at the highest level, elevating the efficiency of PM$_{2.5}$ formation at this altitude. Although the concentrations of VOCs were not measured from the SZMGT, measurements in Kaohsiung, Taiwan have shown that these compounds also increase with altitude, up to a peak of 300–400 m. As such, the VOCs provide an ample supply of reactants for photochemical reactions at high altitudes (Vo et al., 2018). Although there is a distance of ~660 km between Kaohsiung and Shenzhen, both are located in the subtropical monsoon climate zone and with developed industry and transportation; this means the observations in Kaohsiung offer a point of reference for Shenzhen. At mid-altitudes (220 m), the PM$_{2.5}$ concentration was not significantly affected by primary pollutant sources, and PM$_{2.5}$-forming photochemical reactions were also less efficient at this point than higher altitudes. Consequently, the PM$_{2.5}$ concentrations were lower at mid-altitudes than at higher altitudes.

O$_3$ concentrations increased monotonically with altitude (Fig. 8b); this occurred even during the lockdown, where the average O$_3$ concentration remained high without showing any significant change. By contrast, vehicular emissions had plummeted to a very low level during the lockdown, as clearly evidenced in Fig. 8c. This figure shows that NO$_x$ concentrations had decreased considerably at near-ground altitudes, particularly at 120 m, where concentrations had decreased by >75% compared with pre-lockdown levels. Given the significant decrease in NO$_x$ concentrations (as much as ~78.2% in this study), the concentrations of VOCs did not experience the same change as observed in NO$_x$. In recent studies, Qi et al. (2021) reported that the decrease in VOCs in the PRD during the lockdown was much lower than that in NO$_x$, whereas Liu et al. (2021) reported that formaldehyde (HCHO) abundance in the PRD area experienced an even slight increase during lockdown based on TROPOspheric Monitoring Instrument (TROPOMI) satellite measurements.
observations. The different reduction degrees of NOx and VOCs during lockdown may largely shift ozone formation sensitivity to NOx and VOC.

Fig. 9 and 8i-1 display the vertical distributions of pollutants and O3 during the day and night, respectively; day-time and night-time distributions of PM$_{2.5}$, NOx, and O3 did not significantly differ. By contrast, the vertical distribution of O3 varied significantly between day and night. At all altitudes, day-time O3 concentrations were generally lower during the lockdown, whereas night-time concentrations were higher. This paradoxical trend may be attributed to the weakening of atmospheric chemical activity during the lockdown. As reduced human activity also decreased primary pollutant emissions, there was substantially lower availability of precursors for photochemical O3 generation, resulting in decreased day-time O3 concentrations. At night, dark chemical reactions that consume O3 also became less active during the lockdown, resulting in significantly higher night-time O3 concentrations at the near-surface atmosphere; these changes are consistent with the diurnal variations in O3 (Fig. 5d).

Regional transport is another important factor affecting the atmospheric chemical activity during the lockdown. As reduced human activity also decreased primary pollutant emissions, there was substantially lower availability of precursors for photochemical O3 generation, resulting in decreased day-time O3 concentrations. At night, dark chemical reactions that consume O3 also became less active during the lockdown, resulting in significantly higher night-time O3 concentrations at the near-surface atmosphere; these changes are consistent with the diurnal variations in O3 (Fig. 5d).

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3.4. Correlations at different altitudes

Fig. 10 depicts scatterplots and fit lines of O3 and its relationship with PM$_{2.5}$ at each level of the SZMGT, before and during the lockdown. Prior to the lockdown, there was a weak correlation between the O3 and PM$_{2.5}$ concentrations, where none of the correlation coefficients ($R$) passed the significance test. During the lockdown, there was a significantly stronger correlation between PM$_{2.5}$ and O3, where $R$ values for the 0, 120, 220, and 335 m scatter plots were significant at $p < 0.1$. In the PRD region, VOCs significantly contributed to the formation of fine particles (Liu et al., 2008; Zheng et al., 2009), particularly secondary organic aerosols (Huang et al., 2006; Chang et al., 2019; Zhang et al., 2019). Although the advent of COVID-19 did trigger reductions in the concentrations of NOx, SO$_2$, and other primary pollutants, VOC emissions may not have experienced such dramatic changes (Liu et al., 2021). The VOCs may act as important precursors for O3 and the secondary organic aerosols during the lockdown, strengthening the correlation between the PM$_{2.5}$ and O3 concentrations.

Li et al. (2020) analysed the correlation coefficients of O3 and PM$_{2.5}$ at different heights of the SZMGT in December 2017, formulating different conclusions from this study. In December 2017, the correlation coefficient of O3 and PM$_{2.5}$ increased significantly with altitude; they stated that this is because PM$_{2.5}$ was also mainly generated by photochemical reaction at high altitudes, thus having a strong correlation with O3. At lower altitudes, there may be a greater contribution from the primary source to PM$_{2.5}$, resulting in a weaker correlation with O3. In this study, the correlation between PM$_{2.5}$ and O3 was weak at all altitudes during the pre-lockdown period. This may have occurred because Shenzhen had conducted a large number of pollution emission control strategies over the past two years, resulting in a significant decrease in the levels of primary pollutants. When compared with the measured

Fig. 9. Potential PM$_{2.5}$ source areas at different altitudes of the Shiyan Base: (a) 110 m; (b) 220 m; and (c) 320 m. Different colours indicate the probability that airflow affecting the PM$_{2.5}$ concentration of the Shiyan Base passes through that area. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

Fig. 10. Scatter plots of PM$_{2.5}$ and O3 concentrations at different heights of the meteorological tower before and during the lockdown: (a) and (b) ground level; (c) and (d) low level; (e) and (f) middle level; and (g) and (h) high level. The fit lines of plots were produced as per Cantrell (2008).
data in the winter of 2017 (Li et al., 2020), the average concentration of PM$_{2.5}$ in the whole surface layer during the pre-lockdown period decreased by 18.1%, whereas the average O$_3$ concentration had declined by 36.2%. The decrease in the O$_3$ concentration in the surface layer was twice that of PM$_{2.5}$, indicating that there were much fewer products from photochemical reactions and secondary aerosol formation; as such, the correlation coefficient between O$_3$ and PM$_{2.5}$ concentrations was no longer high even in greater altitudes. During the lockdown, the average PM$_{2.5}$ concentration had once again decreased due to drastic reductions in primary emissions. During this process, PM$_{2.5}$ from primary emissions had become insignificant, and photochemical oxidation became an important source of PM. This strengthened the correlation coefficients between O$_3$ and PM$_{2.5}$ compared to those observed in pre-lockdown.

Fig. 11 compares the correlation between PM$_{2.5}$ and NO$_x$ concentrations before and during the lockdown. The correlation trend between PM$_{2.5}$ and NO$_x$ was the exact opposite of that between PM$_{2.5}$ and O$_3$; this means it was strong pre-lockdown (R = ~0.5 at all altitudes), and much weaker after the lockdown (R = ~0.2 at all altitudes). This indicates that there may be significant differences between PM$_{2.5}$ sources before and during the lockdown. It was not possible to carry out composition analysis to determine the underpinning reason for the close correlation between PM$_{2.5}$ and NO$_x$ emissions prior to the lockdown and not during the lockdown, due to a lack of PM$_{2.5}$ compounds observation. Some recent studies have identified particulate nitrate as an important component of water-soluble aerosols in this region (Wu et al., 2020; Yang et al., 2021), which is conducive to the results shown in Fig. 11. One possible reason for this is that the primary emissions of PM$_{2.5}$ in the PRD may have contributed a large proportion of the total PM$_{2.5}$ emissions before the lockdown; as NO$_x$ may be treated as an indicator of anthropogenic emissions, the primary emissions of PM$_{2.5}$ decreased significantly during the lockdown. The other possible explanation is that the nitrate content of PM$_{2.5}$ in the PRD decreased significantly during the lockdown. This is because a previous study reported that nitrate accounts for a large percentage of PM$_{2.5}$, prior to the year 2020 (Yang et al., 2020).

Fig. 12 displays the correlation between the O$_3$ and NO$_x$ concentrations before and during the lockdown. Prior to the pandemic, O$_3$ and NO$_x$ were negatively correlated with each other. The relationship between O$_3$ and NO$_x$ concentrations was fitted with an exponential function. During the lockdown, there was significant weakening of the (negative) correlation between O$_3$ and NO$_x$; this means at very low NO$_x$ concentrations, variations in the concentration of this pollutant appeared to have no clear effect on O$_3$ concentrations.

A comparison of scatter plots before and during the lockdown showed that PM$_{2.5}$ was poorly correlated to O$_3$, albeit closely correlated to NO$_x$ before the lockdown. This indicates that a relatively large proportion of PM$_{2.5}$ may originate from primary emissions or nitrate aerosol, although secondary aerosols may still account for a major part of PM$_{2.5}$. Following the implementation of lockdown, PM$_{2.5}$ became closely correlated to O$_3$, and not to NO$_x$. This indicates that the formation of PM$_{2.5}$ and O$_3$ may be highly regulated by one precursor (e.g., VOC), or the formation of PM$_{2.5}$ during lockdown may primarily be limited by atmospheric oxidants, such as O$_3$, where the fraction of primary PM$_{2.5}$ may have been nearly eradicated.

4. Conclusions and implications

This study investigated changes in NO$_x$, O$_3$, and PM$_{2.5}$ concentrations over the PRD caused by local COVID-19 lockdown. These changes were examined through the analysis of the vertical distribution of pollutants (NO$_x$, O$_3$, and PM$_{2.5}$) before and during the lockdown by using data from the SZMGT. The conclusions of this study are as follows:

![Fig. 11. Scatterplots of the PM$_{2.5}$ and NO$_x$ concentrations at different heights of the meteorological tower before and during the lockdown: (a) and (b) ground level; (c) and (d) low level; (e) and (f) middle level; and (g) and (h) high level.](image1)

![Fig. 12. Scatter plots of O$_3$ and NO$_x$ concentrations at different heights of the meteorological tower before and during the lockdown: (a) and (b) ground level; (c) and (d) low level; (e) and (f) middle level; and (g) and (h) high level.](image2)
The advent of the COVID-19 pandemic forced a dramatic decrease in human activity. This greatly reduced the emission of primary pollutants, such as NO\(_x\), changing the chemical environment of the near-surface atmosphere. The PM\(_{2.5}\) concentration had also reduced significantly due to the decrease in precursor availability.

The reduction in primary pollutant emissions during the COVID-19 lockdown significantly decreased MDA8O\(_3\) whereas it did not decrease the daily average O\(_3\) concentration. The diurnal O\(_3\) concentration patterns were changed by the lockdown, where day-time concentrations were lower and night-time concentrations higher than pre-pandemic concentrations at all levels.

The correlation between PM\(_{2.5}\) and O\(_3\) concentrations was insignificant before the lockdown, and strengthened following the lockdown (\(p < 0.05\)) regardless of altitude. By contrast, the correlation between PM\(_{2.5}\) and NO\(_x\) was much weaker during the lockdown. The results imply the PM\(_{2.5}\) composition may have changed by being predominantly from primary emissions or nitrate aerosols before the lockdown, to being predominantly a secondary organic aerosol, but the validation of this hypothesis required in further studies.

Prior to the COVID-19 pandemic, O\(_3\) and NO\(_x\) concentrations were significantly negatively correlated. This correlation virtually disappeared following the outbreak of the pandemic. It may be concluded that at very low NO\(_x\) concentrations, variations to its concentration have nearly no effect on the O\(_3\) concentration.

Overall, the advent of COVID-19 has devastated economies and societies around the world. However, the dramatic reduction in human activity from the lockdown measures provides unique opportunity for check the response of the atmosphere to human activities. The data indicate that the atmospheric chemical environment of the PRD has changed during the pandemic, leading to a drastic change in pollutants concentrations. These results provide a clear indication of the outcomes of the pollution mitigation policy. In the past, a number of environmental policy studies cast doubt as to whether it was necessary to further reduce traffic emissions. This was because in some areas, decreasing NO\(_x\) concentration led to an increase in the O\(_3\) concentration. While this study shows that the continuous reduction in NO\(_x\) emissions may reduce the peak O\(_3\) and MDA8O\(_3\), but not further reduce the daily average O\(_3\) concentration.

CRediT authorship contribution statement

Lei Li: Conceptualization, Methodology, Software, Writing – review & editing, and, Project administration. Chao Lu: Methodology, Software, Writing – review & editing. Pak-Wai Chan: Data curation. Zijuan Lan: Data curation. Wenhai Zhang: Data curation. Honglong Yang: Data curation. Haichao Wang: Conceptualization, Methodology, Software, Writing – review & editing, Supervision, and, Project administration.

Declaration of competing interest

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

Acknowledgements

This study was supported by the National Natural Science Foundation of China (grant numbers 42075059, 42175111 and U21A6001), Guangdong Basic and Applied Basic Research Foundation (grant number 2019A1515012008) and Science and Technology Projects of Guangdong Province (grant number 2019B121201002).

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L. Li et al.

Atmospheric Environment 276 (2022) 119068

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