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Spatiotemporal Ozone Level Variation in Urban Forests in Shenzhen, China

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Abstract: *Research Highlights:* This study is among the first to investigate ozone levels in urban forests in China. It establishes that urban forest air quality in Yuanshan Forest Park, Shenzhen, is suitable for recreational activities and identifies spatial, seasonal, and diurnal O₃ patterns and relationships with micrometeorological parameters, suggesting the possibility of manipulating relevant forest characteristics to reduce O₃ levels. *Background and Objectives:* An understanding of O₃ levels of urban forest environments is needed to assess potential effects on human health and recreational activities. Such studies in China are scarce. This study investigated urban forest O₃ levels to improve understanding and support residents engaging in forest recreational activities. *Materials and Methods:* We monitored O₃ levels in 2015–2016 for three urban forests representing common habitats (foothill, valley, and ridge) in Yuanshan Forest Park, Shenzhen, and for an adjacent square. *Results:* The overall mean daily and daily maximum 8-h mean (MDA8) O₃ concentrations were highest for the ridge forest and lowest for the valley forest. Each forest's O₃ concentrations were highest in summer. Diurnally, forest O₃ concentrations peaked between 13:00 and 17:00 and reached a minimum between 03:00 and 09:00. The correlation between forest O₃ concentrations and air temperature (AT) was strongly positive in summer and autumn but negative in spring. In each season, O₃ concentration was negatively correlated with relative humidity (RH). No MDA8 or hourly O₃ concentrations in the forests exceeded National Ambient Air Quality Standard Grade I thresholds (100 and 160 µg m⁻³, respectively). *Conclusions:* O₃ accumulation is present in ridge urban forest in all seasons. Foothill and valley urban forests have better air quality than ridge forestation. Urban forest air quality is better in spring and autumn than in summer and is better from night-time to early morning than from noon to afternoon.

Keywords: urban forest; portable ozone monitor; NAAQS; micrometeorological parameter; seasonal variation

1. Introduction

With the acceleration of urbanization in China, the construction of urban forests has increased, and the area covered by urban forest has been expanding, especially in metropolitan areas. Urban forests can provide a high-quality environment that includes clean air, a comfortable microclimate, low noise, and high biodiversity, which benefit physical and mental health [1–2]. An increasing number of urban citizens visit urban forests for leisure and for recreational or fitness activities such as walking or running, requiring close monitoring of the air quality of urban forests [3–5].

Surface ozone (O_3) is a main secondary gaseous pollutant in urban areas; it forms in reactions in which volatile organic compounds (VOCs) interact with NO_x in the presence of sunlight [6–8]. Numerous medical studies have demonstrated that high levels of O_3 can affect human health. For instance, it can increase the frequency of occurrence of lung disease and mortality in urban inhabitants under long-term exposure [9–13]. Thus, O_3 levels are an important indicator of air quality, and elevated O_3 levels in the urban environment require a deeper understanding of O_3 levels in urban forests to help residents engage in healthful recreational and fitness activities.

Most previous studies conducting modelling-based evaluation, such as observations of 86 cities in Canada, 10 metropolitan cities in Italy, and areas in Florence (Italy) and Strasbourg (France) [14–17], demonstrated that urban forests are capable of reducing O_3 levels. In addition, studies using sap flow measurements and eddy covariance systems to investigate the effect of urban trees on O_3 showed that urban trees can remove O_3 through the canopy stomata uptake and non-stomatal deposition [18–20].

Some recent studies have focused on biogenic emissions from urban forests and their effects on O_3 levels. Results from these studies indicate that urban trees can increase O_3 concentrations by emitting a variety of O_3 precursors—e.g. biogenic volatile organic compounds (BVOCs) such as isoprene and (mono)terpenes, which are estimated to be two to three times more photochemically reactive than hydrocarbons of anthropogenic origin—and different plant species feature different O_3 formation potential [7,21,22]. Thus, existing research on the effects of urban forest on O_3 provides contradictory results.

Most investigations conducted in China focus on the toxic effects of O_3 on plants [23–25], or the contribution of BVOCs emitted from trees to O_3 formation [26,27], whereas O_3 levels in urban forests have rarely been characterised. Herein, in order to improve the understanding of the O_3 level in urban forests as well as to help residents engage in more healthful forest recreational activities, we empirically characterise O_3 levels measured in 2015–2016 for (a) three types of forest representing common habitats in Yuanshan Forest Park, Shenzhen, and (b) an adjacent square with little vegetation. Additionally, the micrometeorological parameters of air temperature (AT), relative humidity (RH), wind speed (WS), and solar radiation (SR) were monitored simultaneously with O_3 concentration at each site. The objective of this study was to 1) understand the effect of urban forest on O_3 levels, 2) investigate O_3 level dynamics in urban forests and the best time for residents to engage in recreation, and 3) explore the effects of micrometeorological parameters on O_3 levels in urban forests.

2. Materials and Methods

2.1. Study Area

The study area was located in Shenzhen, Guangdong Province, in southern China. During the past twenty years, Shenzhen has become one of the most prosperous cities in China, having a residential population of over 10 million in 2015 (Shenzhen Statistics and Information Bureau, 2015) and covering an area of 1996.85 km², with urban forests currently accounting for more than 60% of the green space.

The primary terrain of Shenzhen consists of rolling hills; it also features some low mountains and coastal plains. The climate is dominated by the southern subtropical ocean monsoon. The precipitation period is from April to September, and vegetation is largely represented by secondary forests and plantations of southern subtropical evergreen broadleaf forests, with the most common plants including *Acacia mangium* and those of the *Eucalyptae* tribe [28].

For this study, field measurements were performed in Yuanshan Forest Park, which is located in eastern Shenzhen at a distance of 20 km from the city centre and which has become an important locale for recreational activities of nearby residents. The park area totals ~10.9 km², and the elevation ranges from 60 to 599 m. Importantly, no industrial or traffic facilities are located within the park, and more than 85% of its area is covered by vegetation (mainly evergreen broadleaf forest).

2.2. Monitoring Sites

For systematically characterising O₃ levels in urban forest, three types of forest—located in the foothills, in the valley, and on the ridge of the main peak in Yuanshan Forest Park—were selected as monitoring sites. Each area had a size of no less than 600 m², featured a gentle slope ($\leq 35^\circ$), and was suitable for recreation. An aerial photograph of the study area and monitoring sites is shown in Figure 1.

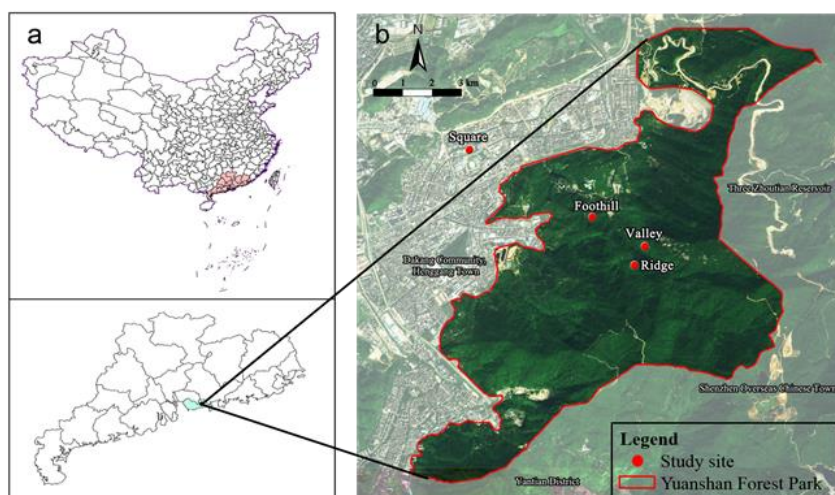


Figure 1. (a) Map of China and the Guangdong province (red area), with the blue area representing the city of Shenzhen (113°46′–114°37′E, 22°27′–22°52′N). (b) Aerial image of Yuanshan Forest Park (red solid line), with the red circles indicating monitoring sites.

Each site comprised six monitoring points located 30 m from the forest margin and situated under the canopies of trees similar in size. Thus, a total of 18 monitoring points was established in the three forests. The distance between any two points was set to a minimum of 50 m to allow good exposure to the surrounding environment.

In addition, a square with little vegetation which is about 2.1 km away from the park was used for comparison. This plot (50 × 50 m) was located in a residential area surrounded by a low-traffic road and low-rise buildings and therefore had an environment similar to that of the park except with less vegetation. Six monitoring points were set in the square using the same criteria described above.

2.3. Monitoring Methods and Dates

O₃ concentrations were monitored using 24 portable O₃ monitors (Aeroqual Series 500, Auckland, New Zealand) having a detection range of 0–1000 $\mu\text{g m}^{-3}$, a resolution of 2 $\mu\text{g m}^{-3}$, and an accuracy of within $\pm 16 \mu\text{g m}^{-3}$ from 0 to 200 $\mu\text{g m}^{-3}$ and $\pm 20 \mu\text{g m}^{-3}$ from 200 to 1000 $\mu\text{g m}^{-3}$ [29–30]. The monitor had proven to be reliable and accurate in numerous previous studies [31–33]. Micrometeorological parameters (AT, RH, WS, and SR) were monitored using a pocket weather station (Kestrel 5500, Nielsen-Kellerman, Boothwyn, PA, USA) and a digital luminance meter (TES-1332A, TES Electrical Electronic Corp., Taiwan). O₃ concentrations and micrometeorological parameters were measured at an elevation of ~1.5 m above ground, which is commonly considered the typical height at which human respiration occurs. All metrics were observed manually, and one observer was established at each point, for a total of 24 observers. Monitoring was nominally performed for 24 h each day (from 09:00 to 09:00 of the following day) at 2-h intervals. Sampling was performed 30 min each time, and data were automatically recorded by an internal memory logger, stored on the monitor, and converted into hourly averages at each point. The metrics were monitored simultaneously at the same times for all points.

Observations were conducted in three different months, representing three different seasons: April 2016, spring; August 2015, summer; January 2016, autumn (April 2016, spring; August 2015, summer; January 2016, autumn). For each season, six sunny days were selected for monitoring.

2.4. Vegetation

To understand the vegetation composition of three urban forests, surveying was performed in November and December 2015 within a 30 × 40 m plot in each experimental forest, and all trees and tall shrubs with a diameter at breast height (DBH) of >2 cm were recorded. For trees, five variables were collected (canopy cover, species, number, height, DBH), and dominant species were determined according to the method of Wang et al. [34]. The main plant species in the three forest plots are listed in Table 1.

Table 1. Vegetation parameters surveyed at three forest plots. Trees with a diameter at breast height (DBH) of <0.8 cm are not included.

Site	Location	Elevation /m	Canopy cover	Arbor trees		
				Average height /m	Average DBH /cm	Dominat species
Foothill	22°38'34"N, 114°14'33"E	158	0.65	10.75	12.97	<i>Acacia mangium</i>
						<i>Cunninghamia lanceolata</i>
						<i>Schefflera heptaphylla</i>
						<i>Dalbergia benthamii</i>
Valley	22°38'34"N, 114°14'33"E	174	0.75	7.6	10.48	<i>Cinnamomum camphora</i>
						<i>Ficus virens</i>
						<i>Schima superba</i>
						<i>Ehretia thyrsoiflora</i>
Ridge	22°38'34"N, 114°14'33"E	332	0.60	8.58	13.57	<i>Dalbergia benthamii</i>
						<i>Gironniera subaequalis</i>
						<i>Schima superba</i>
						<i>Schefflera heptaphylla</i>
						<i>Celtis sinensis</i>
						<i>Dalbergia benthamii</i>
						<i>Cinnamomum camphora</i>

2.5. Data Analysis

To determine and compare the effect of urban forests on O₃ levels, we averaged the values for the daily concentrations of O₃ supplied by the Meteorological Bureau of Shenzhen Municipality and the Shenzhen Environmental Monitoring Centre Station for each monitoring period and used them as the background data for the city of Shenzhen (<http://www.szhec.gov.cn/ztfw/ztl/hjbhxxgkzl/>). There were 11 background stations including Honghu station (urban site, located 14.3 km southwest of the park), Overseas Chinese Town station (urban site, located 28.8 km southwest of the park), Yantian station (urban site, located 34.2 km west of the park), Longgang station (urban site, located 9.6 km north of the park), Xixiang station (suburban site, located 36.6 km west of the park), Nanao station (suburban site, located 27.7 km southeast of the park), Kuiyong station (suburban site, located 19.6 km east of the park), Meisha station (suburban site, located 8.6 km southeast of the park), Guanlan station (urban site, located 19.6 km northwest of the park), Tongxinlingzi (urban site, located 19.1 km southwest of the park) and Nanhaizi station (suburban site, located 28.8 km w of the park), all of which were over 15 km far from Yuanshan Forest Park. The daily (from 01:00 to 01:00 of the

following day) means of O₃ concentration of urban forests were calculated to compare with daily data from background stations. In addition, the O₃ levels in the urban forests were compared to the Grades I and II hourly and daily maximum 8-h (11:00-18:59) mean (MDA8) concentrations of O₃ stipulated by the National Ambient Air Quality Standard (NAAQS Grade I: 160 and 100 µg m⁻³; Grade II: 200 and 160 µg m⁻³, respectively).

One-way analysis of variance (ANOVA) and Duncan's test were used to determine the significance of differences between the overall daily average O₃ concentrations at different sites. Two-way ANOVA and Duncan's test were used to compare the differences of daily mean concentrations of O₃ between different seasons and sites. The Pearson correlation test was applied to detect possible correlations between O₃ and micrometeorological parameters. For all tests, *p* values of < 0.05 were considered to represent statistical significance. Statistical analyses were performed using SPSS Statistics, Version 22 (SPSS Inc., Chicago, USA). Plots were created in Origin 9.0 (OriginLab, Hampton, USA). Tables were prepared using Microsoft Excel 2016 (Microsoft, Redmond, USA).

3. Results

3.1. O₃ Concentration

3.1.1. Overall Characteristics

The overall mean daily O₃ concentration ([O₃]_{DA}) was highest for the ridge forestation and lowest for the valley forestation (Figure 2). Notably, the [O₃]_{DA} of the ridge forestation was significantly higher than that of the square (by 39.76%). In addition, the [O₃]_{DA} of the ridge forestation was insignificantly (1.06-fold) higher than the background value (53.44 ± 4.17 µg m⁻³; not shown in the figure), whereas the values for the foothill and valley forestation were significantly lower (by 27.18 and 44.12%, respectively).

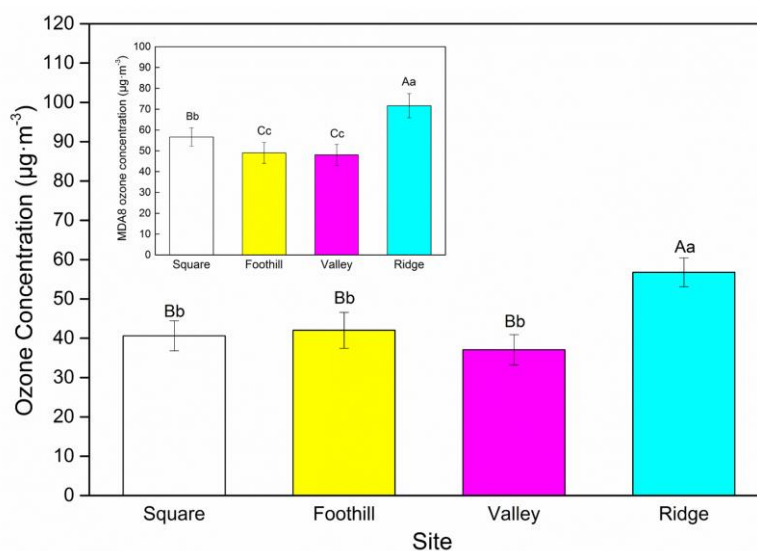


Figure 2. Mean daily and daily maximum 8-h mean (MDA8) concentrations of O₃ ([O₃]_{DA} and [O₃]_{MDA8}, respectively) for the three types of urban forest and the square throughout the monitoring period. Bars represent the standard error of the mean for *n* = 6 determined for each monitoring site. Different capital letters indicate significant differences with *p* < 0.01, and different lower-case letters indicate significant differences with *p* < 0.05.

The MDA8 O₃ concentration ([O₃]_{MDA8}) values for ridge forestation were significantly higher than those for the square (by 26.62%), whereas the corresponding values for foothill and valley forestation were significantly lower than those for the square (by 15.53 and 17.91%, respectively). In addition, the [O₃]_{MDA8} values for the three forests did not exceed the NAAQS Grade I (GB3095-2012) threshold

of $100 \mu\text{g m}^{-3}$ for O_3 , which was set for clean-air areas such as scenic spots and represents a level that has no effect on human health.

3.1.2. Seasonal Variation

For all forest sites, the highest $[\text{O}_3]_{\text{DA}}$ and $[\text{O}_3]_{\text{MDA8}}$ values generally appeared in summer, whereas for the square, the summer values of $[\text{O}_3]_{\text{DA}}$ and $[\text{O}_3]_{\text{MDA8}}$ were the lowest (Figure 3), in agreement with the background values of $[\text{O}_3]_{\text{DA}}$ (70.67 , 57.00 , and $32.67 \mu\text{g m}^{-3}$ for spring, autumn, and summer, respectively; not shown in the figure).

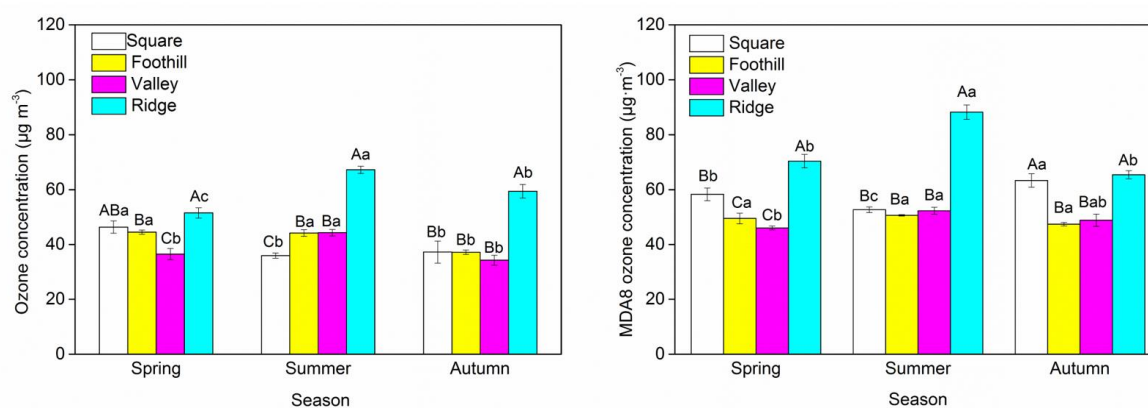


Figure 3. Seasonal and spatial variation of $[\text{O}_3]_{\text{DA}}$ and $[\text{O}_3]_{\text{MDA8}}$ for the three types of urban forest and the square. Bars represent standard errors of the mean for $n = 6$ determined for each monitoring site. Different capital letters indicate significant differences between monitoring sites for a given season ($p < 0.05$), and different lower-case letters indicate significant differences between different seasons for a given monitoring site ($p < 0.05$).

For each season, the highest $[\text{O}_3]_{\text{DA}}$ and $[\text{O}_3]_{\text{MDA8}}$ values were observed for the ridge forestation, whereas the lowest values were observed for the foothill or valley forestation except in summer. In spring, the $[\text{O}_3]_{\text{DA}}$ values for the four sites were significantly lower than background values (not shown in the figure) by $>30\%$. In summer, the $[\text{O}_3]_{\text{DA}}$ values for the three forest sites were significantly higher than those for the square and the background values (not shown in the figure) by 22.82 – 86.83% and 35.26 – 105.75% , respectively. In autumn, the $[\text{O}_3]_{\text{DA}}$ values for the foothill and valley forestation were close to that of the square and were significantly lower than the background value (not shown in the figure) by $>34.50\%$, whereas the corresponding $[\text{O}_3]_{\text{MDA8}}$ values were lower than that of the square by 20.93 and 18.56% , respectively. In each season, the $[\text{O}_3]_{\text{MDA8}}$ values for the three forest sites did not exceed the NAAQS Grade I threshold of $100 \mu\text{g m}^{-3}$ for O_3 , but the summer attainment efficiency for the ridge forestation was only 11.79% .

3.1.3. Diurnal Variation

The average diurnal cycles of O_3 concentration for all sites were similar in each season (Figure 4). In spring, the O_3 concentration was generally minimal between $03:00$ and $07:00$, rapidly increasing to reach a noon-to-afternoon maximum between $13:00$ and $17:00$ and then stably decreasing during evening hours (Figure 4a). However, the curve's shape is strongly site-dependent. For example, a steep plateau and the highest daily variation ($57.19 \mu\text{g m}^{-3}$) was observed for the ridge forestation, and flatter shapes were observed in cases of lower daily variation for foothill and valley forestation and for the square (36.04 , 31.83 , and $15.44 \mu\text{g m}^{-3}$, respectively).

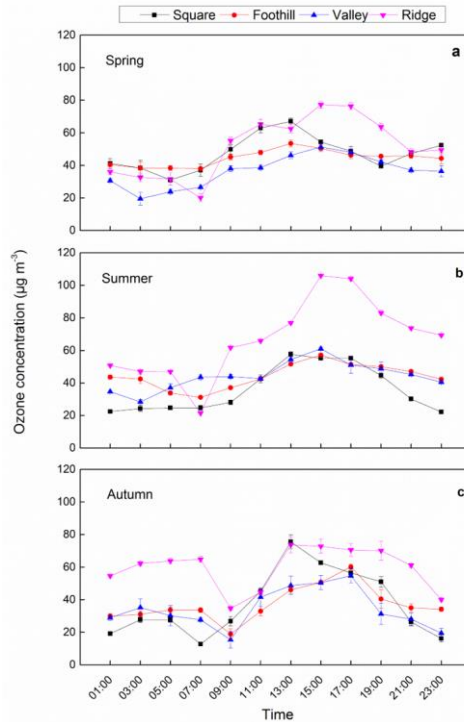


Figure 4. Mean diurnal cycles of O₃ concentration in the three types of urban forest and the square for (a) spring, (b) summer, and (c) autumn.

In summer, the mean diurnal cycles for all sites were consistent with those observed in spring (Figure 4b). The largest daily variation observed for the ridge forestation ($84.58 \mu\text{g m}^{-3}$) was significantly (1.38-fold) higher than that of the square, whereas a smaller value was observed for the valley forestation ($32.7 \mu\text{g m}^{-3}$, close to that of the square), and the smallest variation was observed for the foothill forestation ($25.94 \mu\text{g m}^{-3}$).

In autumn, the mean diurnal cycles for all sites featured a small flat plateau from 01:00 to 07:00 followed by a sharp decrease to a morning (07:00–09:00) minimum and a later rapid rise to an afternoon (13:00–17:00) maximum (Figure 4c). The largest daily variation was observed for the square, and significantly smaller values were observed for the three forest sites (decreases of 34.20–37.85%). In addition, none of the hourly O₃ concentrations in the three types of urban forest exceeded the NAAQS Grade I threshold of $160 \mu\text{g m}^{-3}$ in any season, and the attainment efficiency exceeded 34%. Thus, the ozone levels in the three types of urban forest in Yuanshan Forest Park did not reach the level of harm to human health and ranged within the clean level, which is in line with the requirements for air quality of the environment for residents' forest recreation.

For a specific site, the daily variation varied from season to season. For foothill and valley forestation, the daily variation was largest in autumn and smallest in spring. For ridge forestation, the daily variation in summer significantly exceeded those for spring and autumn (by 47.89 and 116.76%, respectively). However, for the square, the daily variation in autumn was significantly higher (by ~75%) than those determined for the other two seasons.

3.2. Micrometeorological Parameters

Figure 5 shows that the average diurnal cycles of AT, RH, and SR, but not of WS, in the three seasonal monitoring periods were similar for the four monitoring sites. In particular, hourly AT values steadily increased from 01:00 to reach a maximum between 13:00 and 17:00 and then decreased during the evening hours. Additionally, the daily variation curves for the three forest sites were milder than those for the square, and spring curves were flatter than those observed in the other two seasons for the four sites.

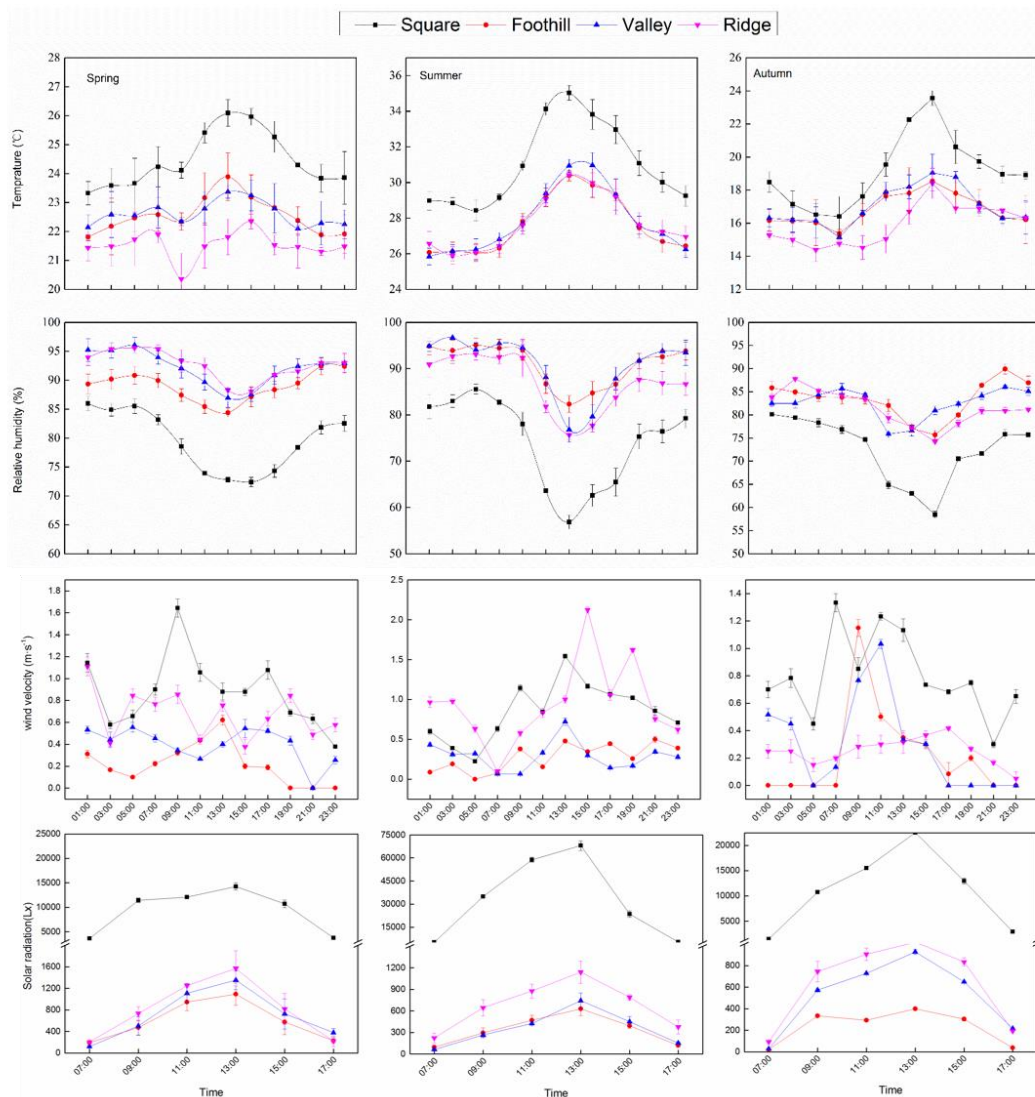


Figure 5. Mean diurnal cycles of air temperature (AT), relative humidity (RH), wind speed (WS), and solar radiation (SR) for the three types of urban forest and the square in spring, summer, and autumn. Note the different scales of the y -axis.

For RH, the diurnal cycles for all sites were opposite to those of AT in each season. Specifically, the hourly values steadily declined from 01:00, reaching a minimum between 13:00 and 15:00 and then gradually increasing. In addition, the RH values of the three forest sites were all significantly higher than that of the square in each season.

With regard to WS, the daily variation at the four sites was unstable in each season, with large WS values typically observed in the daytime (07:00–17:00) and low values in the night-time hours (19:00–05:00). Furthermore, the hourly WS values at the four sites were all lower than 2 m s^{-1} .

In each season, the SR values for the four sites exhibited a gradual rise from 07:00, reaching a maximum at 13:00 and then decreasing. The hourly SR values for the three forest sites were all significantly lower than that for the square.

3.3. Correlation of O_3 Concentration with Micrometeorological Parameters

Table 2 presents the results of Pearson correlation analysis, which reveal that the correlation between O_3 concentration and micrometeorological factors is site- and season-dependent. In spring, for all sites, O_3 concentration was significantly negatively correlated with AT ($r = -0.838$, $p < 0.0001$ for foothill forestation; $r = -0.693$, $p < 0.0005$ for valley forestation; $r = -0.655$, $p < 0.0005$ for ridge forestation; $r = -0.534$, $p = 0.001$ for the square) and RH ($r = -0.656$, $p < 0.0005$ for foothill forestation; $r = -0.656$, $p < 0.0005$ for valley forestation; $r = -0.656$, $p < 0.0005$ for ridge forestation; $r = -0.656$, $p < 0.0005$ for the square).

= -0.646, $p < 0.0005$ for valley forestation; $r = -0.480$, $p = 0.002$ for ridge forestation; $r = -0.439$, $p = 0.007$ for the square).

Table 2. Correlations between O₃ concentration and micrometeorological parameters.

Season	Site	Air Temperature	Relative Humidity	Wind Speed	Solar Radiation
Spring	Foothill	-0.838**	-0.656**	0.497**	-0.260
	Valley	-0.693**	-0.646**	0.298	-0.149
	Ridge	-0.655**	-0.480**	0.062	-0.191
	Square	-0.534**	-0.439*	0.091	-0.250
Summer	Foothill	0.485**	-0.382*	0.141	0.256
	Valley	0.780**	-0.677**	0.046	0.447*
	Ridge	0.657**	-0.590**	0.354*	0.173
	Square	0.825**	-0.806**	0.493**	0.211
Autumn	Foothill	0.634**	-0.389*	-0.247	-0.266
	Valley	0.583**	-0.441**	-0.012	0.109
	Ridge	0.499**	-0.028	0.171	-0.207
	Square	0.756**	-0.587**	0.231	0.573*

*Correlation is significant at the 0.05 level (two-tailed). **Correlation is significant at the 0.01 level (two-tailed).

In summer, for all sites, O₃ concentration was significantly positively correlated with AT ($r = 0.485$, $p = 0.003$ for foothill forestation; $r = 0.780$, $p < 0.0005$ for valley forestation; $r = 0.657$, $p < 0.0005$ for ridge forestation; $r = 0.825$, $p < 0.0001$ for the square) and significantly negatively correlated with RH ($r = -0.382$, $p = 0.022$ for foothill forestation; $r = -0.677$, $p < 0.0005$ for valley forestation; $r = -0.590$, $p < 0.0005$ for ridge forestation; $r = -0.806$, $p < 0.0001$ for the square).

In autumn, O₃ concentration was significantly positively correlated with AT ($r = 0.634$, $p < 0.0005$ for foothill forestation; $r = 0.583$, $p < 0.0005$ for valley forestation; $r = 0.499$, $p = 0.002$ for ridge forestation; $r = 0.756$, $p < 0.0005$ for the square) and significantly negatively correlated with RH for foothill forestation, valley forestation, and the square ($r = -0.389$, $p = 0.019$; $r = -0.441$, $p = 0.007$; $r = -0.587$, $p < 0.0005$, respectively). However, O₃ concentration was generally not significantly correlated with WS or SR in any season.

4. Discussion

4.1. Effect of Urban Forests on O₃ Levels

The impact of urban forests or tree canopies on O₃ concentration has been investigated by performing measurements inside and outside forests using passive samplers, but the results obtained have not been consistent. In this study, the simultaneous monitoring of O₃ levels in three kinds of urban forest representing different habitats and in a square with few trees showed that the effects of urban forests on O₃ vary with their habitat type. The spring and autumn [O₃]_{MDAS} values of foothill and valley forestation decreased significantly by over 15% compared to those of the square; this indicates that these urban forest types can reduce O₃ levels in those two seasons. Some scholars have reported based on direct empirical measurements that urban forests have the effect of reducing O₃ levels. For example, Yli-Pelkonen et al. [35] and Harris and Manning [36] showed that O₃ levels in tree-covered areas were significantly lower than those in adjacent open areas. Fantozzi et al. [37] reported that O₃ concentrations under *Quercus ilex* canopies were lower than those in open-field areas, but only in autumn. The results of this study are generally consistent with the findings of those studies. However, in this study the overall levels of O₃ in ridge forestation were significantly higher than the values measured in the square; these results suggest that the level of O₃ in ridge-type urban forest exhibits accumulation effects. This is much more likely ascribed to that the ridge site is intercepting airmasses that have been less influenced by near-surface deposition and titration by NO_x. In addition, according to the the forest canopy cover data shown on the table 1, the value of ridge forest was lower than that of foothill and valley forest, leading to more solar radiation entering

into it, and causing greater photochemical formation of O₃. On the other hand, the transport of BVOCs from foothill and/or valley to ridge by mountain valley breezes during daytime could induce their accumulation as O₃ precursors and thus promote the photochemical formation of O₃. In our study, the summer O₃ levels in the three urban forests were significantly higher than the values in the square, indicating that O₃ in urban forests accumulates in summer. These results are in agreement with the findings of Yli-Pelkonen et al. [38] and Grundstrom and Pleijel [39]. This behaviour can be ascribed to (a) the emission of BVOCs (primarily isoprene or monoterpenes) from dominant species such as *Acacia mangium*, *Schima superba*, and *Schefflera heptaphylla* in the three forests [40,41], which enhance the photochemical production of O₃, and (b) the fact that the levels of (mainly traffic-emitted) NO_x in the square exceeded those in the forests, which could lead to increased O₃ loss in the former case [42]. Notably, both of the above effects were most pronounced in summer. Sea-land breezes may be another important factor accounting for the differences between the forests and the square, i.e. land breezes during daytime could bring O₃ from the square into forests and thus induce O₃ accumulation [43].

In addition, the spring and autumn [O₃]_{DA} values for the square were significantly lower than the background data, which suggests that these urban forests do not increase local O₃ levels during those seasons. The summer [O₃]_{DA} for the square, on the other hand, was significantly higher than the background data, indicating that these urban forests may increase local O₃ levels in summer. However, the O₃ levels in the three kinds of urban forest did not exceed the NAAQS Grade I threshold, thus demonstrating that the overall air quality of these urban forests is good and suitable for recreation purposes. Additionally, the effect of urban mountain forestation on O₃ may differ from that of other types of urban forest, such as road shelter forest and residential green space. In this study, we chose only three types of urban forest representing different habitats to investigate the effect of urban forest on O₃. In order to further clarify the role of urban forests in O₃, we suggest that more systematic studies on O₃ levels in urban forests representing a wider variety of habitats be conducted.

4.2. Dynamic Change in O₃ Levels in Urban Forests

4.2.1. Spatial Variation of O₃ Levels

In our results, the levels of O₃ in ridge forestation (elevation 332 m) in each season were significantly higher than those for valley forestation (elevation 174 m) and foothill forestation (elevation 158 m), although the difference in O₃ levels between valley and foothill elevations was not obvious (Figures 2 and 3). From foothill elevation to ridge elevation, O₃ levels in the urban forests tended to increase. This result is consistent with those of previous studies conducted in mountain areas [44-46], most of which demonstrated that the concentration of O₃ increases with altitude. For example, Guo et al. [47] conducted simultaneous field measurements at various elevations on Tai Mo Shan (a mountain located in Hong Kong) and found that the O₃ concentration was greater near the summit than at the foot of the mountain, and similar results were obtained in a study carried out in the Southern Rocky Mountains [48]. Moreover, an investigation of O₃ content in Aspe (France) and Canfranc (Spain) valleys showed that the mean O₃ concentration increases upon moving from the valley bottom to the upper parts [49]. Reasons for this tendency may be explained by the fact that from foothill to ridge, the forest canopy closure gradually decreases, allowing more solar radiation to enter the forest, leading to greater photochemical formation of O₃. On the other hand, the transport of BVOCs (including isoprene, mono-/sesquiterpenes, and oxygenated compounds) as O₃ precursors from foothill and/or valley to ridge by mountain valley breezes during daytime could induce the accumulation of these species and thus promote the photochemical formation of O₃ [50-52]. In addition, the increases in WS and SR from foothill to ridge (related to forest structure and topography differences; Figure 5) could also result in O₃ level discrepancies between sites. The relationship between WS and SR and O₃ concentration in urban forests is discussed in detail in Section 4.3.

Compared to mountainous areas, urban forests are more frequently affected by urban artificial environments—e.g. urban heat islands, traffic emissions, and human disturbance—which can

promote BVOC emissions [53], and the spatial variation of O₃ concentration in urban forests may differ from that in mountainous areas. In this study, however, the spatial distribution of O₃ in urban forests representing three types of habitat is similar to that in mountain areas; this may be attributable to the better background air environment in the city of Shenzhen. For cities where air pollution is more serious, further study is needed to determine whether the spatial distribution of O₃ in urban forest presents the same characteristics.

4.2.2. Seasonal Variation of O₃ Levels

Of the seasons, the highest O₃ concentrations in the sites with three kinds of urban forest in Yuanshan Forest Park were observed in summer (Figure 3), in agreement with the results of most previous studies conducted in urban, rural, and forest areas [54-58], and in compliance with the seasonal variation of O₃ levels in Joshua Tree National Park, USA [59], as well as with the seasonal variation under tree canopies in the urban area of Siena, Italy [60]. This finding can be attributed primarily to the high BVOC levels observed in this period, especially during daytime, when tree activity and the intensity of photochemical reactions are at a maximum [61-62]. However, Wang et al. [63] characterising the levels of surface O₃ in Hong Kong, found that at most sites, maximum and minimum concentrations were observed in autumn and in summer, respectively. The difference between our study's finding and that of Wang et al. [63] may be due to differences in the seasonal cycles of sea-land breezes and wind direction.

The levels of O₃ in foothill forestation were significantly higher in spring than in autumn, whereas the reverse was true for ridge forestation; levels in the valley did not show a marked seasonal variation, which can be ascribed to the fact that the seasonal variation of BVOC emissions depends on the tree species, canopy cover, and/or forest microtopography [64-65]. The high levels of O₃ in foothill forestation can be explained by the increased BVOC emissions in spring [66], whereas the microtopography of the valley is thought to facilitate the formation of an inversion layer in spring and autumn, which is not conducive to the diffusion of O₃. On the other hand, one of the main valley species, *Ficus virens*, has been reported to be a poor isoprene emitter, resulting in the stable photochemical formation of O₃ in spring and autumn. For ridge forestation, the high levels of O₃ in autumn can be ascribed mainly to the high elevation of this area, which favours the formation of a stable boundary layer during this season and thus facilitates the NO-promoted decomposition of O₃. Thus, both our results and those previously obtained confirm the important influence of BVOCs (mainly isoprene and terpenes) on the seasonal variation of O₃ levels in urban forests, highlighting the need for future synchronous studies of O₃ and BVOC levels in such forests to clarify the corresponding quantisation relationship and thereby facilitate the construction of better recreational forest areas.

With regard to the daily variation of O₃ concentration, the diurnal cycles of all three urban forests feature a typical shape during the spring and summer periods similar to those observed in many previous studies [43,58,59,67,68]. Specifically, relatively stable concentrations were observed from midnight to early morning (with a minimum observed in the night-time or morning hours), then a maximum between 13:00 and 15:00, followed by a decrease until midnight. This trend can be explained by the diurnal cycling of O₃ source and sink levels. During the night, when photochemical production of O₃ does not occur, the titration of O₃ by NO becomes the dominant chemical process, leading to significant O₃ loss. At night, the main sources of NO in forests are from outside the area (transported in) and from soil microbial activities [69]. The night-time loss of O₃, on the other hand, can be caused by its stomatal absorption by trees and by non-stomatal removal through deposition to ground surfaces and leaf cuticles [70,71]. However, the role of these pathways is limited, which, in combination with the decreased height of the night-time boundary layer, leads to **fast** loss of O₃. Thus, **the O₃ concentration is minimal just before sunrise because of the overnight depletion**. After sunrise, the O₃ concentration begins to increase as a result of photochemical reactions and BVOC emission triggered by solar radiation. The progressively increasing difference between temperatures inside and outside the forest results in a strengthening of air convection, thus facilitating the transport of O₃ and its outside precursors into the forest, causing a constant superposition and accumulation of O₃.

At noon, there is the most photochemical production of O₃ with the largest solar radiation and enhances the accumulation of O₃ so that it reaches a maximum level in the afternoon. Subsequently, the progressive decrease in solar radiation intensity results in decreased emission of BVOCs, thus promoting O₃ depletion.

The diurnal curves of O₃ concentration obtained for autumn feature an additional small peak at nightfall or dawn. This observation can be explained by the ease of inversion layer formation in the night-time during this season, which is conducive to the intrusion of O₃-rich air from aloft down to the forest and results in O₃ accumulation, in agreement with the results of a study conducted in the Pearl River Delta [18,71,72]. In addition, we found that the times at which O₃ levels reached maxima or minima were slightly different between urban forests in each season, which might be related to differences in the factors affecting O₃ sources and sinks, e.g. forest tree composition and/or the daily variation of micrometeorological parameter values between sites.

4.3. Impact of Micrometeorological Parameters on O₃ Levels

Urban forest forms a microclimate that differs from that of an urban environment because of its ecological characteristics such as its large canopy cover, the special underlying surface, and the physiological activities of plants [73-75]. Microclimate parameters such as air temperature, relative humidity, wind speed, and solar radiation may play an important role in the formation, dispersion, and transport of O₃ [76-78].

In this study, we examined the relationship between O₃ concentrations and micrometeorological variables in urban forests to understand the effects of microclimate on O₃ levels. The results demonstrate that O₃ concentration is significantly positively correlated with AT in summer and autumn; this is similar to the finding of many existing studies in the literature [58,79,80]. However, we also found that the correlation between O₃ and AT varies with the season and that AT is significantly negatively correlated with O₃ in spring. This behaviour can be explained mainly by the fact that temperature influences O₃ levels in forests by influencing many temperature-dependent reactions, such as photochemical reactions of O₃ formation and chemical titration of O₃ loss [81]. In summer, although the solar radiation is strongest outside the forest, trees grow vigorously and the forest canopy cover is larger, which has the greatest reduction on solar radiation, so the light entering the forest is less than that in spring. But during this season, trees have the largest emission of BVOCs and temperature affects O₃ levels in the forest mainly by influencing the rate of photochemical O₃ formation; i.e. elevated temperatures promote BVOC emission and thus accelerate the rate of photochemical O₃ generation, so that O₃ concentration is significantly positively correlated with AT. In addition, based on the findings of this study, solar radiation which is related to photochemical reaction to form O₃ in forest locations is significantly higher in the spring than during summer. This can be explained that spring is characterised by the onset of the physiological activity of trees, at which time the new leaves of trees are in the stage of germination and the canopy cover of forests is relatively low. At the same time, the solar radiation increases with the increase of the solar altitude angle, while the reduction of tree canopy on solar radiation, such as reflection and scattering, is less. Therefore, the solar radiation flux into the forest is more and the solar radiation is stronger which may cause more photochemical formation of O₃ at higher temperature. However, an anti-correlation between O₃ and air temperature is seen at all of the sites in spring, this may be due to the effect of air temperature on the boundary layer height, high boundary layer height means a better dispersion condition, which may spread O₃ to aloft and decrease O₃ in the surface. The decrease of air temperature may cause the dropping of boundary layer, which is not conducive to the dispersion of O₃, and cause the accumulation of O₃. In addition, the decrease of boundary layer may also be conducive to the sinking of O₃-rich air from aloft into the forest to increase O₃ concentrations. However overall, based on the findings of this study and previous studies, it is still unclear why this correlation is seen, so that we suggest that further in-depth studies on the relationship between temperature and O₃ in different seasons should be carried out in order to clarify the effect of temperature on O₃ levels in urban forest.

With regard to the relationship between O₃ concentrations and RH, a negative correlation was found for each season, and this is consistent with most previous studies [58,78,82]. The reasons may be explained as follows. On the one hand, O₃ can deposit on water droplets. On the other hand, O₃ photolysis, followed by reaction of the O(1D) atom produced with water would increase at higher RH, and therefore contributes to O₃ loss. The formation of large amounts of water vapour at high RH increases the degree of solar radiation scattering and therefore negatively affects the photochemical production of O₃.

Many studies in urban areas have pointed out that O₃ is positively correlated with WS because of the dependence of the diffusion and transport of O₃ on WS. However, the results of Sari et al. [58] in a study of the relationship between surface O₃ levels and WS in the forest area of the Biga Peninsula, Turkey—show that the correlation coefficient between surface O₃ and WS is not high. In our study, the O₃ concentration was not found to be significantly correlated with WS, and this is in agreement with the findings of Sari et al. [58]. This behaviour can be ascribed to the fact that during our monitoring period, WS values in the forests usually did not exceed 2 m s⁻¹, whereas the tendency of forest air to form turbulent flows caused the wind speed and direction to be unstable during daytime. Therefore, under these conditions, WS had little effect on the diffusion and transport of O₃. In addition, we found that solar radiation did not significantly affect the concentration of O₃ in the forests, in contrast to results previously reported by Zhao et al. [82], Shan et al. [78], and other researchers. This difference may be related to the fact that forest crowns can significantly reduce solar radiation. In addition, a large number of investigations have shown that forest microclimate parameters such as AT, RH, WS, and SR are strongly affected by or dependent on certain ecological characteristics of forests such as tree density, speciation, canopy density, and leaf area index [83–85]. Based on this, we suggest that micrometeorological parameter values can be adjusted by changing the above factors to control O₃ levels in urban forests.

5. Conclusions

In this study, we used portable monitors to synchronously record O₃ concentrations and meteorological parameters in three types of forest representing common habitats of Yuanshan Forest Park and an adjacent square from August 2015 to April 2016. The results include the following observations and findings:

- The effects of urban forests on O₃ vary with their habitat type: In ridge urban forestation, O₃ accumulates in all seasons, but in foothill and valley urban forests, it decreases in spring and autumn.
- From foothill elevations to ridge elevations, the O₃ concentrations in the forests gradually increased, indicating that the air quality of urban forests in foothill and valley forests is better than that of ridge forestation.
- For all forest sites, the highest O₃ concentrations were observed in summer; this seems to be related to the fact that BVOC emissions during this period are at a maximum. Thus, air quality of the urban forests in spring and autumn was better than that in summer. The levels of O₃ were always high in the afternoon (13:00–17:00) and lower at night or in the early morning (03:00–09:00); this means that the best times for residents to participate in recreational activities in the forests are before 09:00.
- In the urban forests, O₃ concentration was significantly correlated with AT and RH but not with WS and SR; i.e. AT and/or RH may be the main micrometeorological factors influencing the O₃ levels. This suggests that when the habitat of urban forest is known, we can regulate the forest characteristics that affect the microclimate, such as tree density, to reduce O₃ levels in the forests.
- MDA8 and hourly concentrations of O₃ in the three types of urban forest in Yuanshan Forest Park did not exceed the NAAQS Grade I thresholds of 100 and 160 µg m⁻³, respectively, during the entire monitoring period. Thus, the air quality of these urban forests is good and is suitable for recreation purposes.

Author Contributions: W.D. analyzed data and drafted the manuscript. C.W. was involved in planning of study and designing of the work. N.P., C.Z., Z.H., X.X., participated in collecting the experiment data. The remaining authors contributed to refining the ideas, carrying out additional analyses and finalizing this paper. All authors discussed the results and revised the manuscript.

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