Ozone Trends from Two Decades of Ground Level Observation in Malaysia

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Abstract: We examine the change in surface ozone and its precursor behavior over 20 years at four locations in western Peninsular Malaysia which have undergone urban-commercial development. Trend and correlation analyses were carried out on ozone and oxides of nitrogen observation data over the periods of 1997–2016 as well as the decadal intervals of 1997–2006 and 2007–2016. Diurnal variation composites for decadal intervals were also plotted. Significant increasing ozone concentrations were observed at all locations for the 20-year period, with a range between 0.09 and 0.21 ppb yr⁻¹. The most urbanized location (S3) showed the highest ozone trend. Decadal intervals show that not all stations record significant increasing trends of ozone, with S1 recording decreasing ozone at a rate of −0.44 ppb yr⁻¹ during the latter decade. Correlation analysis showed that only oxides of nitrogen ratios (NO/NO₂) had significant inverse relationships with ozone at all stations corresponding to control of ozone by photostationary state reactions. The diurnal composites show that decadal difference in NO/NO₂ is mostly influenced by change in nitric oxide concentrations.

Keywords: ozone precursors; long term ozone measurements; gaseous pollutant ratios

1. Introduction

Surface ozone (O₃) is a pollutant that affects human health and crop yields [1–4]. O₃ studies in urban areas, particularly in the urban-commercial hub within and around Kuala Lumpur, the capital city of Malaysia, have shown frequent incidences of high O₃ and other pollutant concentrations such as particulate matter [5–7]. Within the greater Klang Valley conurbation, which is the most densely populated area in Malaysia, surface O₃ exposure has reached levels that pose significant risks to health [4]. However, a study on public perception on air quality in the area indicates that more than two-thirds of respondents did not perceive any threats to their health and have a positive outlook on the air quality status in the area. Concerns on air quality discussed in popular media in Malaysia are typically associated with severe haze episodes caused by large scale biomass burning in the region that causes perceivable reduction in visibility [8,9]. Since O₃ is a colorless gas that does not have a pungent odor, there is likely less awareness of the severity of O₃ pollution when it is not accompanied by haze episodes.
Mitigation and control of O₃ pollution is challenging as it is not a pollutant that is directly emitted into the atmosphere. O₃ is formed through reactions of precursors such as oxides of nitrogen (NOx) and volatile organic compounds (VOC) that contribute to the formation of atomic oxygen (O). Reaction of this atomic oxygen with molecular oxygen (O₂) results in the formation of O₃. Although O₃ formation from oxygen appears straightforward, O₃ photochemistry is complex. The NOx pathway of O₃ formation, for example, also involves the destruction of O₃ by nitric oxide (NO), when NO concentrations are sufficiently high [10,11]. In urban environments, O₃ formation can be classified into NOx-sensitive and VOC-sensitive regimes. In the NOx-sensitive regime, reducing NOx will result in greater reduction in O₃ compared to reducing VOC, while the opposite is true for the VOC-sensitive regime [12]. Formation of surface O₃ also requires the presence of sunlight. Hence, its level is strongly influenced not only by the complex chemical pathways involved in its formation and destruction, but also by meteorological factors that drive these reactions [10,13–15].

In Malaysia, studies on surface O₃ pollution have mostly focused on relatively short study periods of ten years or less [16–18]. These studies have explained the relationship between O₃ and its precursors as well as meteorological parameters at diurnal and seasonal scales. The monsoon seasons in Malaysia have been shown to influence the intra-annual variability of O₃ with both local and regional transport associated with seasonal winds influencing O₃ episodes in Malaysia [5,17,19]. Variability of O₃ during high particulate matters events associated with haze and non-haze episodes has also been studied, as O₃ showed a positive relationship with high particulates events at diurnal scale [20,21].

Although the seasonal and diurnal variability of O₃ in Malaysia has been extensively studied, very few studies have focused on determining long term O₃ trends, particularly in the western coast of the peninsula where the Klang Valley is located. A long term study on a background surface O₃ monitoring site showed a positive O₃ trend for the period between 1997 and 2011, associated with expanding anthropogenic activity in the surrounding area [22]. In contrast, daily maximum O₃ trends in Malaysian Borneo showed that only four out of the six available monitoring stations recorded increasing O₃ trends for the period between 2002 and 2013. It would appear that not all locations show consistently increasing trends in O₃ within the country and it is unclear if differences in O₃ trends would directly relate to its precursor trends. Given that Malaysia is a tropical country that has markedly different seasonal weather profile from countries in mid-latitudes and has been undergoing rapid urban expansion since the early 1990s, analyzing its long term O₃ behavior is expected to provide some insight into O₃ behavior in a developing country over the tropical region.

The main aim of this study is to identify O₃ and oxides of nitrogen trends over two decades at four locations in western Peninsular Malaysia that have undergone urban-commercial development. O₃ and precursor trends as well as correlation were determined, and diurnal variation composites for decadal intervals were further plotted to determine the relationship between O₃ and oxides of nitrogen over the periods of 1997–2016, 1997–2006, and 2007–2016. Decadal intervals were also included in the analysis for comparing patterns in O₃ trends to determine if the trends are still consistent when different intervals are analyzed.

2. Data and Methodology

Gaseous pollutant records between 1997 and 2016 at four stations within the Department of Environment (DoE) Malaysia’s ambient air quality network were selected and analyzed (Figure 1). Station selection was done based on pollutant data availability for the duration of the study and its location within Peninsular Malaysia. The Malaysian peninsula can be divided into the western, eastern, and southern region as the Titiwangsa mountain range bisects the peninsula from the north to more than two-thirds of Peninsular Malaysia toward the south. The topography influences meteorology such as the difference in seasonal rainfall between the east and west [23]. Western Peninsular Malaysia has more densely populated areas and commercial-industrial zones compared to the east.
Hourly O$_3$ measurements were made using a UV absorption O$_3$ analyzer (Teledyne Model 400A, San Diego, CA, USA). NO and NOx measurements as well as NO$_2$ readings were obtained from the Teledyne Model 200A analyzer (San Diego, CA, USA). Carbon monoxide (CO) measurements were taken using a Teledyne Model 300 analyzer (San Diego, CA, USA). Sulphur dioxide (SO$_2$) measurements were made using Teledyne Model 100A/E (San Diego, CA, USA). Additional information on instruments can be found in Latif et al. (2014) [22]. For the period between 1997 and 2016, the DoE contracted the measurements of pollutants and the calibration of equipment for the continuous air quality monitoring network to Alam Sekitar Malaysia Sdn. Bhd. Calibration and maintenance schedules include daily autocalibration for all pollutants and monthly maintenance. Data transferred to the DoE used here are data that have undergone calibration and maintenance schedules that were designed based on United States Environmental Protection Agency standards.

Data from the DoE were preprocessed to discard zero readings for pollutant concentration, and no computational method was used to replace or impute hourly missing value for the pollutants. To reduce the impact on data homogeneity, if large continuous missing values were present in O$_3$ data, only stations that recorded 10% or less hourly missing data within the 20-year period were selected. These were then further checked to determine that no more than 25% of these hourly data were missing each year. For all other pollutants, the total missing value had to be less than 30%, while the annual missing value had to be less than 50% to fulfil station selection criteria. The 50% cut-off is deemed acceptable, given that Malaysia is a tropical country without large seasonal variability such as those...
observed in mid latitudes. A similar cut-off point has also been employed in a Hong Kong study on long term O₃ trends [24]. Information on station location and data availability is presented in Table 1. Missing values for the monthly data are visually represented in the time series plots shown and discussed in Section 3 (Figures 4 and 6).

Table 1. Station location and data availability.

| Station ID | S1 | S2 | S3 | S4 |
|------------|----|----|----|----|
| Location   | Sungai Petani, Kedah | Tasek Ipoh, Perak | Klang, Selangor | Bukit Rambai, Melaka |
| Latitude (°N) | 5.6314 | 4.6297 | 3.0103 | 2.2585 |
| Longitude (°E) | 100.47 | 101.11 | 101.40 | 102.17 |
| % missing data for 20-year period | O₃ | 9.9 | 10.0 | 10.0 | 9.4 |
| | NOx | 9.8 | 7.7 | 10.5 | 8.9 |
| | NO | 27.6 | 21.9 | 15.1 | 18.1 |
| | NO₂ | 11.1 | 8.6 | 10.7 | 9.4 |
| | CO | 7.1 | 8.8 | 8.0 | 6.6 |
| | SO₂ | 26.7 | 17.4 | 9.0 | 14.1 |

Monthly mean (Mmean) was calculated from hourly data if 50% or more of the hourly data were available within the month. If this criterion was not fulfilled, the resultant missing monthly data were replaced with median values calculated over a sliding window of length 10 months using “movmedian” function within MATLAB 2019b. In addition to O₃, Mmean was calculated for oxides of nitrogen (NO, NO₂ and NOx) and selected pollutant ratios such as NO/NO₂, CO/NOx, and SO₂/NOx. Monthly mean for daily maximum (Mmax) values were also calculated for O₃ as the daily maximum for the period between 12 p.m. and 6 p.m. if more than 3 h of data were available within a day. The moving median method was also used to replace missing values for Mmax O₃ concentration as required.

Trend analysis on Mmean and Mmax was done using Theil-Sen estimator, which is a non-parametric method that is robust in the presence of outliers and requires little prior information regarding measurement errors [24,25]. The trend analysis was performed in R (version 3.6.2), using the “stl” function in the openair package to deseasonalize the data with Loess smoothing [26]. Loess smoothing applies a weighted least squares method for its polynomial fit and is also robust against presence of outliers [27,28]. Spearman’s Rank-Order Correlation analysis was carried out on the monthly mean (Mmean) values of the pollutants to determine the relationship between O₃ and other gaseous parameters.

Emissions data ranging from 1997 to 2015 for NOx, CO, and SO₂ were obtained from EDGARv5.0 [29,30]. The data extracted have a yearly temporal resolution and are gridded at horizontal grid spacing of 0.1° x 0.1°. To allow comparison between station point data and EDGAR’s gridded data, the “point-to-pixel comparison” approach [31] was used, whereby the value of the grid where the station point is in was extracted as station data. The number of active vehicles on road by state was obtained from the Road Transport Department of Malaysia [32].

3. Results and Discussion

3.1. Overview of Ozone Distribution

Kuala Lumpur, the capital city of Malaysia, and its surrounding area, the greater Klang Valley region, is a highly dense urban-commercial hub in Malaysia. Station S3 is located within the Klang Valley region and is close to an international shipping port. Station S2 is located north of Kuala Lumpur and the Klang Valley, while stations S1 and S4 are the locations furthest north and south, respectively, from Kuala Lumpur. Distribution of hourly O₃ within the 20-year period for all four of these stations are presented in Figure 2. The mean values were within the range of 18–21 ppb, while the medians were in the range of 11–17 ppb. Stations S1 and S4 show higher median and mean values within the 20-year period compared to stations S2 and S3. The mirror image line on each side of the boxplot shows the distribution of the hourly data as a probability density plot. These so-called violin plots
show some skewness in the distribution, as hourly values at S2 and S3 are more densely populated below the mean. S1 and S4 data also have a higher density of data distributed below the mean, but the probability density plot peak is broader at these two stations. Although the overall density and mean values indicate O$_3$ concentrations extending to higher values at stations S1 and S4, neither stations recorded the highest observations of O$_3$, and in fact, S3 recorded the highest hourly O$_3$ value of 171 ppb, followed by S2 with 158 ppb.

The violin plot provides a mirror image of the probability density function for each station. Box plots are also shown and mean values are labeled with diamond shaped markers.

The ambient air quality standard in Malaysia for hourly O$_3$ is 100 ppb [33]. Calculation of the fraction of hourly O$_3$ values higher than this threshold shows that S3 records the highest non-compliance (Figure 3). The station is also the only location to record O$_3$ non-compliance that is higher in the first decade of the study, while all the other locations show much higher occurrence of non-compliance to O$_3$ in the latter decade (2007–2016). Time series plots of O$_3$ Mmean and Mmax are shown in Figure 4a,b, respectively. Most of the monthly mean O$_3$ readings fall within the range of 10–25 ppb, while the monthly mean of daily maximum O$_3$ was mostly within the 50–100 ppb range. Mmean at S1 records a much higher occurrence of Mmean falling within the upper range of 25–35 ppb O$_3$. S3 records the highest occurrence of Mmax falling in the upper range of 100–150 ppb mostly in the earlier part of the decade (1997–2006), consistent with the results of hourly exceedance.
Figure 3. Fraction of hourly O$_3$ concentrations that were higher than 100 ppb. The fraction is calculated from total hours of O$_3$ exceedance divided by total available data for each station within the selected period.

Figure 4. Time series (1997–2016) for (a) Monthly mean O$_3$ (Mmean) and (b) Monthly mean of daily max O$_3$ (Mmax).
Although the area around all four stations has been undergoing development within the 20-year period, the locales of stations S2 and, particularly, S3 were already more urbanized compared to S1 and S4 prior to 1997 (Supplementary Figure S1 provides satellite images for the stations during December 1996 and December 2016 for comparison). Station S3 has been shown to be among the locations that record very high O$_3$ in Peninsular Malaysia [5,6,34]. Hence, the observed higher non-compliance and Mmax values at this location are largely to be expected. The hourly O$_3$ distribution and Mmean values, however, indicate that the smaller and less densely urbanized areas such as around S1 are showing higher frequency of O$_3$ concentrations falling in the upper range of the observations. To understand long term trends in O$_3$ at the monitoring stations and its possible relation to other pollutants such as NO, deseasonalized trends (Section 3.2), correlation (Section 3.3), and diurnal composites (Section 3.4) are analyzed over the 20-year study period as well as for ten year intervals of 1997–2006 and 2007–2016.

### 3.2. Trends in Ozone, Oxides of Nitrogen, and Selected Pollutant Ratios

Deseasonalized trends for O$_3$ and selected parameters are presented in Table 2. The Mmean O$_3$ for the entire study period indicates significant increasing O$_3$ at S2, S3, and S4 at $p < 0.05$, with rates of 0.19, 0.21, and 0.13 ppb yr$^{-1}$, respectively. At S1, the trend is much lower, with an increase of only 0.09 ppb yr$^{-1}$ ($p < 0.10$). Overall, these results correspond to global trends, which show increasing surface and tropospheric O$_3$ [24,35–40]. Decadal intervals, however, show that not all stations record significant increasing trends of O$_3$. For the period between 1997 and 2006, only S1 and S2 recorded significant increases in O$_3$ trends, with S1 recording the highest significant increase (0.51 ppb yr$^{-1}$) between all stations for all periods studied. Between 2007 and 2016, S1 showed a decreasing O$_3$ trend instead, at a rate of −0.44 ppb yr$^{-1}$ ($p < 0.05$), which contributed to it recording the lowest increase in O$_3$ over the entire 1997–2016 period. Stations S2, S3, and S4, meanwhile, showed significant increasing trends for the period between 2007 and 2016. S4 and S2 recorded the second and third highest rates of O$_3$ increase with 0.44 and 0.42 ppb yr$^{-1}$ ($p < 0.05$), respectively, during this period. Although the 20-year trend showed increasing O$_3$ at all stations, the O$_3$ trend over the decadal period was less consistent between stations.

|          | 1997–2006 | 2007–2016 | 1997–2016 | 1997–2006 | 2007–2016 | 1997–2016 |
|----------|-----------|-----------|-----------|-----------|-----------|-----------|
|          | Deseasonalized Mmean O$_3$ (ppb yr$^{-1}$) | Deseasonalized Mmax O$_3$ (ppb yr$^{-1}$) |          |          |          |          |
| S1       | 0.51      | −0.44     | 0.09      | 1.25      | −0.24     | 0.13      |
| S2       | 0.36      | 0.42      | 0.19      | 1.06      | 0.15      | 0.03      |
| S3       | −0.17     | 0.25      | 0.21      | −1.35     | 0.33      | −0.15     |
| S4       | −0.09     | 0.44      | 0.13      | −0.21     | 0.38      | 0.3       |

|          | Deseasonalized Mmean NO (ppb yr$^{-1}$) | Deseasonalized Mmean NO (ppb yr$^{-1}$) |          |
| S1       | 0.30      | −0.18     | 0.12      | 0.20      | 0.01      | 0.16      |
| S2       | 0.07      | −0.31     | −0.13     | 0.63      | −0.27     | 0.02      |
| S3       | −1.33     | −0.62     | −0.98     | 0.06      | 0.10      | −0.01     |
| S4       | 0.09      | 0.13      | 0.39      | 0.42      | 0.24      | 0.21      |

|          | Deseasonalized Mmean NOx (ppb yr$^{-1}$) | Deseasonalized Mmean NO/NO$_2$ (yr$^{-1}$) |          |
| S1       | 0.43      | −0.23     | 0.24      | 0.01      | −0.01     | 0.00      |
| S2       | 0.61      | −0.44     | −0.08     | −0.05     | −0.01     | −0.01     |
| S3       | −1.27     | −0.47     | −0.99     | −0.07     | −0.02     | −0.04     |
| S4       | 0.54      | 0.43      | 0.62      | −0.03     | −0.01     | 0.02      |

|          | Deseasonalized Mmean CO/NOx (yr$^{-1}$) | Deseasonalized Mmean SO$_2$/NOx (yr$^{-1}$) |          |
| S1       | −4.30     | 3.95      | −1.45     | −0.07     | 0.00      | −0.02     |
| S2       | −2.18     | 1.47      | −0.23     | −0.08     | 0.00      | −0.03     |
| S3       | −0.99     | 0.46      | −0.13     | −0.02     | 0.00 *    | −0.01     |
| S4       | −2.14     | 0.34      | −0.91     | −0.05     | 0.00      | −0.02     |

Note: Significant trends at $p < 0.05$ in bold; Significant trend at $p < 0.10$ in italics. * trend value is −0.0035 yr$^{-1}$.
Mmean for oxides of nitrogen were also examined for comparison with O\textsubscript{3} trends, since these are pollutants that play an important role in O\textsubscript{3} photochemistry. Photochemical O\textsubscript{3} formation involves a two-step process involving the dissociation of NO\textsubscript{2} in the presence of sunlight \cite{10,12}:
\[
\text{NO}_2 + h\nu \rightarrow \text{NO} + \text{O}, \tag{1}
\]
and the reaction of the oxygen atom with oxygen molecules in the presence of a third body (M):
\[
\text{O} + \text{O}_2 \overset{\text{M}}{\rightarrow} \text{O}_3. \tag{2}
\]

However, the NO from Equation (1) can rapidly react with the O\textsubscript{3}, forming NO\textsubscript{2}:
\[
\text{NO} + \text{O}_3 \rightarrow \text{NO}_2 + \text{O}_2. \tag{3}
\]

Hence, typically, O\textsubscript{3} peaks do not occur until NO concentrations have fallen, as NO can titrate O\textsubscript{3}. The NO and NO\textsubscript{x} trends over 1997–2016 both show negative trends for S2 and S3 and a non-significant trend for NO\textsubscript{2}. S4 shows significant increase in NO, NO\textsubscript{2} and NO\textsubscript{x} for all three periods studied. These trends do not consistently correspond to the Mmean O\textsubscript{3} trends either directly or inversely, and this is expected, since O\textsubscript{3} concentrations in ambient air are not solely influenced by O\textsubscript{3} photochemistry. Comparing the differences in Mmean O\textsubscript{3} trends between some of the stations, such as S3 and S4 or S2 and S3 for the period of 1997–2016, gives better insight into the ozone-precursor behavior. The difference in Mmean O\textsubscript{3} trends for the 1997–2016 period is relatively high between S3 and S4, with a value of 0.08 ppb yr\textsuperscript{-1}. However, a smaller difference of 0.02 ppb yr\textsuperscript{-1} is recorded between S2 and S3. Similarly, S1 and S4 pairing recorded a difference of only 0.04 ppb yr\textsuperscript{-1} between them. The NO and NO\textsubscript{2} trends show that it is only S2 and S3 that record decreasing levels in these species, while S1 and S4 showed increasing trends in both NO and NO\textsubscript{x} level. The NO\textsubscript{2} trends for S1 and S4 both show significant increase within a 20-year period at \( p < 0.05 \), while both S2 and S3 have non-significant trends, even at \( p < 0.10 \). The distinctive pairing reflects combination of locations that were more urbanized (S2 and S3) or less urbanized (S1 and S4) prior to 1997.

Trends of Mmax O\textsubscript{3} were more varied between stations and between the selected periods compared to Mmean trends. Only S4 shows a significant positive trend in Mmax O\textsubscript{3}, despite the increase in O\textsubscript{3} exceedance in the period between 2007–2016 compared to 1997–2006 at S1, S2, and S4. The Mmax O\textsubscript{3} trends were only significant at S4, with a rate of 0.3 ppb yr\textsuperscript{-1} for the period between 1997 and 2016. Station S3 recorded a non-significant decreasing Mmax O\textsubscript{3} trend between the 1997 and 2016 period, despite recording the highest Mmean trends for the same period. For the first decadal interval of 1997–2006, S3 showed a significant decrease in O\textsubscript{3} maxima at a rate of −1.35 ppb yr\textsuperscript{-1}, while S1 and S2 recorded significant increasing trends. In the latter interval of 2007–2016, none of the stations recorded significant trends. Given that O\textsubscript{3} maxima are more likely linked to localized influence rather than a combination of regional and local precursor distribution and meteorology \cite{41}, fewer significant trends in O\textsubscript{3} maxima in comparison to mean O\textsubscript{3} concentrations at the stations can be expected. Although there is an overall global increase in O\textsubscript{3} and regional photochemical production is an important source of O\textsubscript{3} in decadal time scales \cite{42}, local emission profiles or saturation of precursor species are sufficiently dominant to influence O\textsubscript{3} trends. It would appear that peak values of O\textsubscript{3} are less dependent upon an expected increase in emission from urban-commercial expansion, but instead reflect a unique chemistry–meteorology combination that varies on a day to day basis.

Ratios of NO/NO\textsubscript{2}, CO/NO\textsubscript{x}, and SO\textsubscript{2}/NO\textsubscript{x} were also analyzed, as these can provide some indications as to whether the location is influenced by mobile or point sources. Given that mobile sources typically have higher emissions of CO and NO\textsubscript{x}, while point sources have higher SO\textsubscript{2} and NO\textsubscript{x} emissions, high SO\textsubscript{2}/NO\textsubscript{x} paired with low CO/NO\textsubscript{x} ratios, for example, could indicate point sources \cite{43–45}. Increasing NO/NO\textsubscript{2} ratios indicate locations closer to traffic emissions \cite{46,47}. The trend for the ratios shows a decrease for all combinations at S2 and S3, despite these stations...
showing urban expansion, which is expected to cause an increase in traffic volume (Figure 5a). Figure 5a
does, however, highlight the more urbanized profile of stations S2 and S3, with vehicular counts
that are a magnitude higher than stations S1 and S4. The total emissions derived from the EDGAR
database (Figure 5b–d) also indicate that S3 has the highest emissions from all sources due to its high
population, traffic density, and urban-commercial expansion. It also shows that S1 and S2 have a more
similar emission profile to each other, unlike the pairing for the number of active vehicles on the road
(Figure 5a).

Figure 5. Time series of total active vehicle count by state for the period 2008–2015 (a) and total
emissions (all sources) for NOx, CO and SO2 for the period 1997–2015 (a–c).

3.3. Correlation of Monthly Mean Ozone with Selected Parameters

The correlation analysis is carried out on monthly means to smooth out meteorologically influenced
diurnal and intra-seasonal signals that could influence O3 behavior. However, O3 and other pollutant
concentrations are also influenced by emissions, planetary boundary layer height and long-distance
transport, in addition to chemistry and meteorology in varying degrees, depending on the time scale
chosen [39,48–51]. All of this contributes to the potentially non-linear relationship between O3 and
other pollutants. Hence, a non-parametric method was selected, as the focus is on identifying potential
relationship between O3 and the selected pollutants over the period of study that may provide insight
into relative behavior of other pollutants in relation to O3.

The correlation analysis results between O3 and selected parameters over the individual decades
are shown in Table 3. NO and NO2 showed negative and positive correlation with O3, respectively,
at all stations with the exception of negative NO2 correlation with O3 at S4 for the period between 1997
and 2006. Additionally, data from both S3 and S4 showed insignificant correlation between O3 and NO
at selected durations. Figure 6 presents time series for NO, NO2, CO, and SO2, in which S3 records
the overall highest pollutant concentrations, while S4 is the only station to show increasing NO in the
latter decade. NOx also showed no significant relationship with O3, except for S4 in the first decade
and S3 for the total study duration. With the exception of NO/NO2 ratios, none of the parameters
showed a similar significant relationship between stations when the results were compared between
the decadal and total study duration. These results are similar to the trend results, supporting our
finding that there is no clear link between ambient O3 and oxides of nitrogen observations when the
results are seen individually.
Table 3. Spearman’s Rank-Order Correlation of Mmean O3.

|   | NO  | NO2 | NOx | NO/NO2 | CO/NOx | SO2/NOx |
|---|-----|-----|-----|--------|--------|---------|
|   | 1997–2006 |     |     |        |        |         |
| S1 | -0.28 | 0.27 | -0.17 | -0.5 | 0.12 | -0.04 |
| S2 | -0.46 | 0.64 | 0.33 | -0.69 | -0.19 | -0.34 |
| S3 | -0.17 | 0.43 | 0.04 | -0.34 | 0.44 | 0.22 |
| S4 | -0.41 | -0.07 | -0.25 | -0.22 | 0.26 | 0.29 |
|   | 2007–2016 |     |     |        |        |         |
| S1 | -0.23 | 0.25 | 0.02 | -0.39 | -0.06 | 0.12 |
| S2 | -0.55 | 0.38 | 0.01 | -0.67 | 0.09 | -0.07 |
| S3 | -0.37 | 0.36 | -0.05 | -0.52 | 0.18 | 0.07 |
| S4 | -0.16 | 0.29 | 0.08 | -0.4 | 0.18 | 0.02 |

Note: Significant correlation at \( p < 0.05 \) in bold.

Figure 6. Time series of Mmean for NO (a), NO2 (b), CO (c), and SO2 (d). Data points in red are missing observations that have been filled with computed values.

All the stations showed a significant negative relationship with NO/NO2 ratios, that is, less O3 at higher NO levels. S2, for example, consistently obtained coefficient values above 0.5 within all study periods for O3 relationship with NO/NO2 ratios. O3 relationship with NO and NO2 (Equations (1)–(3)) at steady state can be represented by \( \text{O}_3 = j_{NO2} [\text{NO}_2]/k_1[\text{NO}] \), where \( j_{NO2} \) is the photolysis rate for NO2 and \( k_1 \) is the rate constant for the reaction between NO and O3 [11]. Hence, the results are in
fact more consistent with control of monthly mean O₃ levels by increasing titration of O₃ by NO into NO₂. The S1 station had shown a large difference in O₃ trends between the first decade and the last decade. However, results of the correlation analysis do not show large differences in the NO, NO₂, and NO/NO₂ relationship with O₃ between the decades. The only observable difference is in the trend of NO itself (Table 2), where NO is increasing in the first decade and decreasing in the next. Without additional information on other precursor species, such as VOC and localized emission profile, it is not possible to determine with certainty if O₃ titration caused the significant change in O₃ in the last few years of the latter decade. The CO/NOx and SO₂/NOx ratios only showed a significant relationship with O₃ at S2, S3, and S4 for the first decade and were not significant during other periods. The lack of consistency in O₃ and pollutant ratio relationship is also reflected in the differing trends of O₃ and pollutant ratio between stations (Table 2).

3.4. Diurnal Variation Composites

In order to determine if there are any changes in the diurnal profile between the decadal intervals at each station, a composite of hourly data was plotted for the period of 1997–2006 and 2007–2016 (Figure 7). The difference between the two (the latter decade minus the earlier decade) was also plotted. The decadal diurnal composites show a change in magnitude of pollutant concentration but no temporal shift (peaks occurring at similar times). O₃ shows an increase at all stations, with S3 showing the largest difference between the decades overall. NO at S2 shows a relatively small decrease in the latter decade compared to S3 that records the largest decrease in NO in the same period. S1 and S4 show an increase in NO, but with an almost similar magnitude of change to S2 and S3, respectively. NO₂ shows a much smaller decadal difference between all the stations compared to NO and hence, the NO/NO₂ differences are primarily influenced by the change in NO rather than NO₂. The change in NO, either an increase or decrease, makes only a relatively small difference to NO₂ levels. At S3, which is highly urbanized, the observations suggest that NO to NO₂ conversion (Equation (3)) and O₃ levels are controlled by local NO emissions. At S3, O₃ increases in the latter decade, while NO decreases over the same period. This is consistent with S3 being situated close to NO emission sources and strong titration of O₃ by NO. However, NO to NO₂ conversion can also be affected by formation of NO₂ via the VOC pathway. In contrast to station S3, station S4 shows increase in O₃ and increase in NO between the decades, which is consistent with increased production of NO₂ via reactions of peroxyl radicals with NO, e.g., HO₂/RO₂ + NO → OH/RO + NO₂ [10,52]. Different stations appear to show different NOx sensitivity and presumably, VOC sensitivity. Having stations with different NOx and VOC sensitivities poses additional challenge in air pollution mitigation as reduction in NOx, for example, could actually result in increasing O₃ at some locations such as S3.
Figure 7. Composite of diurnal plots for $O_3$, NO, NO$_2$, and NO/NO$_2$. 

**4. Conclusions**
4. Conclusions

The trends in deseasonalized Mmean O$_3$ show that there has been an increase in O$_3$ within the 20-year period at all the stations. Station S3, which is the most densely populated and urbanized location, recorded the highest rate of increase (0.21 ppb yr$^{-1}$, $p < 0.05$). This is followed by stations S2 and S4 at rates of 0.19 and 0.13 ppb yr$^{-1}$ ($p < 0.05$), respectively. The lowest increase in O$_3$ was recorded at S1, with a rate of 0.09 ppb yr$^{-1}$ ($p < 0.10$). Decadal intervals showed a more varied pattern in O$_3$ trends. In the first decade (1997–2006), S1 showed the highest recorded significant increase in O$_3$ (0.51 ppb yr$^{-1}$), but it then recorded the largest significant decrease in O$_3$ in the 2007–2016 period ($-0.44$ ppb yr$^{-1}$). S2 and S4 showed the largest increment over the latter decade (2007–2016), with rates of 0.42 and 0.44 ppb yr$^{-1}$, respectively. Both the NO and NOx trends were negative at S2 and S3, while S1 and S4 showed positive trends ($p < 0.05$) during the 1997–2016 period. Mmax O$_3$ trends were only significant at S4 within the 20-year period (0.3 ppb yr$^{-1}$). Correlation analysis showed that the NO/NO$_2$ ratio more consistently produced a significant negative correlation with Mmean O$_3$ irrespective of the period of analysis, which corresponds to O$_3$ control by photostationary state reactions. The diurnal composites for decadal changes suggest that the stations may have different NOx and VOC sensitivities. However, further analysis on O$_3$ sensitivity to NOx and VOC is required for conclusive evidence on the potential saturation of NOx or VOC at the locations.

Supplementary Materials: The following are available online at http://www.mdpi.com/2073-4433/11/7/755/s1, Figure S1: Satellite image of station locations in December 1996 and December 2016.

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