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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/NO_2) 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/NO_2 is mostly influenced by change in nitric oxide concentrations.

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

1. Introduction

Surface ozone (O_3) is a pollutant that affects human health and crop yields [1–4]. O_3 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 O_3 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 O_3 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 O_3 is a colorless gas that does not have a pungent odor, there is likely less awareness of the severity of O_3 pollution when it is not accompanied by haze episodes.

Mitigation and control of O_3 pollution is challenging as it is not a pollutant that is directly emitted into the atmosphere. O_3 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 (O_2) results in the formation of O_3. Although O_3 formation from oxygen appears straightforward, O_3 photochemistry is complex. The NOx pathway of O_3 formation, for example, also involves the destruction of O_3 by nitric oxide (NO), when NO concentrations are sufficiently high [10,11]. In urban environments, O_3 formation can be classified into NOx-sensitive and VOC-sensitive regimes. In the NOx-sensitive regime, reducing NOx will result in greater reduction in O_3 compared to reducing VOC, while the opposite is true for the VOC-sensitive regime [12]. Formation of surface O_3 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 O_3 pollution have mostly focused on relatively short study periods of ten years or less [16–18]. These studies have explained the relationship between O_3 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 O_3 with both local and regional transport associated with seasonal winds influencing O_3 episodes in Malaysia [5,17,19]. Variability of O_3 during high particulate matters events associated with haze and non-haze episodes has also been studied, as O_3 showed a positive relationship with high particulates events at diurnal scale [20,21].

Although the seasonal and diurnal variability of O_3 in Malaysia has been extensively studied, very few studies have focused on determining long term O_3 trends, particularly in the western coast of the peninsula where the Klang Valley is located. A long term study on a background surface O_3 monitoring site showed a positive O_3 trend for the period between 1997 and 2011, associated with expanding anthropogenic activity in the surrounding area [22]. In contrast, daily maximum O_3 trends in Malaysian Borneo showed that only four out of the six available monitoring stations recorded increasing O_3 trends for the period between 2002 and 2013. It would appear that not all locations show consistently increasing trends in O_3 within the country and it is unclear if differences in O_3 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 O_3 behavior is expected to provide some insight into O_3 behavior in a developing country over the tropical region.

The main aim of this study is to identify O_3 and oxides of nitrogen trends over two decades at four locations in western Peninsular Malaysia that have undergone urban-commercial development. O_3 and precursor trends as well as correlation were determined, and diurnal variation composites for decadal intervals were further plotted to determine the relationship between O_3 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 O_3 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.

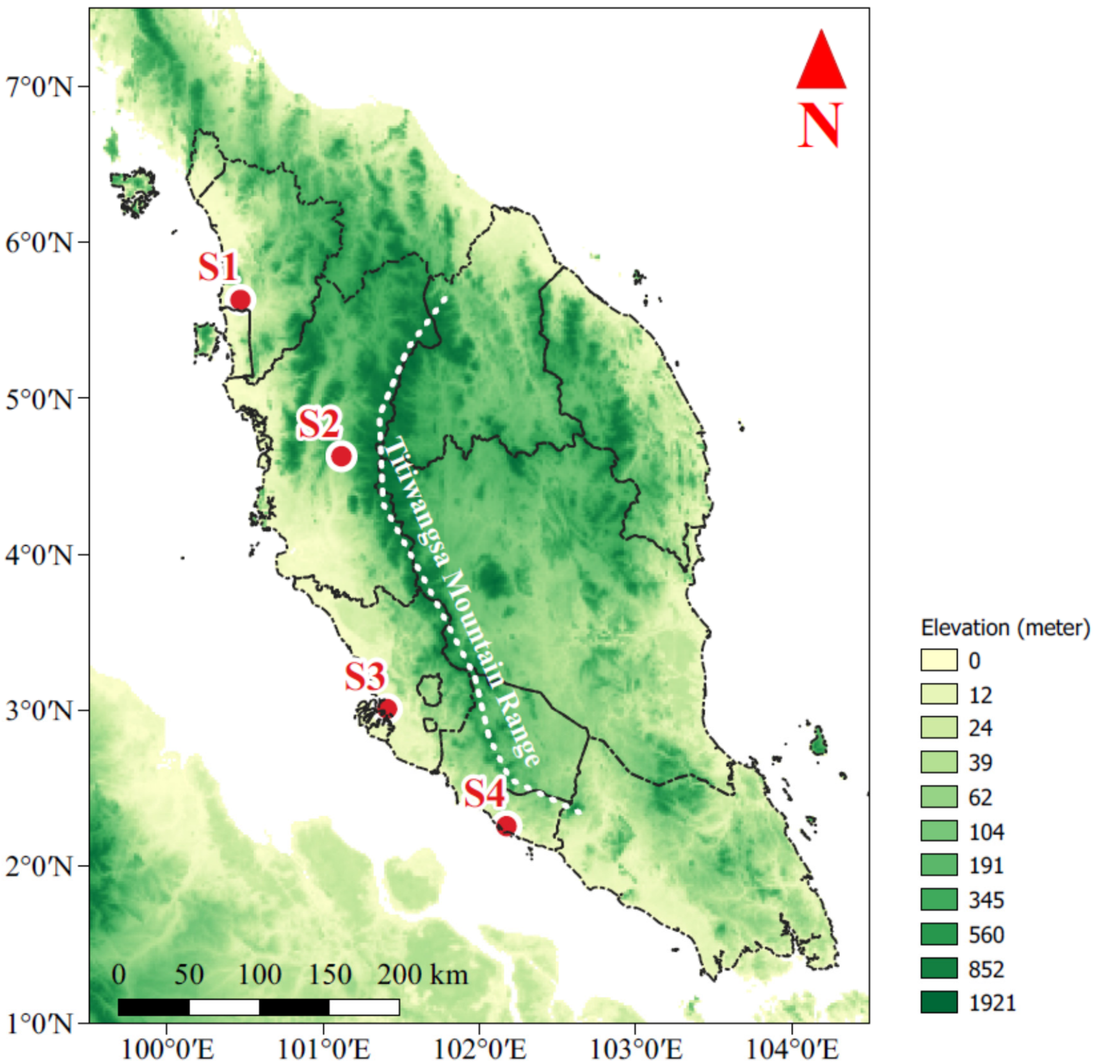

Figure 1. Location of the four monitoring stations within Peninsular Malaysia.

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 O_3 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	O_3	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
	NO_2	11.1	8.6	10.7	9.4
	CO	7.1	8.8	8.0	6.6
	SO_2	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 O_3, Mmean was calculated for oxides of nitrogen (NO, NO_2 and NOx) and selected pollutant ratios such as NO/NO_2, CO/NOx, and SO_2/NOx. Monthly mean for daily maximum (Mmax) values were also calculated for O_3 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 O_3 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 O_3 and other gaseous parameters.

Emissions data ranging from 1997 to 2015 for NOx, CO, and SO_2 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° × 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 O_3 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.

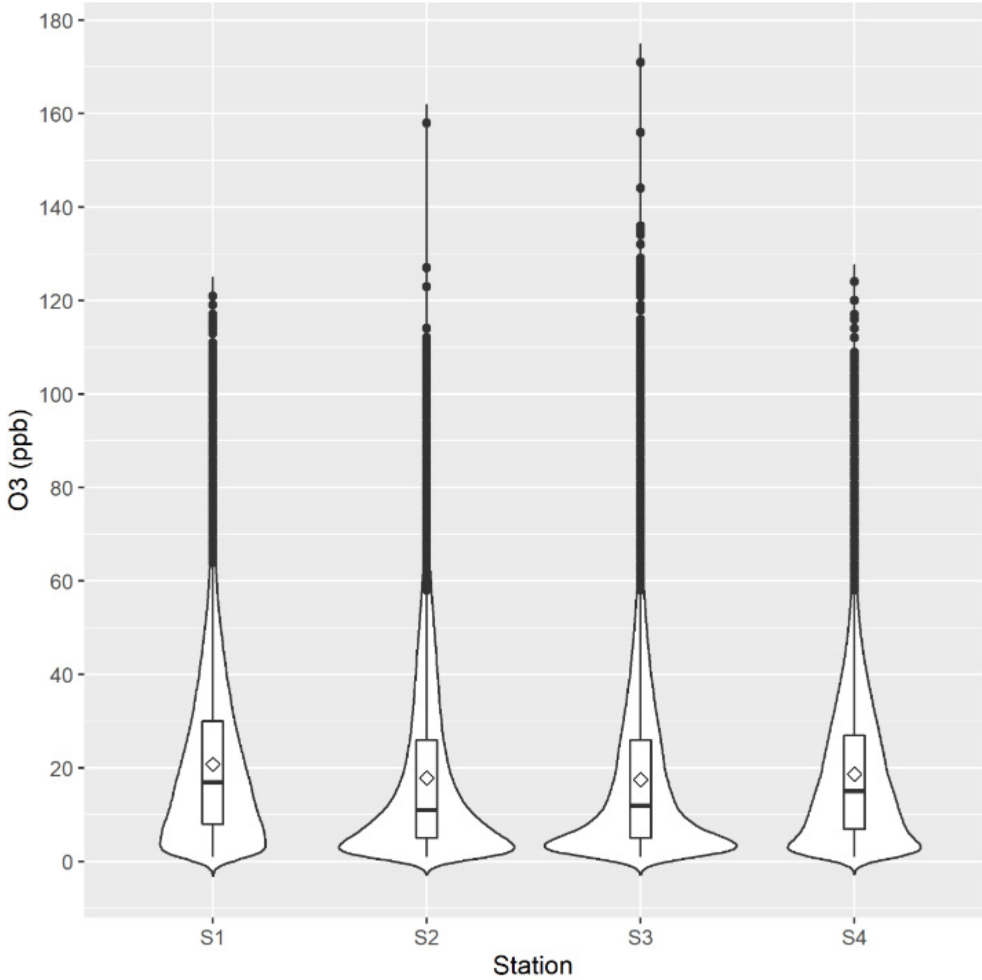

Figure 2. The violin plot provides a mirror image of the probability density function for each station. Box plots are also shown and mean values are labeled with diamond shaped markers.

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.

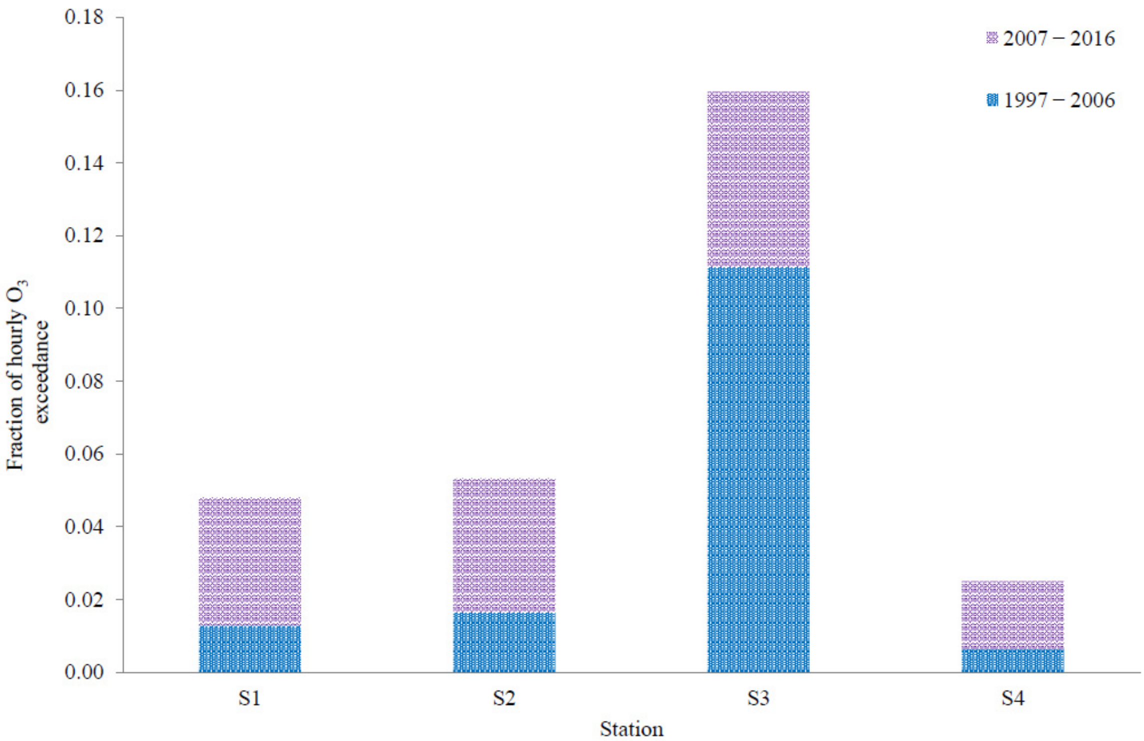

Figure 3. Fraction of hourly O_3 concentrations that were higher than 100 ppb. The fraction is calculated from total hours of O_3 exceedance divided by total available data for each station within the selected period.

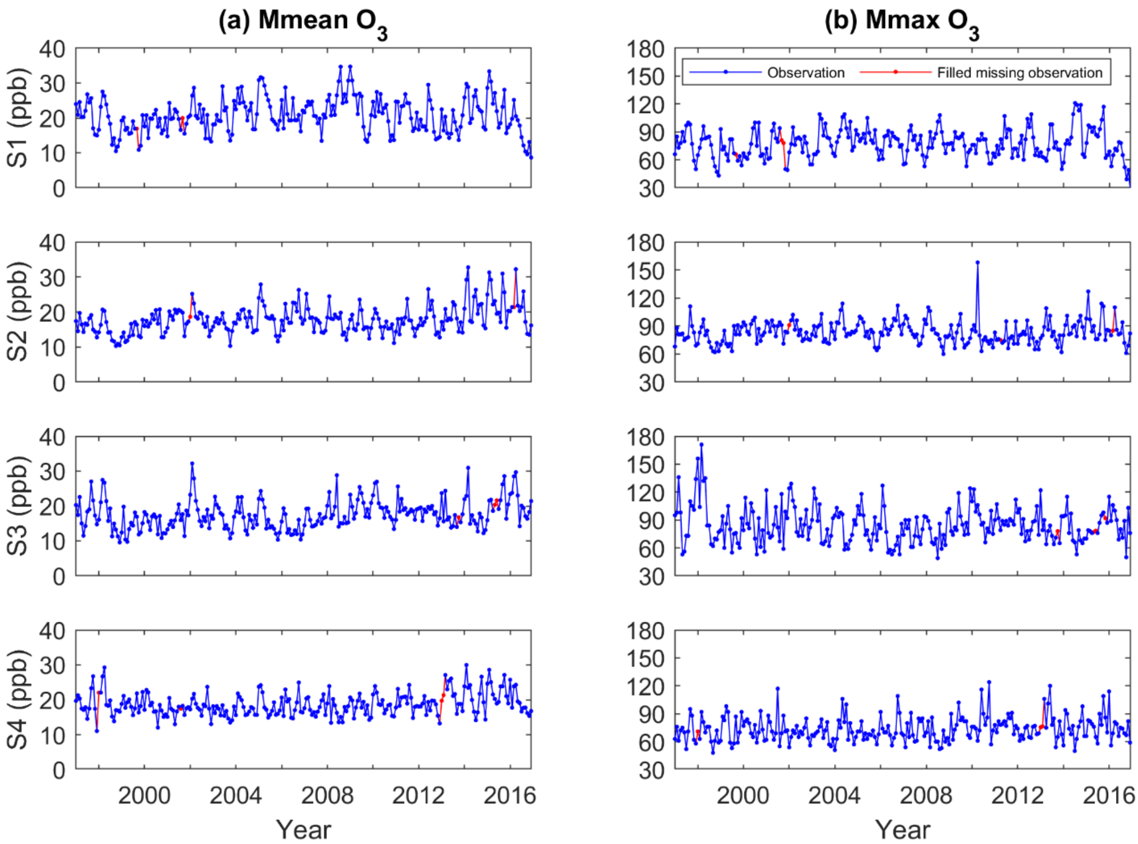

Figure 4. Time series (1997–2016) for (**a**) Monthly mean O_3 (Mmean) and (**b**) Monthly mean of daily max O_3 (Mmax).

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.

Table 2. Deseasonalized trends for monthly mean (Mmean) pollutant concentrations and monthly mean of daily maximum O_3 (Mmax O_3) concentrations.

	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_2 (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_3 trends, since these are pollutants that play an important role in O_3 photochemistry. Photochemical O_3 formation involves a two-step process involving the dissociation of NO_2 in the presence of sunlight [10,12]:

$$NO_2 + h\nu \rightarrow NO + O, \tag{1}$$

and the reaction of the oxygen atom with oxygen molecules in the presence of a third body (M):

$$O + O_2 \overset{M}{\rightarrow} O_3. \tag{2}$$

However, the NO from Equation (1) can rapidly react with the O_3, forming NO_2:

$$NO + O_3 \rightarrow NO_2 + O_2. \tag{3}$$

Hence, typically, O_3 peaks do not occur until NO concentrations have fallen, as NO can titrate O_3. The NO and NOx trends over 1997–2016 both show negative trends for S2 and S3 and a non-significant trend for NO_2. S4 shows significant increase in NO, NO_2 and NOx for all three periods studied. These trends do not consistently correspond to the Mmean O_3 trends either directly or inversely, and this is expected, since O_3 concentrations in ambient air are not solely influenced by O_3 photochemistry. Comparing the differences in Mmean O_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_3 trends for the 1997–2016 period is relatively high between S3 and S4, with a value of 0.08 ppb yr^{-1}. However, a smaller difference of 0.02 ppb yr^{-1} is recorded between S2 and S3. Similarly, S1 and S4 pairing recorded a difference of only 0.04 ppb yr^{-1} between them. The NO and NO_x 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 NOx level. The NO_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_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_3, despite the increase in O_3 exceedance in the period between 2007–2016 compared to 1997–2006 at S1, S2, and S4. The Mmax O_3 trends were only significant at S4, with a rate of 0.3 ppb yr^{-1} for the period between 1997 and 2016. Station S3 recorded a non-significant decreasing Mmax O_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_3 maxima at a rate of −1.35 ppb yr^{-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_3 maxima are more likely linked to localized influence rather than a combination of regional and local precursor distribution and meteorology [41], fewer significant trends in O_3 maxima in comparison to mean O_3 concentrations at the stations can be expected. Although there is an overall global increase in O_3 and regional photochemical production is an important source of O_3 in decadal time scales [42], local emission profiles or saturation of precursor species are sufficiently dominant to influence O_3 trends. It would appear that peak values of O_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_2, CO/NOx, and SO_2/NOx 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 NOx, while point sources have higher SO_2 and NO_x emissions, high SO_2/NOx paired with low CO/NOx ratios, for example, could indicate point sources [43–45]. Increasing NO/NO_2 ratios indicate locations closer to traffic emissions [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).

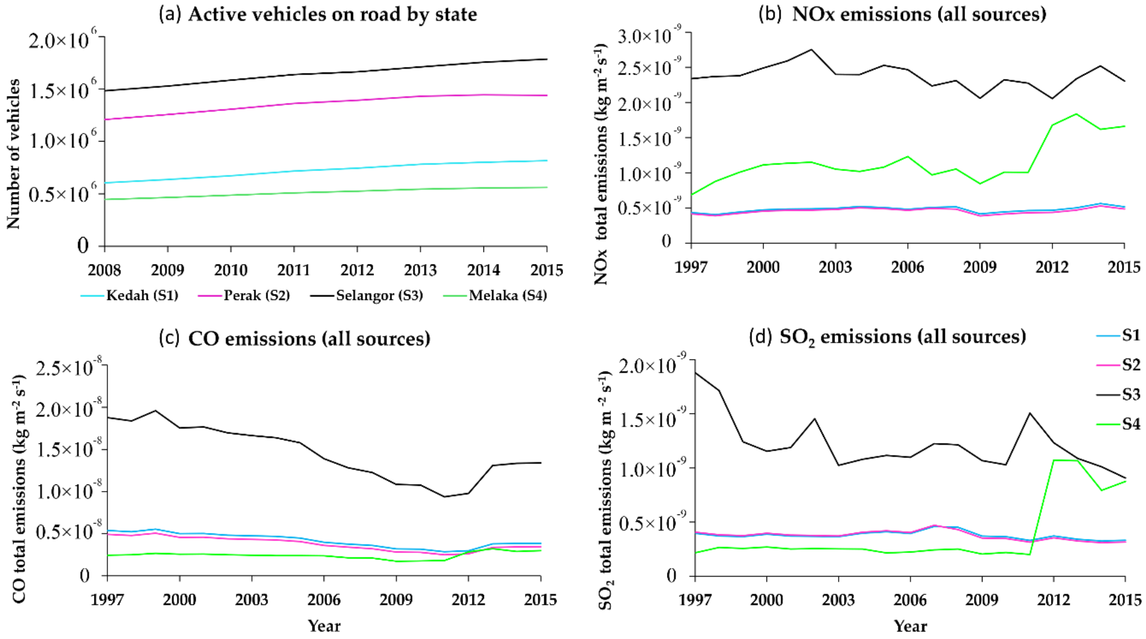

Figure 5. Time series of total active vehicle count by state for the period 2008–2015 (**a**) and total emissions (all sources) for NOx, CO and SO2 for the period 1997–2015 (**a**–**c**).

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 O_3 behavior. However, O_3 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 O_3 and other pollutants. Hence, a non-parametric method was selected, as the focus is on identifying potential relationship between O_3 and the selected pollutants over the period of study that may provide insight into relative behavior of other pollutants in relation to O_3.

The correlation analysis results between O_3 and selected parameters over the individual decades are shown in Table 3. NO and NO_2 showed negative and positive correlation with O_3, respectively, at all stations with the exception of negative NO_2 correlation with O_3 at S4 for the period between 1997 and 2006. Additionally, data from both S3 and S4 showed insignificant correlation between O_3 and NO at selected durations. Figure 6 presents time series for NO, NO_2, CO, and SO_2, 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 O_3, except for S4 in the first decade and S3 for the total study duration. With the exception of NO/NO_2 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 O_3 and oxides of nitrogen observations when the results are seen individually.

Table 3. Spearman's Rank-Order Correlation of Mmean O_3.

		NO	NO_2	NOx	NO/NO_2	CO/NOx	SO_2/NOx
				1997–2006			
S1	O_3	**−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	O_3	**−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
				1997–2016			
S1	O_3	**−0.18**	**0.27**	−0.01	**−0.43**	−0.03	−0.04
S2		**−0.51**	**0.5**	0.11	**−0.69**	−0.06	**−0.24**
S3		**−0.38**	**0.36**	**−0.18**	**−0.50**	**0.29**	−0.04
S4		−0.04	**0.18**	0.04	**−0.14**	0.12	0.01

Note: Significant correlation at $p < 0.05$ in bold.

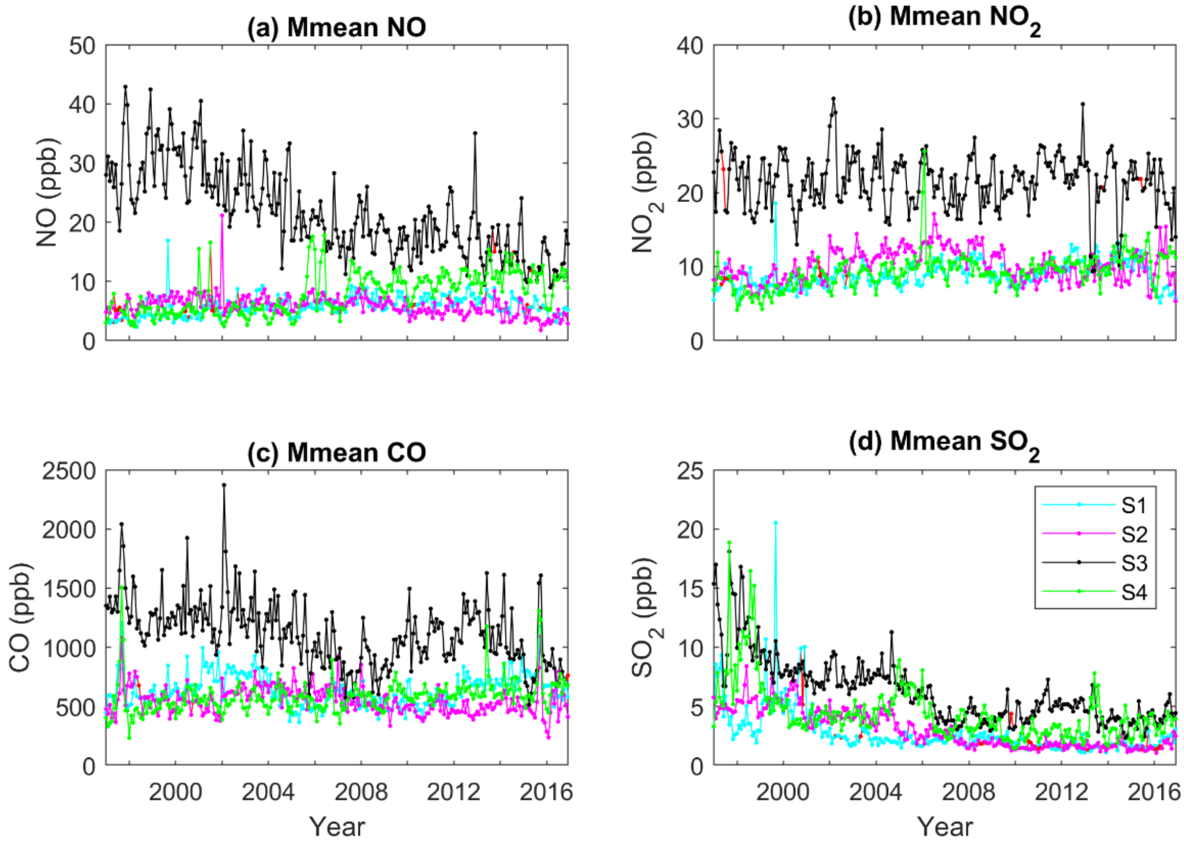

Figure 6. Time series of Mmean for NO (**a**), NO_2 (**b**), CO (**c**), and SO_2 (**d**). Data points in red are missing observations that have been filled with computed values.

All the stations showed a significant negative relationship with NO/NO_2 ratios, that is, less O_3 at higher NO levels. S2, for example, consistently obtained coefficient values above 0.5 within all study periods for O_3 relationship with NO/NO_2 ratios. O_3 relationship with NO and NO_2 (Equations (1)–(3)) at steady state can be represented by $O_3 = j_{NO2}\,[NO_2]/k_1[NO]$, where j_{NO2} is the photolysis rate for NO_2 and k_1 is the rate constant for the reaction between NO and O_3 [11]. Hence, the results are in fact more consistent with control of monthly mean O_3 levels by increasing titration of O_3 by NO into NO_2. The S1 station had shown a large difference in O_3 trends between the first decade and the last decade. However, results of the correlation analysis do not show large differences in the NO, NO_2, and NO/NO_2 relationship with O_3 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 O_3 titration caused the significant change in O_3 in the last few years of the latter decade. The CO/NOx and SO_2/NOx ratios only showed a significant relationship with O_3 at S2, S3, and S4 for the first decade and were not significant during other periods. The lack of consistency in O_3 and pollutant ratio relationship is also reflected in the differing trends of O_3 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). O_3 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. NO_2 shows a much smaller decadal difference between all the stations compared to NO and hence, the NO/NO_2 differences are primarily influenced by the change in NO rather than NO_2. The change in NO, either an increase or decrease, makes only a relatively small difference to NO_2 levels. At S3, which is highly urbanized, the observations suggest that NO to NO_2 conversion (Equation (3)) and O_3 levels are controlled by local NO emissions. At S3, O_3 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 O_3 by NO. However, NO to NO_2 conversion can also be affected by formation of NO_2 via the VOC pathway. In contrast to station S3, station S4 shows increase in O_3 and increase in NO between the decades, which is consistent with increased production of NO_2 via reactions of peroxyl radicals with NO, e.g., $HO_2/RO_2 + NO \rightarrow OH/RO + NO_2$ [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 O_3 at some locations such as S3.

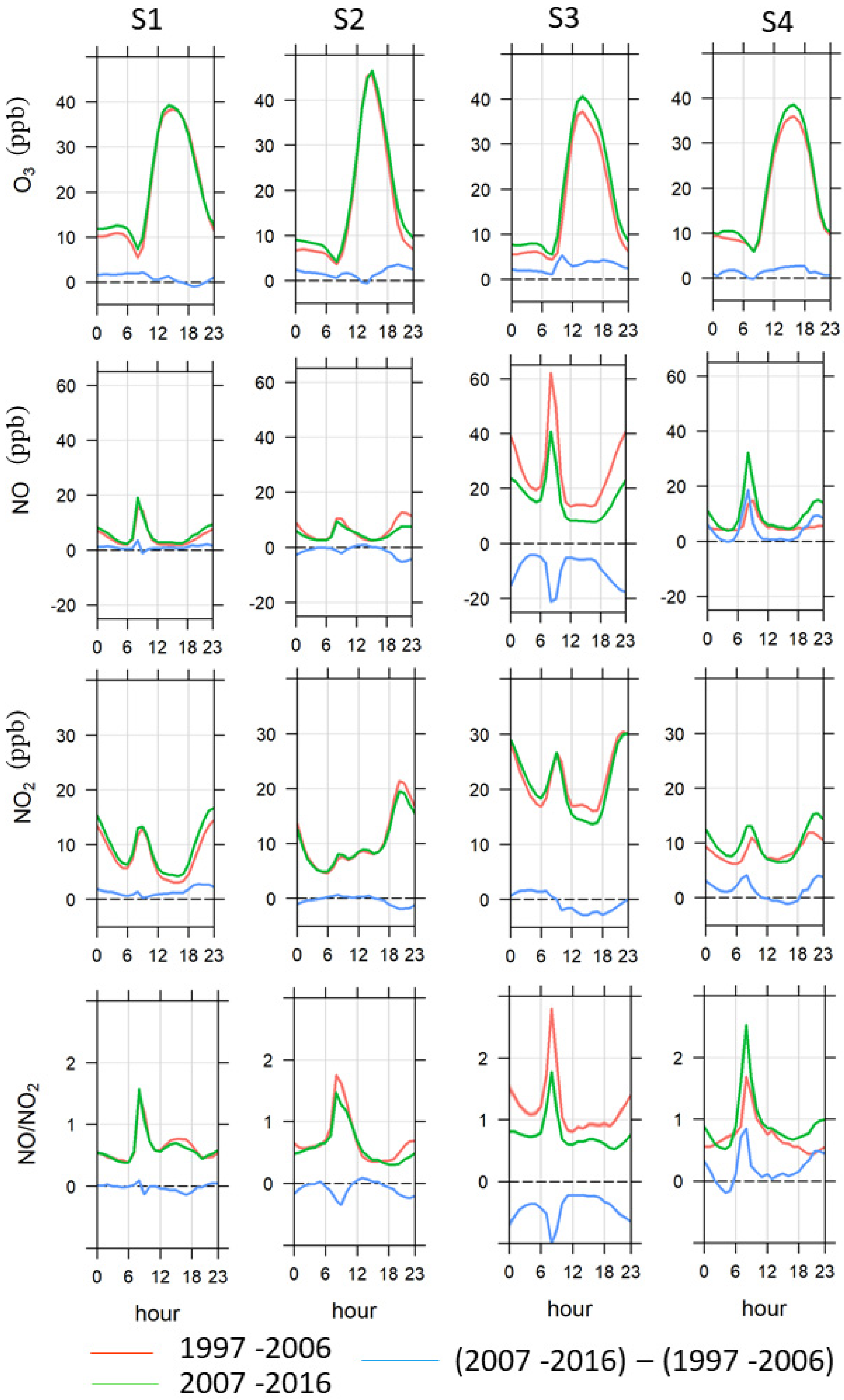

Figure 7. Composite of diurnal plots for O_3, NO, NO_2, and NO/NO_2.

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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References

1. Fleming, Z.L.; Doherty, R.; von Schneidemesser, E.; Malley, C.; Cooper, O.; Pinto, J.; Colette, A.; Xu, X.; Simpson, D.; Schultz, M.; et al. Global Ozone Distribution relevant to Human Health: Metrics and present day levels from the Tropospheric Ozone Assessment Report (TOAR). *Elem. Sci. Anth.* **2018**, *6*. [CrossRef]
2. Pleijel, H.; Broberg, M.C.; Uddling, J.; Mills, G. Current surface ozone concentrations significantly decrease wheat growth, yield and quality. *Sci. Total Environ.* **2018**, *613*, 687–692. [CrossRef] [PubMed]
3. Ishii, S.; Bell, J.; Marshall, F. Phytotoxic risk assessment of ambient air pollution on agricultural crops in Selangor State, Malaysia. *Environ. Pollut.* **2007**, *150*, 267–279. [CrossRef]
4. Wan Mahiyuddin, W.R.; Sahani, M.; Aripin, R.; Latif, M.T.; Thach, T.-Q.; Wong, C.-M. Short-term effects of daily air pollution on mortality. *Atmos. Environ.* **2013**, *65*, 69–79. [CrossRef]
5. Latif, M.T.; Huey, L.S.; Juneng, L. Variations of surface ozone concentration across the Klang Valley, Malaysia. *Atmos. Environ.* **2012**, *61*, 434–445. [CrossRef]
6. Mohtar, A.A.A.; Latif, M.T.; Baharudin, N.H.; Ahamad, F.; Chung, J.X.; Othman, M.; Juneng, L. Variation of major air pollutants in different seasonal conditions in an urban environment in Malaysia. *Geosci. Lett.* **2018**, *5*, 21. [CrossRef]
7. Azmi, S.Z.; Latif, M.T.; Ismail, A.S.; Juneng, L.; Jemain, A.A. Trend and status of air quality at three different monitoring stations in the Klang Valley, Malaysia. *Air Qual. Atmos. Health* **2010**, *3*, 53–64. [CrossRef]
8. Latif, M.T.; Othman, M.; Idris, N.; Juneng, L.; Abdullah, A.M.; Hamzah, W.P.; Khan, M.F.; Nik Sulaiman, N.M.; Jewaratnam, J.; Aghamohammadi, N.; et al. Impact of regional haze towards air quality in Malaysia: A review. *Atmos. Environ.* **2018**, *177*, 28–44. [CrossRef]

9. Keywood, M.; Ayers, G.; Gras, J.; Boers, C. Haze in the Klang valley of Malaysia. *Atmos. Chem. Phys. Discuss.* **2003**, *3*, 615–653. [CrossRef]
10. Finlayson-Pitts, B.J.; Pitts, J.N. *Chemistry of the Upper and Lower Atmosphere: Theory, Experiments and Applications*; Academic Press: San Diego, CA, USA, 2000.
11. Seinfeld, J.H.; Pandis, S.N. *Atmospheric Chemistry and Physics: From Air Pollution to Climate Change*, 2nd ed.; JohnWiley and Sons, Inc.: NewYork, NY, USA, 2006.
12. Sillman, S. The relation between ozone, NOx and hydrocarbons in urban and polluted rural environments. *Atmos. Environ.* **1999**, *33*, 1821–1845. [CrossRef]
13. Chameides, W.; Fehsenfeld, F.; Rodgers, M.; Cardelino, C.; Martinez, J.; Parrish, D.; Lonneman, W.; Lawson, D.; Rasmussen, R.; Zimmerman, P. Ozone precursor relationships in the ambient atmosphere. *J. Geophys. Res.* **1992**, *97*, 6037–6055. [CrossRef]
14. Lu, X.; Zhang, L.; Chen, Y.; Zhou, M.; Zheng, B.; Li, K.; Liu, Y.; Lin, J.; Fu, T.M.; Zhang, Q. Exploring 2016–2017 surface ozone pollution over China: Source contributions and meteorological influences. *Atmos. Chem. Phys.* **2019**, *19*, 8339–8361. [CrossRef]
15. Ellis, A.W.; Hildebrandt, M.L.; Thomas, W.M.; Fernando, H. Analysis of the climatic mechanisms contributing to the summertime transport of lower atmospheric ozone across metropolitan Phoenix, Arizona, USA. *Clim. Res.* **2000**, *15*, 13–31. [CrossRef]
16. Banan, N.; Latif, M.T.; Juneng, L.; Ahamad, F. Characteristics of Surface Ozone Concentrations at Stations with Different Backgrounds in the Malaysian Peninsula. *Aerosol Air Qual. Res.* **2013**, *13*, 1090–1106. [CrossRef]
17. Toh, Y.Y.; Lim, S.F.; Von Glasow, R. The influence of meteorological factors and biomass burning on surface ozone concentrations at Tanah Rata, Malaysia. *Atmos. Environ.* **2013**, *70*, 435–446. [CrossRef]
18. Ismail, M.; Suroto, A.; Ismail, N.A. Time series analysis of surface ozone monitoring records in Kemaman, Malaysia. In *Air Pollution—A Comprehensive Perspective*; Haryanto, B., Ed.; InTechOpen: London, UK, 2012. [CrossRef]
19. Ashfold, M.; Latif, M.; Samah, A.; Mead, M.I.; Harris, N.R. Influence of Northeast Monsoon cold surges on air quality in Southeast Asia. *Atmos. Environ.* **2017**, *166*, 498–509. [CrossRef]
20. Awang, N.R.; Ramli, N.A.; Shith, S.; Zainordin, N.S.; Manogaran, H. Transformational characteristics of ground-level ozone during high particulate events in urban area of Malaysia. *Air Qual. Atmos. Health* **2018**, *11*, 715–727. [CrossRef]
21. Awang, N.R.; Ramli, N.A.; Shith, S.; Md Yusof, N.F.F.; Zainordin, N.S.; Sansuddin, N.; Ghazali, N.A. Time effects of high particulate events on the critical conversion point of ground-level ozone. *Atmos. Environ.* **2018**, *187*, 328–334. [CrossRef]
22. Latif, M.T.; Dominick, D.; Ahamad, F.; Khan, M.F.; Juneng, L.; Hamzah, F.M.; Nadzir, M.S.M. Long term assessment of air quality from a background station on the Malaysian Peninsula. *Sci. Total Environ.* **2014**, *482*, 336–348. [CrossRef]
23. Jamaluddin, A.F.; Tangang, F.; Chung, J.X.; Juneng, L.; Sasaki, H.; Takayabu, I. Investigating the mechanisms of diurnal rainfall variability over Peninsular Malaysia using the non-hydrostatic regional climate model. *Meteorol. Atmos. Phys.* **2018**, *130*, 611–633. [CrossRef]
24. Wang, T.; Dai, J.; Lam, K.S.; Nan Poon, C.; Brasseur, G.P. Twenty-Five Years of Lower Tropospheric Ozone Observations in Tropical East Asia: The Influence of Emissions and Weather Patterns. *Geophys. Res. Lett.* **2019**, *46*, 11463–11470. [CrossRef]
25. Fernandes, R.G.; Leblanc, S. Parametric (modified least squares) and non-parametric (Theil–Sen) linear regressions for predicting biophysical parameters in the presence of measurement errors. *Remote Sens. Environ.* **2005**, *95*, 303–316. [CrossRef]
26. Carslaw, D.C.; Ropkins, K. openair—An R package for air quality data analysis. *Environ. Modell. Softw.* **2012**, *27–28*, 52–61. [CrossRef]
27. Cleveland, R.B.; Cleveland, W.S.; McRae, J.E.; Terpenning, I. STL: A seasonal-trend decomposition. *J. Off. Stat.* **1990**, *6*, 3–73.
28. Bigi, A.; Ghermandi, G.; Harrison, R.M. Analysis of the air pollution climate at a background site in the Po valley. *J. Environ. Monit.* **2012**, *14*, 552–563. [CrossRef]

29. Crippa, M.; Oreggioni, G.; Guizzardi, D.; Muntean, M.; Schaaf, E.; Lo Vullo, E.; Solazzo, E.; Monforti-Ferrario, F.; Olivier, J.; Vignati, E. *Fossil CO2 and GHG Emissions of All World Countries*; Publication Office of the European Union: Luxembourg, 2019.
30. EDGAR v5.0 Global Air Pollutant Emissions. Available online: https://edgar.jrc.ec.europa.eu/overview.php?v=50_AP (accessed on 23 June 2020). [CrossRef]
31. Tan, M.L.; Samat, N.; Chan, N.W.; Roy, R. Hydro-meteorological assessment of three GPM satellite precipitation products in the Kelantan River Basin, Malaysia. *Remote Sens.* **2018**, *10*, 1011. [CrossRef]
32. Number of Vehicles On The Road by State, Malaysia, 2008–2015. Available online: http://www.data.gov.my/data/ms_MY/dataset/bilangan-kenderaan-di-atas-jalan-raya-mengikut-negeri (accessed on 21 June 2020).
33. *Laporan Kualiti Alam Sekeliling 2016 (Environmental Quality Report)*; Department of Environment Malaysia: Putrajaya, Malaysia, 2017.
34. Awang, N.R.; Elbayoumi, M.; Ramli, N.A.; Yahaya, A.S. Diurnal variations of ground-level ozone in three port cities in Malaysia. *Air Qual. Atmos. Health* **2016**, *9*, 25–39. [CrossRef]
35. Cooper, O.R.; Parrish, D.; Ziemke, J.; Balashov, N.; Cupeiro, M.; Galbally, I.; Gilge, S.; Horowitz, L.; Jensen, N.; Lamarque, J.-F.; et al. Global distribution and trends of tropospheric ozone: An observation-based review. *Elem. Sci. Anth.* **2014**, *2*, 000029. [CrossRef]
36. Anet, J.G.; Steinbacher, M.; Gallardo, L.; Velásquez Álvarez, P.A.; Emmenegger, L.; Buchmann, B. Surface ozone in the Southern Hemisphere: 20 years of data from a site with a unique setting in El Tololo, Chile. *Atmos. Chem. Phys.* **2017**, *17*, 6477–6492. [CrossRef]
37. Nair, P.R.; Ajayakumar, R.S.; David, L.M.; Girach, I.A.; Mottungan, K. Decadal changes in surface ozone at the tropical station Thiruvananthapuram (8.542° N, 76.858° E), India: Effects of anthropogenic activities and meteorological variability. *Environ. Sci. Pollut. Res.* **2018**, *25*, 14827–14843. [CrossRef]
38. Fu, Y.; Liao, H.; Yang, Y. Interannual and decadal changes in tropospheric ozone in China and the associated chemistry-climate interactions: A review. *Adv. Atmos. Sci.* **2019**, *36*, 975–993. [CrossRef]
39. Guicherit, R.; Roemer, M. Tropospheric ozone trends. *Chemosphere Glob. Chang. Sci.* **2000**, *2*, 167–183. [CrossRef]
40. Assareh, N.; Prabamroong, T.; Manomaiphiboon, K.; Theramongkol, P.; Leungsakul, S.; Mitrjit, N.; Rachiwong, J. Analysis of observed surface ozone in the dry season over Eastern Thailand during 1997–2012. *Atmos. Res.* **2016**, *178–179*, 17–30. [CrossRef]
41. Ahamad, F.; Latif, M.T.; Tang, R.; Juneng, L.; Dominick, D.; Juahir, H. Variation of surface ozone exceedance around Klang Valley, Malaysia. *Atmos. Res.* **2014**, *139*, 116–127. [CrossRef]
42. Nagashima, T.; Sudo, K.; Akimoto, H.; Kurokawa, J.; Ohara, T. Long-term change in the source contribution to surface ozone over Japan. *Atmos. Chem. Phys.* **2017**, *17*, 8231–8246. [CrossRef]
43. Parrish, D.D.; Trainer, M.; Buhr, M.P.; Watkins, B.A.; Fehsenfeld, F.C. Carbon monoxide concentrations and their relation to concentrations of total reactive oxidized nitrogen at two rural U.S. sites. *J. Geophys. Res. Atmos.* **1991**, *96*, 9309–9320. [CrossRef]
44. Aneja, V.P.; Agarwal, A.; Roelle, P.A.; Phillips, S.B.; Tong, Q.; Watkins, N.; Yablonsky, R. Measurements and analysis of criteria pollutants in New Delhi, India. *Environ. Intern.* **2001**, *27*, 35–42. [CrossRef]
45. Goyal, P. Present scenario of air quality in Delhi: A case study of CNG implementation. *Atmos. Environ.* **2003**, *37*, 5423–5431. [CrossRef]
46. Coppalle, A.; Delmas, V.; Bobbia, M. Variability of NOx and NO2 concentrations observed at pedestrian level in the city centre of a medium sized urban area. *Atmos. Environ.* **2001**, *35*, 5361–5369. [CrossRef]
47. Mavroidis, I.; Ilia, M. Trends of NOx, NO2 and O3 concentrations at three different types of air quality monitoring stations in Athens, Greece. *Atmos. Environ.* **2012**, *63*, 135–147. [CrossRef]
48. Zhang, J.; Ouyang, Z.; Miao, H.; Wang, X. Ambient air quality trends and driving factor analysis in Beijing, 1983–2007. *J. Environ. Sci.* **2011**, *23*, 2019–2028. [CrossRef]
49. Gardner, M.W.; Dorling, S.R. Meteorologically adjusted trends in UK daily maximum surface ozone concentrations. *Atmos. Environ.* **2000**, *34*, 171–176. [CrossRef]
50. Vingarzan, R. A review of surface ozone background levels and trends. *Atmos. Environ.* **2004**, *38*, 3431–3442. [CrossRef]

51. Pusede, S.E.; Steiner, A.L.; Cohen, R.C. Temperature and recent trends in the chemistry of continental surface ozone. *Chem. Rev.* **2015**, *115*, 3898–3918. [CrossRef]
52. Manahan, S.E. *Fundamentals of Environmental Chemistry*; CRC Press: Boca Raton, FL, USA, 2011.