Variations of Selected Criteria Air Pollutants During High Particulate Event

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Abstract Nitrogen Dioxide (NO_2), Ground Level Ozone (O_3), and Particulate Matter with size less than 10 μ (PM_{10}) are air pollutants measured under the Malaysia Ambient Air Quality Guideline requirements. The focus of this research is the interaction between each criteria pollutant as well as the effects of daytime (DT), nighttime (NT), four monsoon seasons [northeast monsoon (NE), southwest monsoon (SW), 1st intermonsoon (AM) and 2nd intermonsoon (SO)] and high particulate events (HPEs) that occurred in one year towards O_3 concentrations. The hourly concentration trends of air pollutants were compared and contrasted using descriptive analysis and graphical analysis. Pearson correlation coefficient was used to analyze the relationship between PM_{10} with O_3 and O_3 with NO_2. The results show that seasonal variation has the least effect for each pollutant. Even the correlation on each pollutant is less significant, the effect to monthly mean value indicates that HPE has the highest mean value of PM_{10} concentration at 116.16 μg/m³. April–May inter-monsoon has the lowest level of all three air quality parameters with PM_{10} (24.09 μg/m³), O_3 (5.35 and 8.83 ppb) and NO_2 (6.61 and 7.93 ppb), respectively. September–October inter-monsoon has higher mean concentration than April–May (PM_{10}, 53.20 μg/m³; O_3, 22.33 ppb and NO_2, 8.29 ppb). DT and NT provide the information whereby O_3 and NO_2 are highly dependent on the daily human activities and sunlight as these two pollutants are significantly differenced between DT and NT. Besides, the study also showed that the mean concentration of PM_{10} in Taiping monitoring station has a positive correlation coefficient towards O_3, which indicate that the increase of PM_{10} will increase O_3. Essentially, during HPE, a high concentration of PM_{10} induced high formation of O_3 compared to during non-HPE.

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1 Introduction

Air pollutants measured in Malaysia Ambient Air Quality Guideline are Sulphur dioxide (SO_2), Nitrogen Dioxide (NO_2), Ground Level Ozone (O_3), Carbon Monoxide (CO), and Particulate Matter [with an aerodynamic diameter less than 10 μ (PM_{10}) and with an aerodynamic diameter less than 2.5 μ ($PM_{2.5}$)] [11]. Air Pollutant Index (API) is established to provide easy understandable information about air pollution for the public. Hourly API readings are published to the public to enable the citizen to be informed and prepare themselves if the air quality worsens [12]. Afroz et al. [1] suggest that primary sources of air pollutants in Malaysia are from land vehicles, operating industrial, and biomass burning, whereas PM_{10} and NO_2 are the primary pollutants.

In Malaysia, updated in 2019, there are 68 monitoring stations [10] designated to monitor and record the air quality continuously for 24 h per day. Malaysia has suffered from numerous particulate pollutions since 1994. Effect of these haze episodes are not only limited to human health but as well as towards economy, plants and vegetation [19]. Therefore, it's important to study the behaviour of each air pollutant.

Air pollution is affected by seasonal monsoons [2, 16] and meteorological [4–7]. PM_{10} is mainly released from the combustion of agricultural activities and forest biomasses burning [8, 9]. NO_2 is the production of burning fuel in land vehicles and factories waste gaseous [13]. Meanwhile, O_3 formed from both natural and anthropogenic sources contribute to the high level of ground-level O_3 concentration, and the spatial variation of emission sources has been widely studied [22].

PM_{10} and O_3 are air pollutants that are under most attention from many types of research as well as NO_2 that act as a precursor of ground-level O_3. Photochemical reaction of ground-level O_3 is greatly affected by the presence of UV light and its precursors. However, the effect of the existence of PM_{10} usually has been ignored because of the inactivity of both air pollutants. This study is giving focus on the screening effect of PM_{10} towards the formation of O_3 as well as towards the concentration of other pollutants. The objectives of this study are to study the behaviour of air pollutants during the non-high particulate events (non-HPEs) and high particulate events (HPEs), to study the diurnal variation of air pollutants and to establish the influence of PM_{10} towards concentration of O_3 and NO_2.

2 Methodology

2.1 Site Location

Air pollution data at Taiping monitoring station (4° 53′ 56.5″ N 100° 40′ 44.3″ E) of 2014 has been studied based on daytime/nighttime, seasonal monsoons and HPE conditions. Taiping monitoring station is categorized as an industrial area. The main contributors of O_3 precursors are vehicle emission from expressway especially during school hours. Average ambient temperatures of Taiping are around 29 °C, and annual rainfall intensity is 537.3 mm with a relative humidity approximately 85%.

2.2 Statistical Analysis

The research focuses on data collection and analysis of the concentration of O_3, NO_2, and PM_{10} to study their behavior based on each criterion and condition. Department of Environment Malaysia has provided the three types of air pollutants data, which are PM_{10}, NO_2, and O_3 at Taiping monitoring station during 2014 to carry out the objectives mentioned above. HPE incidence in Taiping gives higher value during 2014 and Taiping station was chosen as the wettest are across peninsular Malaysia. The data analysis looks into the effect of seasonal monsoons, high particulate event, daytime and nighttime. Then the hourly concentration trends of air pollutants were compared and contrasted using descriptive analysis and graphical analysis. Correlation coefficient will be used to analyse the relationship between PM_{10} with O_3 and O_3 with NO_2. Figure 1 shows the flow of this study. The analysis used 8760 data of hourly mean concentration of PM_{10}, O_3 and NO_2.

Seasonal monsoons were categorized according to the months [3] as shown in Table 1. Early November until late March is Northeast monsoon termed as NE. Early April until late May is the first inter-monsoon season termed as AM. Early June until late September is Southwest monsoon which termed as SW. Late September until late October is the second inter-monsoon season which term as SO [16]. Daytime (DT) and nighttime (NT) are categorized by time duration for DT are 7.00 a.m. until 7.00 p.m. while NT from 7.00 p.m. till 7.00 a.m.

The high particulate event (HPE) was declared when API value more than 100 for more than 72 h while second parts used the definition of HPE that stated duration whereby the concentration of PM_{10} is more than 150 µg/m^3 for more than 72 h [17]. This study adopted the New MAAQS for the concentration of PM_{10}, O_3, and NO_2 as a guideline for data analysis, as shown in Table 2. According to the new Malaysia Ambient Air Quality Standards (MAAQS), the standard value for 24 h basis of PM_{10} is 100 µg/m^3 and 90 ppb for the hourly basis of O_3 concentration. For NO_2 concentration, the guideline given a limit of 70 µg/m^3, which is
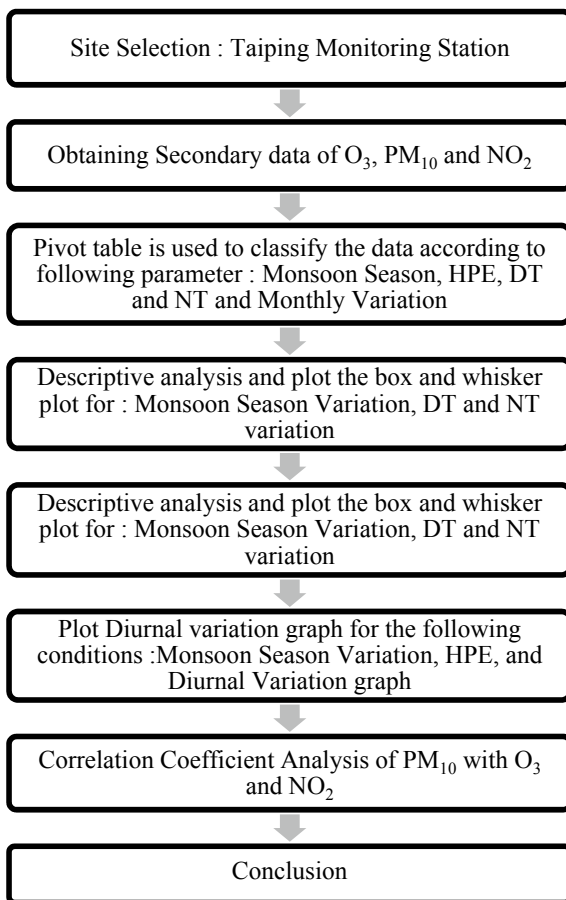
Fig. 1 Flow chart of this
study methodology

| Site Selection : Taiping Monitoring Station |

| Obtaining Secondary data of O_3, PM_{10} and NO_2 |

| Pivot table is used to classify the data according to following parameter : Monsoon Season, HPE, DT and NT and Monthly Variation |

| Descriptive analysis and plot the box and whisker plot for : Monsoon Season Variation, DT and NT variation |

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| Plot Diurnal variation graph for the following conditions :Monsoon Season Variation, HPE, and Diurnal Variation graph |

| Correlation Coefficient Analysis of PM_{10} with O_3 and NO_2 |

| Conclusion |

Table 1 Monsoonal category

Monsoon (ID)	Duration (month)
Northeast (NE)	November–March
1st Intermonsoon (AM)	April–May
Southwest (SW)	June–September
2nd Intermonsoon (SO)	October

36 ppb for 24-h basis. Meanwhile, for O_3, the guideline given a limit of 100 μg/m^3 for 8-h basis [11].

Data analysis of air pollutants is using time-series plot, descriptive analysis, diurnal plot and Pearson correlation coefficient. Time series plot is a graph of data against time whereby the time is the horizontal axis and data recorded as variables is the vertical axis. Diurnal plots have similar axis unit as time series plot. The difference is the horizontal axis represents as daily 24-h average instead of monthly

Table 2 New Malaysia ambient air quality standards 2015 [11]

Pollutants	Averaging time	Standard (2020) ($\mu g/m^3$)
Particulate Matter with the size of less than 10 μ (PM_{10})	1 Year	40
	24 h	100
Particulate Matter with the size of less than 2.5 μ ($PM_{2.5}$)	1 Year	15
	24 h	35
Sulphur dioxide (SO_2)	1 h	250
	24 h	80
Nitrogen dioxide (NO_2)	1 h	280
	24 h	70
Ground level ozone (O_3)	1 h	180
	8 h	100
Carbon monoxide (CO)	1 h	30
	8 h	10

hours average. Box and whisker plot is part of the descriptive analysis whereby comparison of mean and quartile value between different sets of results can be easily made. For correlation coefficients, Eq. (1) is used to calculate the R-value.

$$\text{Correlation coefficient, } p_{xy} = \frac{\text{cov}(x,y)}{\sigma_x \sigma_y} \tag{1}$$

where
cov (x, y): covariance of two variable x and y
$\sigma_x \sigma_y$: product of standard deviation of two variables.

Pearson Correlation coefficient takes no units and always have a value between −1.0 to +1.0. In the correlation coefficient, zero value indicates that both variables do not react with each other. The positive and negative signs of the result determine the type of interaction.

3 Results and Discussion

3.1 Variations of PM_{10}, O_3, and NO_2

Descriptive analysis of PM_{10}, O_3, and NO_2 of Taiping in 2014 are illustrated using a box and whisker plot in Fig. 2. This analysis has been carried out for three pollutants namely PM_{10}, O_3 and NO_2 during HPE, difference of seasonal variation, daytime and nighttime variation.
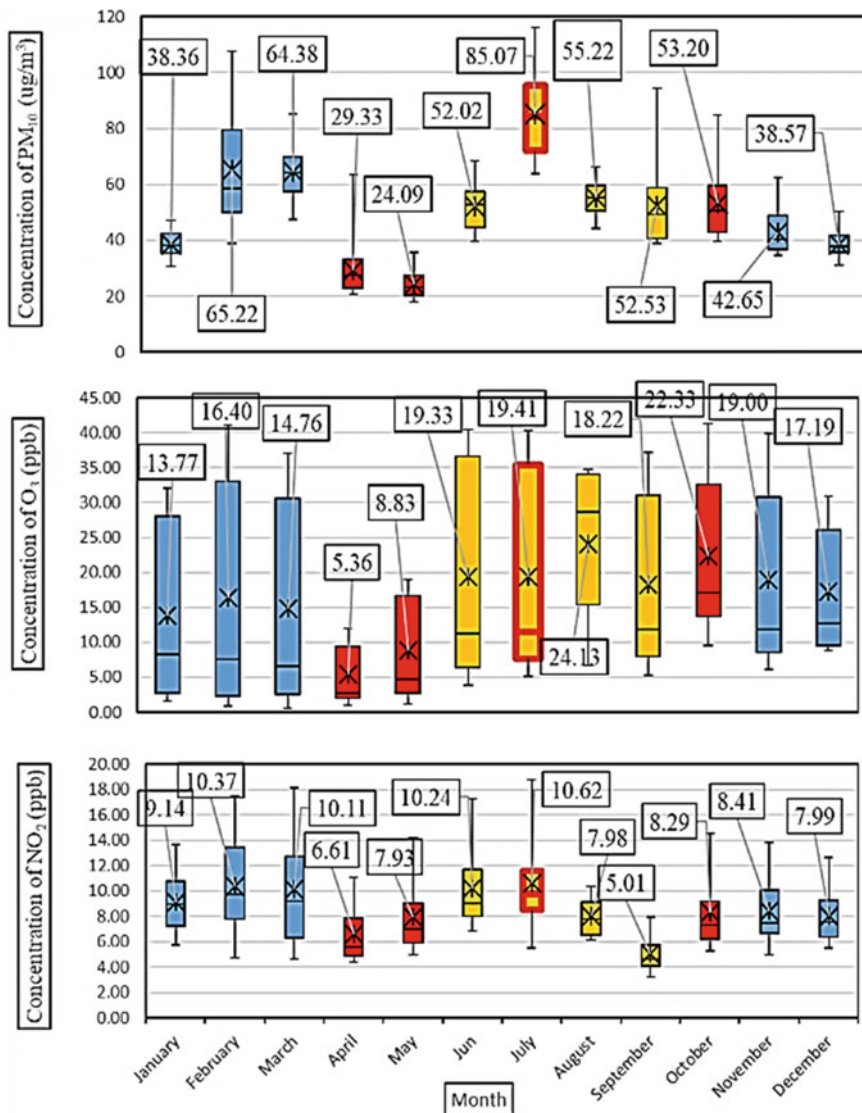
Fig. 2 Box and whisker plot of PM$_{10}$, O$_3$ and NO$_2$ (light blue: NE monsoon; Red: inter-monsoon (AM and SO); Yellow: SW monsoon, Red-Line: HPE)

For PM$_{10}$ concentration, highest mean occurred during HPE (85.07 μg/m^3). The lowest mean PM$_{10}$ concentration happened during AM, which is 29.33 μg/m^3 (April) and 24.09 μg/m^3 (May). SW and SO have an almost consistent mean value of 52.02 μg/m^3 (June), 52.53 μg/m^3 (August), 52.53 μg/m^3 (September), and 53.20 μg/m^3 (October). The highest mean O$_3$ concentration occurred during August

(24.13 ppb), then followed by SO (22.33 ppb). The lowest mean concentration shares the same trait as PM_{10} whereby April (5.36 ppb) and May (8.83 ppb), AM have the lowest concentration. Results from NO_2 concentration showed that the highest mean concentration is also during HPE (10.62 ppb). However, the lowest mean concentration is during September with only 5.01 ppb. Inter-monsoon AM having 6.61 ppb (April) and 7.93 ppb (May) while SO have 8.29 ppb. NE and SW monsoon has an average concentration ranging from 8.41 ppb (November) to 10.24 ppb (June).

Table 3 shows that from the results, PM_{10}, O_3 and NO_2 recorded the highest mean concentration in July, because the effects of HPE occurrences happen during that month. The overall view, O_3 has most fluctuated concentration from DT to NT similar as found by Tong et al. [20]. The percentage difference is ranging from 46.06% (October) to the highest of 70.37% (February). Then, NO_2 also have high percentage difference of 24.78% (April) to 58.93% (July) from DT to NT. PM_{10} percentage difference has a value of less than 10% (March, June, July, August and December), more than 10% but less than 30% (May, October and November) and rest of the months are more than 30% difference.

3.2   Seasonal Variations of PM_{10}, O_3, and NO_2

The diurnal plot revealed the behaviour of the concentration of air pollutants. In the morning where human activities are low, all three pollutants have a slightly smooth curve until daytime. Since 8.00 a.m., the concentration of O_3 begins to fluctuate until reaching its first peak at around 11.00 a.m. whereas the concentration of PM_{10}

Table 3 Mean average concentrations of PM_{10}, O_3 and NO_2 for DT and NT variation

Month	PM_{10} concentration ($\mu g/m^3$)		O_3 concentration (ppb)		NO_2 concentration (ppb)	
	DT	NT	DT	NT	DT	NT
January	38.39	38.55	20.68	6.85	7.76	10.51
February	56.21	74.24	25.3	7.49	8.54	12.2
March	64.82	63.94	20.7	8.83	7.83	12.39
April	34.72	23.95	7.98	2.75	5.88	7.34
May	25.96	22.22	13	4.66	6.64	9.22
June	53.53	50.52	27.25	10.4	8.36	12.12
July	85.81	84.34	28.21	11.61	8.50	13.03
August	55.22	48.87	24.13	11.25	7.98	11.2
September	56.72	48.34	25.29	11.14	4.27	5.75
October	59.81	46.59	29.02	15.65	7.03	9.56
November	45.84	39.47	27.19	10.85	7.29	9.54
December	38.95	38.19	22.64	11.74	6.88	9.1

increase as well. However, the concentration of NO_2 remains low during the daytime. This condition can be explained from the photochemical reaction of O_3 where the formation of NO can react with VOCs to form the stable NO_2. Therefore, the breaking and reforming of the NO_2 molecule do not affect much on the concentration. After the O_3 achieve its second peak near dusk, the UV intensity started to drop as the loss of sunlight for the transformation of O_3 [21]. However, this promotes the increase in the concentration of NO_2 to reach its peak at night.

Figure 3 illustrated that the maximum PM_{10} concentration occurred during SO with 80.20 µg/m³ and second is during NE with 79.75 µg/m³. The lowest PM_{10} mean value occurs during AM at 46.39 µg/m³. For SE, the PM_{10} maximum mean value is 63.14 µg/m³. Photochemical reaction of formation of O_3 required sunlight [18].
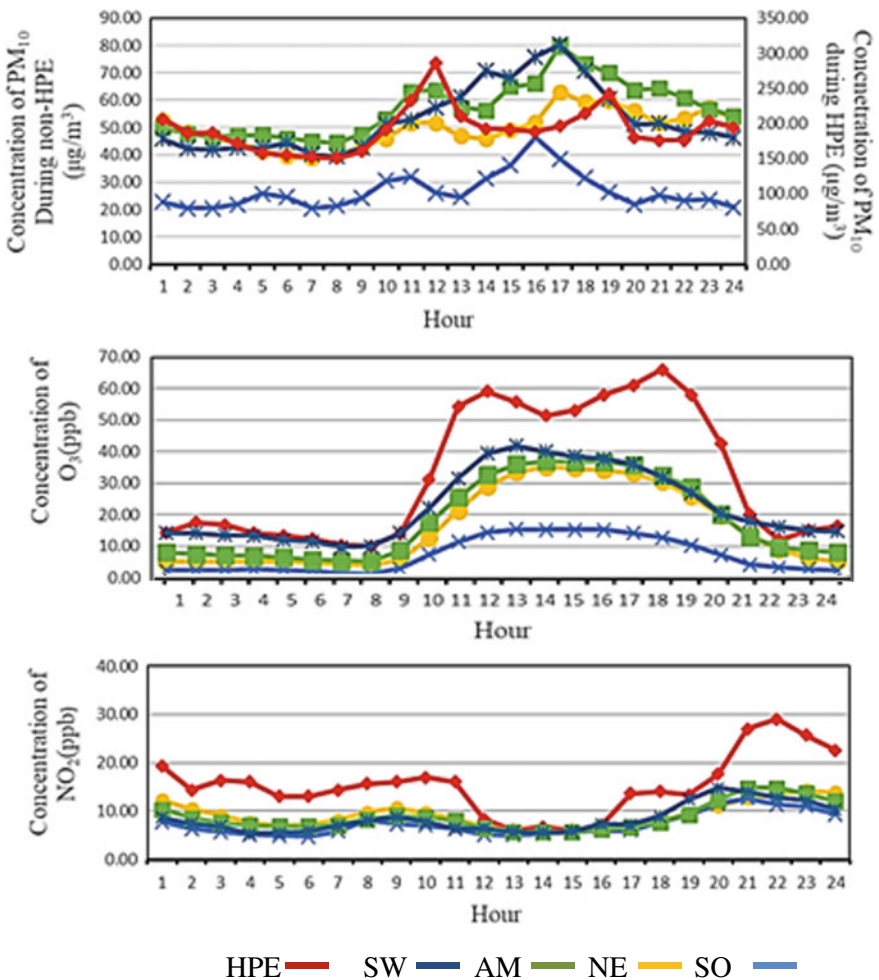

Fig. 3 Diurnal plot of PM_{10}, O_3, and NO_2 under the influence of seasonal monsoon and HPE

In Malaysia, sunrise usually occurred after 7.00 a.m. This trait can be comparable to the daily plot of O_3 concentration as the increase of O_3 concentration started only after 8.00 a.m. O_3 reached its maximum concentration at around 2.00 p.m. to 3.00 p.m. for all seasons except SO, which is at 1.00 p.m. At near dusk (5.00 p.m. to 7.00 p.m.), the sunlight got weaker eventually. Therefore, O_3 concentration started to fall. From an overview of the diurnal plot of O_3, SO has the highest trend, followed by NE and SW. AM has the lowest amongst all the seasons. NO_2 have a remarkable crest and trough pattern. Two crests occurred from 8.00 a.m. to 10.00 a. m. and 8.00 p.m. to 12.00 a.m. Two troughs occurred from 4.00 a.m. to 7.00 a.m. and 12.00 p.m. to 5.00 p.m. However, the trend was almost uniform among the monsoon seasons. This was because no season shows domination of the highest value at all in 24 h. In the morning, SE has the highest NO_2 concentration. In the afternoon, the diurnal plot shows that all seasons are having almost similar NO_2 level of 4.00–8.00 ppb (12.00 p.m. to 5.00 p.m.).

For nighttime, the concentration of NO_2 reaches a peak around 9.00 p.m.to 11.00 p.m. (12–16 ppb). The morning peaks were due to the increase in traffic volume in the morning. However, in the presence of sunlight, the concentration of NO_2 falls for the transformation of O_3 to occur. The condition remained until the night where the intensity of the sun lowered, the formation of NO_2 from NO followed by the destruction of O_3.

HPE shows a different trend compare to other seasons. For PM_{10}, two peaks were observed during HPE, which is at noon (286 $\mu g/m^3$) and 7.00 p.m. (242.33 $\mu g/m^3$). The value is very high compared to the limit set by MAAQS. The situation is similar for O_3 whereby average O_3 concentration has two peaks at noon (59.0 ppb) and 6.00 p.m. (66.0 ppb). NO_2 concentration slightly differs from diurnal plot from seasonal variation. The average concentration of NO_2 about 13.0–19.0 ppb (1.00 a.m. to 10 a.m.) and fall after 10 a.m. to slightly more than 5.0 ppb. However, the progressions of NO_2 showed a step-growth at 5.00 p.m. and maintain around 14.0 ppb. After 7.00 p.m., the concentrations increase gradually and achieve maximum value at 10.00 p.m. (29.0 ppb).

Besides, an observation of double-peaks can be noticed from the concentration of O_3. The trend of double-peaks happened where the first peak occurred during the morning, and the second peak occurred during the afternoon. It also shows that the first peak is lower than the second peak. According to Liu and Liu [14], the first peak occurred due to the vertical or horizontal transport of O_3 in the morning as well as due to a lower concentration of NO. The higher second peak is due to the increase in accumulation of ground-level O_3 due to the photochemical reactions.

3.3 Correlation Coefficient of PM_{10}, O_3, and NO_2

Table 4 shows the correlation coefficient (R-value) of PM_{10} and O_3 have ranged from +0.40 to +0.88, which is showing positive result except for February is −0.13 and this finding is similar to that found by Awang et al. [4, 5]. The correlation

Table 4 Pearson correlation coefficient of PM_{10} with O_3 and NO_2 with O_3 ($p < 0.05$)

Month	Correlation coefficient of PM_{10} and O_3	Correlation coefficient of NO_2 and O_3
January	0.48	−0.65
February	−0.13	−0.75
March	0.73	−0.74
April	0.74	−0.32
May	0.74	−0.27
June	0.76	−0.40
July	0.64	−0.49
August	0.77	−0.47
September	0.73	−0.39
October	0.88	−0.23
November	0.79	−0.24
December	0.40	−0.19

coefficient of O_3 and its precursors NO_2 shows a negative trend which varies from −0.19 to −0.75. All the results were significant at $p < 0.05$.

As NO_2 is the O_3 precursor for the photochemical transformation of O_3, the correlation coefficient of these two variables provide promising negative results that change in one pollutant gives a different influence on the concentration of the other pollutants. Results of the correlation coefficient showed that the R-value decreased from 'during non-HPE' to 'during HPE'. The photochemical formation of O_3 results in breaking a molecule of NO_2 for the completion in DT. Besides, during NT in the absence of sunlight, NO_2 does not form O_3. Therefore, a negative correlation coefficient correctly proved the condition whereby the decrease of O_3 comes together with an increase in NO_2 concentration and vice versa [15]. Thus, O_3 concentration during HPE significantly depends on precursor concentrations because an increment in precursors will promote high production in O_3 concentration. The unfavourable trends of O_3 during HPE can possibly lead to increased health risks that require immediate mitigation and prevention plans.

4 Conclusions

The study looks at the fluctuation in concentrations variabilities of PM_{10} with O_3 and its precursors in 2014 because HPE occurred. Both gaseous maximum values that were observed do not exceed the recommended value in MAAQS. During HPE, the maximum concentration of PM_{10} achieved a very unhealthy level of 346 µg/m³. Analysis of daytime and nighttime results is significant for O_3 and NO_2. O_3 have very high mean concentration during DT and become very low during NT. The situation is directly opposite of NO_2 whereby concentration during

DT is lower than during NT. This condition is supported by the Pearson correlation coefficient between NO_2 and O_3 that shown the negative value which indicates that the changes occurred in one pollutant will result in the opposite result of the other pollutants. Therefore, NO_2 has a direct negative effect on the concentration of O_3. These observations provide useful guidance that increase of PM_{10} concentration will increase in O_3 concentration. During the HPE period, screening effect of PM_{10} has positively correlated with O_3, but during non-HPE the correlation coefficient has decreased. Therefore, in nutshell, during HPE, a high concentration of PM_{10} induced high formation of O_3 compared to during non-HPE.

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