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Exploring Ozone Precursor Patterns in The Urban Area: A Case Study in Peninsular Malaysia

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Abstract

Ozone precursors are chemical compounds that interact with oxygen in the environment, leading to the formation of ozone. Volatile organic compounds (VOCs) are common ozone precursors. Ozone precursors can affect air quality and human health. The objective of this study is to investigate and evaluate ozone precursors in Cheras and Seremban in the central zone of Peninsular Malaysia using monthly data from 2018 to 2021. The Kolmogorov-Smirnov test found a p-value of less than 0.05, significantly rejecting the hypothesis of normal distribution. Exploratory data analysis was used to evaluate the data at both stations based on descriptive statistics, scatter plots, boxplots, and correlations between parameters. The maximum value of toluene from 2018 to 2021, is 5,738 ppb, which is more higher than Seremban's 2,228 ppb and than other ozone precursors in both stations. Meanwhile, the minimum of benzene, ethylbenzene and xylene in Cheras are 0.3201 ppb, 0.1470 ppb and 0.2910 ppb and in Seremban are 0.3794 ppb, 0.1770 ppb and 0.1400 ppb while the maximum value in Cheras are 1.3892 ppb, 0.7826 ppb and 1.3498 ppb and Seremban are 1.6955 ppb, 1.3117 ppb and 1.7801. Spearman's correlation shows that there is a strong positive monotonic relationship between toluene and benzene at both Cheras and Seremban stations (0.71 and 0.91) while most pollutants have a weak correlation with each other. After comparing the two locations, it was found that Cheras had a higher concentration of pollutants than Seremban. Cheras' growing economy and central location mean that there are more manufacturers, fuel-burning vehicles, and chemicals emitting into the air than in Seremban. The results of the study can help governments develop more effective strategies to reduce the release of ozone precursors into the atmosphere, which can harm humans if emission limits are exceeded.

1. Introduction

Air pollution has become a serious issue in most developed countries around the world. The term "air pollution" refers to the contamination of the air with numerous toxic compounds that hurt the ecosystem. The burning of straw, coal, and kerosene is only one of a few examples of anthropogenic sources of air pollution along with emissions from factories, fuel-burning vehicles, and aerosol cans [1-3]. A wide range of harmful pollutants, including carbon monoxide (CO), carbon dioxide (CO_2), particulate matter, nitrogen dioxide (NO_2), nitrogen oxide (NO_x), sulphur dioxide (SO_2), ozone (O3), ammonia (NH_3), volatile organic compound (VOC) and more are released onto our environment [4]. Ozone precursors are substances that react with other chemicals to produce ozone, primarily in the troposphere. Volatile organic compounds (VOCs) react in the atmosphere in the presence of sunlight, particularly the UV spectrum, and this causes much of the tropospheric ozone generation. Ozone precursors are substances like benzene, toluene, ethylbenzene, and xylene in VOCs [5]. The increase in ozone concentration in the atmosphere is causes by the high emission of VOC [6]. The harmful consequences of volatile organic chemicals on the environment and human health have generated much discussion [7, 8]. The creation of this circumstance has been greatly influenced by humans. It has been noted that continuous exposure to these harmful substances has detrimental effects even when these limits are met, even though the USEPA, WHO, and other health-related organisations have established standard limits as non-hazardous levels [9].

One of the biggest issues about human health nowadays is the prevalence of benzene (C_6H_6), toluene (C_7H_8), ethylbenzene (C_8H_{10}), and xylene (C_8H_{10}) in the air outside and within buildings [10]. BTEX also known as benzene, toluene, ethylbenzene, and xylene is the substance of the volatile ozone compound (VOC). These substances have been monitored by the Department of Environment (DOE) from the Ministry of Natural Resources, Environment and Climate Changes from July 2017 until now. BTEX has started to be popular due to the increase of this substance and the production of ozone concentration in the atmosphere [6]. These substances are naturally present in crude oil and can be detected in seawater near natural gas and petroleum sources. Gas releases from volcanoes and forest fires are two more natural sources of BTEX substances [11]. A previous study highlights BTEX as one of the present air pollutants that can affect and harm human health [10, 12] because the concentration exceeds the limit of recommendation of the Environment Protection Agency (EPA).

Exploratory data analysis (EDA) is a data analysis method that employs statistical graphics and visualization techniques to summarize key findings from large data sets. Exploratory data analysis is an important process in data analysis that involves examining a data set to summarize its key features using visual and statistical methods. It helps identify patterns, outliers' detection, test hypotheses, and prepare data for further analysis. EDA includes univariate, bivariate and multivariate analyses, using tools such as histograms, scatter plots and summary statistics. Bose & Roy Chowdhury [13] used the Spearman correlation approach to correlate the concentration of air pollutants with the effect of meteorological variables on air pollutants in India. In Luxembourg, Aggoune-Mtalaa & Laib [14] presented an exploratory data analysis of air pollution and traffic in a few cities in 2022.

Air pollution is a major problem in developed nations across the world, resulting from human activities like as burning coal, straw, and kerosene. Emissions from factories, fuel-burning automobiles, and aerosol cans have an adverse effect on ecosystems. A wide range of harmful pollutants, including volatile organic compounds (VOC) are released into our environment. The prevalence of volatile ozone compounds (VOC) like benzene, toluene, ethylbenzene, and xylene in the air is a significant health concern. Two monitoring stations, Cheras, Kuala Lumpur, and Seremban, Negeri Sembilan, positioned in the central zone and as the city center in different States, were established in response to the rising ozone concentration brought on by ozone precursors in metropolitan and developed cities. In this study, the ozone precursors (BTEX) that cause the production of ozone will be analysed by using exploratory analysis. Exploratory data analysis is a statistical method that uses visualization and graphics to summarize key findings from data sets. The purpose of this study is to explore and compare the ozone precursors in Cheras and Seremban in the central zone of Peninsular Malaysia from 2018 to 2021.

2. Study Area

Cheras is a district and an urban part of Malaysia's Klang Valley (Fig. 1). It is a built-up, self-sufficient township with lots of amenities and attractions. The distance between Cheras and the capital is 6.7 km. Cheras is a growing, self-sufficient municipality that offers a wide range of commercial businesses, educational institutions, and entertainment venues to its densely inhabited area. Seremban is the State capital of Negeri Sembilan in Peninsular Malaysia and a city in the Seremban District. Seremban is situated about 60 km south of Kuala Lumpur, the capital city of Malaysia, 50 km south of the administrative capital Putrajaya, and about 30 km inland from the coast. Part of the Malaysia Vision Valley corridor and the National Growth Conurbation, Seremban is the southern of the Greater Kuala Lumpur metropolitan area.

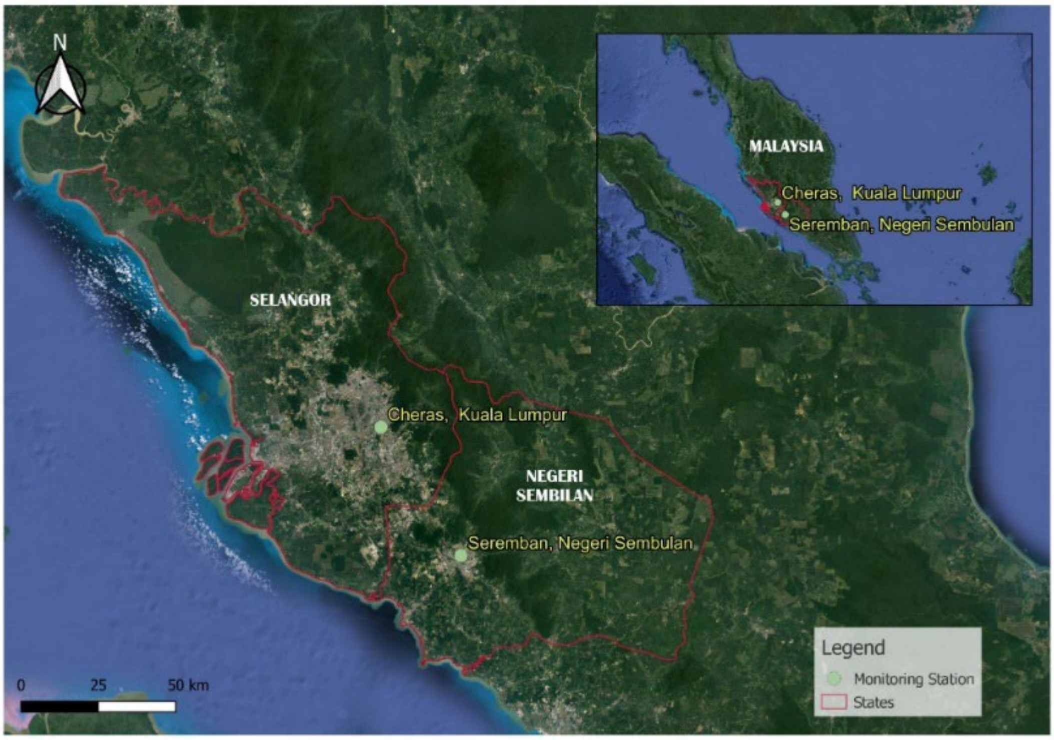


Fig. 1 *The map of Cheras and Seremban monitoring station in Peninsular Malaysia*

3. Methodology

3.1 Data Study

Two continuous air quality monitoring stations (CAQMSs) in Cheras and Seremban, Peninsular Malaysia, were used to gather the concentrations of ozone precursor. Every monitoring station's location in Peninsular Malaysia's urban region is depicted in Fig. 1. Pakar Scieno TW Sdn Bhd oversees all CAQMS on behalf of the Malaysian Department of Environment. The ozone precursor was determined using a Thermo Scientific tapered element oscillating microbalance (TEOM) 1405 DF (USA). Before the data was sent to the Malaysian Department of Environment (DOE), Pakar Scieno TW Sdn Bhd (Shah Alam, Malaysia) handled all calibration processes and quality control/quality assurance (QA/QC) of the data [15]–[19]. To assess the normality of the data, the Kolmogorov-Smirnov test was conducted. For each dataset, the p-value indicated a non-normal distribution, with $p < 0.05$. This result shows significance with a *p*-value of less than 0.05. Consequently, there is strong evidence suggesting that the data do not follow a normal distribution. In this study, ozone with measurement unit, parts per million (ppm) and BTEX in volatile organic compounds (VOC) with measurement unit, parts per billion (ppb) will be analysed in two locations which are Cheras, Kuala Lumpur, and Seremban, Negeri Sembilan. The monthly data used in the study were provided by the Department of Environment (DOE) from 2018 to 2021. Table 1 shows the description of variables in the study in volatile organic compounds (VOC).

Table 1 *Description of variable in volatile organic compound (VOC)*

No	Variable	Chemical Formula
1	Benzene	C_6H_6
2	Toluene	$C_6H_5CH_3$
3	Ethylbenzene	C_8H_{10}
4	Xylene	$C_6H_4(CH_3)_2$
5	Ozone	O_3

3.2 Exploratory Data Analysis

In this study, exploratory data analysis involving descriptive analysis, boxplot, scatter plots and Spearman correlation, was used to analyse the data of each ozone precursor parameter and compare between Cheras and

Seremban monitoring stations. Descriptive analysis, involves summarizing the main features of the data, such as mean, standard deviation (SD), median, first quantiles (Q1) and third quartiles (Q3), minimum (Min) and maximum (Max). It provided a basic understanding of the distribution and central tendencies of the ozone precursor concentrations in both Cheras and Seremban stations. While the boxplot is used to display the distribution of the data and identify any outliers. Boxplots helped in visualizing the spread and skewness of the ozone precursor concentrations, making it easier to compare the variability between the two locations. Scatter plots were utilized to observe the relationships between different ozone precursor parameters. By plotting the data points for Cheras and Seremban, scatter plots helped in identifying patterns, trends, and potential correlations between the variables.

Spearman correlation is used to measure the strength and direction of the monotonic relationship between two continuous variables [20]. Outliers in Spearman's correlation is typically less concerning than those in Pearson's analysis. Spearman's correlation is less sensitive to outliers than Pearson's correlation. This is because the Spearman correlation works with the rank of the data rather than its raw value. By converting the data to rank, the influence of extreme values is minimized, making it a robust measure for data sets that may contain outliers [21] and does not assume a normal distribution of the data. Equation of Spearman correlation in the equation (1) [22] as

$$R_s(X_i, Y_i) = 1 - \frac{6\sum_{i=1}^{k}\left(X_i^l - Y_i^l\right)^2}{k(k^2-1)} \quad (1)$$

where X_i and Y_i are the rank of X (benzene, toluene, ethylbenzene, and xylene) and Y (ozone), respectively. $d_i = X_i^l - Y_i^l$ is the corresponding order difference in equation (1). If the resulting value of d_i is close to 1, indicates a strong positive correlation between the two variables. Conversely, if it is close to -1, there is a strong negative correlation between them [23]. In this study, Spearman correlation was applied to determine the relationships between ozone and BTEX (benzene, toluene, ethylbenzene, and xylene) concentrations in both cities. The correlation coefficients provided insights into how closely related these pollutants were in each location.

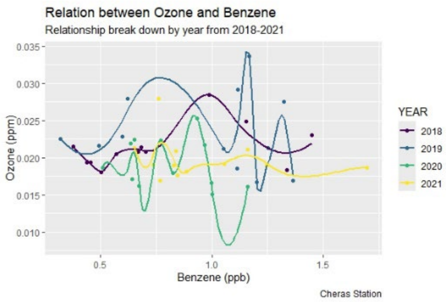
4. Results and Discussion

In the study, R language version 3.41 was used to analyse the data and QGIS 3.26.2 software was used to construct the map. Table 2 shows the descriptive analysis of two monitoring stations namely Cheras and Seremban. It contains five ozone precursors including BTEX and Ozone. Each of them is described using the mean, standard deviation (SD), median, first quantiles (Q1) and third quartiles (Q3), minimum (Min) and maximum (Max) values for each variable. Table 2 displays, the mean of toluene is 2.681 ppb and the standard deviation is 1.2673 ppb at Cheras Station. This value is higher compared to Seremban station which is 1.345 ppb for mean and 0.4452 ppb for standard deviation.

Table 2 *Descriptive statistics of ozone precursor in Cheras and Seremban from year 2018 to 2021*

Location		Mean	SD	Median	Q1	Q3	IQR	Min	Max	Skewness
Cheras	Benzene (ppb)	0.8785	0.3132	0.8337	0.6476	1.1258	0.4782	0.3201	1.6955	0.3601
	Toluene (ppb)	2.681	1.2673	2.787	1.743	3.577	1.8343	0.230	5.738	0.03123
	Ethylbenzene (ppb)	0.6502	0.2719	0.6765	0.4135	0.8008	0.3872	0.1470	1.3117	0.1395
	Xylene (ppb)	0.8582	0.3622	0.8360	0.5729	0.9959	0.4230	0.2910	1.7801	0.6888
	Ozone (ppm)	0.02097	0.0039	0.02080	0.01825	0.02233	0.0041	0.0151	0.0337	1.1323
Seremban	Benzene (ppb)	0.7690	0.2136	0.7549	0.6334	0.8612	0.2278	0.3794	1.3892	0.6115
	Toluene (ppb)	1.345	0.4452	1.340	1.033	1.665	0.6323	0.431	2.228	-0.1019
	Ethylbenzene (ppb)	0.3717	0.1305	0.3580	0.3046	0.4106	0.1060	0.1770	0.7826	1.3357
	Xylene (ppb)	0.5142	0.2718	0.4395	0.3365	0.6299	0.2935	0.1400	1.3498	1.1209
	Ozone (ppm)	0.02073	0.0029	0.02075	0.01837	0.02195	0.0036	0.0155	0.0290	0.7274

When comparing emissions from 2018 to 2021, the highest toluene dispersion value was 5,738 ppb. This is significantly higher than the 2,228-ppb recorded in Seremban, indicating a significant difference in toluene levels between the two locations. Furthermore, this maximum value surpasses other ozone precursors, emphasizing the important contribution of toluene to ozone formation during this period. Toluene is one of the most important precursor contributors to ozone and secondary organic aerosol (SOA) which have negative impact on both human health and air quality [24]. From the skewness value, all the parameters in Cheras show the data have a positive skewed (0.3601 ppb, 0.03123 ppb, 0.1395 ppb, 0.6888 ppb, 1.1323 ppb) which means the data distribution is positively skewed meanwhile, at Seremban station, the toluene shows negative skewed (-0.1019 ppb), while others show positive skewed (0.6115 ppb, 1.3357 ppb, 1.1209 ppb, 0.7274 ppb). BTEX data frequently have a skewed distribution with a lengthy tail that points towards greater concentrations. This is because certain sources, such as traffic or industrial pollutants, may result in noticeably greater BTEX levels at certain times or locations [25]. In Fig. 2, the concentration of ozone in volatile organic compounds (VOC) for BTEX is shown against the year using distinct colour labels: 2018 (purple), 2019 (blue), 2021 (green), and 2021 (yellow). By comparing the two stations namely Cheras and Seremban, the Cheras station gives a high concentration of ozone and BTEX in 2018. This explains that Cheras as an urban area with a high population index, had an increased atmospheric gas emissions from economic industry [26], [27]. Both the rise in the number of cars on the road and the frequent gas leaks from the manufacturing sector are to blame for the gas release.



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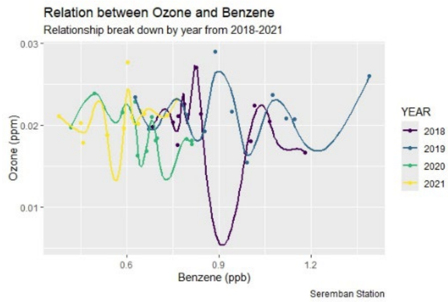

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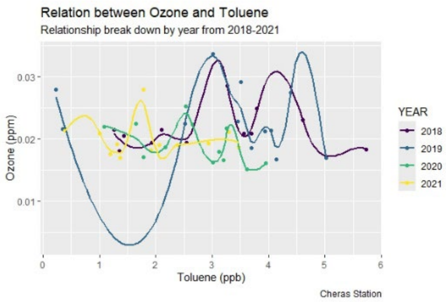

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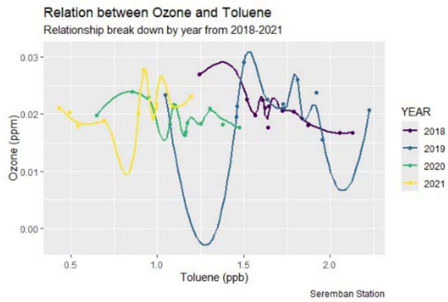

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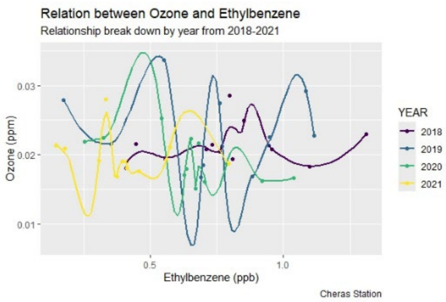

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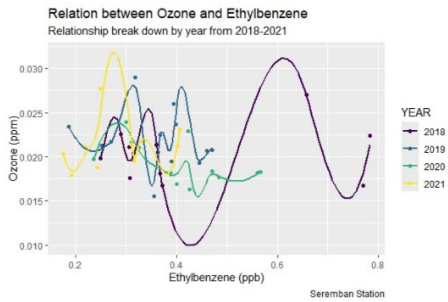

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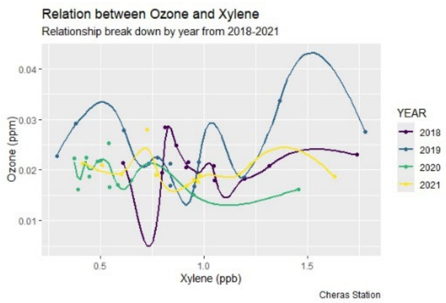

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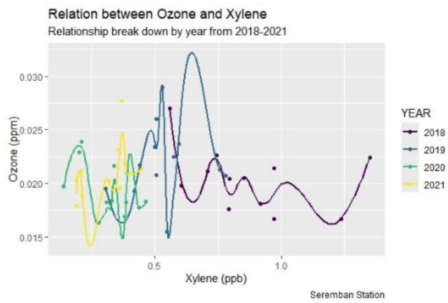

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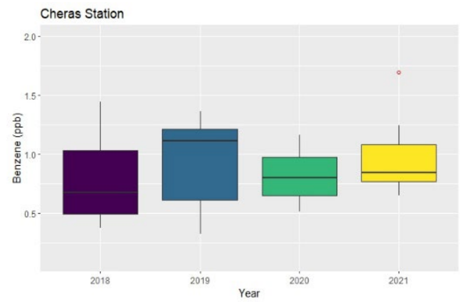
Fig. 2 *The Scatter Plot between Ozone and BTEX in Cheras station and Seremban Station*

The scatter plot from both stations increased significantly in 2019 specifically in September when there was an event of haze [18] that made several Southeast Asian countries curtail their outdoor activities [26], [28]. This episode was caused by a forest fire that occurred in Sumatra, Indonesia [29]. In 2020, it shows a low concentration between ozone and BTEX (Fig. 2). During this time, the whole world was affected by the virus COVID19 pandemic. This is due to the government's implementation of Movement Control Order (MCO) at the time, which prevented individuals from leaving their homes and encouraged them to stay indoors to stop the COVID-19 virus from spreading. As a result, most of the economic activities were temporarily closed and the use of vehicles on the road was lower than usual. The air became healthy due to the lower gas release from the industrial and vehicle sources. The concentrations of BTEX begin to gradually rise when the MCO is lifted [30]. Even though that all businesses begin to run well at this time and individuals begin to go out, some of them continue to work from home and prefer to shop online [31], [32].

Ozone concentration is influenced by the emission of VOC. From Fig. 3, in Cheras and Seremban stations, the distribution of data shows no sudden increase or decrease within 4 years. Based on temporal variability, BTEX concentrations can change dramatically over time due to a variety of factors, including weather, traffic patterns, and industrial activity [25]. The boxplots show that the spread and variation of ozone precursor emissions were lower in 2020 compared to the year before. The COVID-19 outbreak that occurred at the time was what caused most nations around the globe to impose lockdowns or restrictions. After the lockdown was removed and economic activity continued and grow regularly in 2021, emissions began to climb [33].



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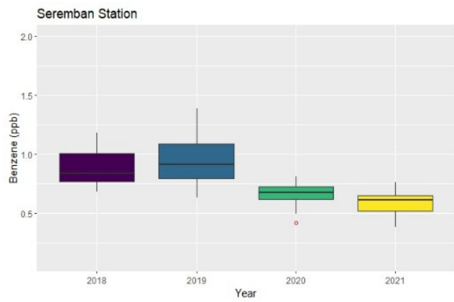

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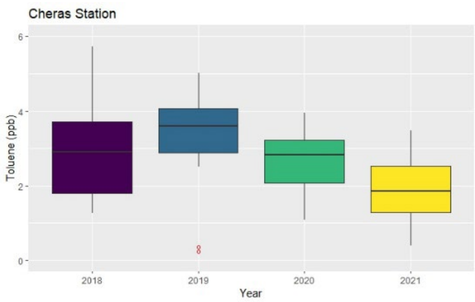

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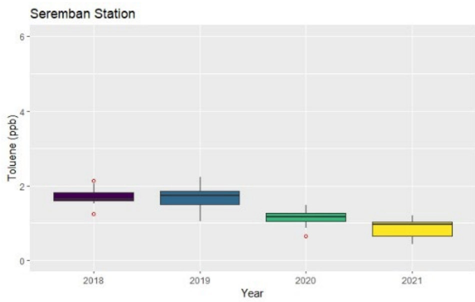

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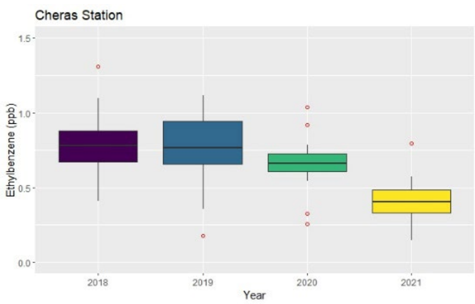

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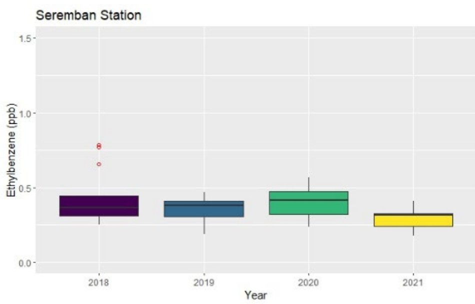

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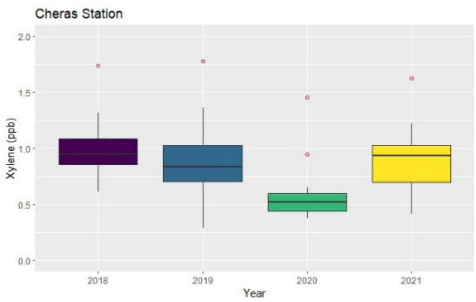

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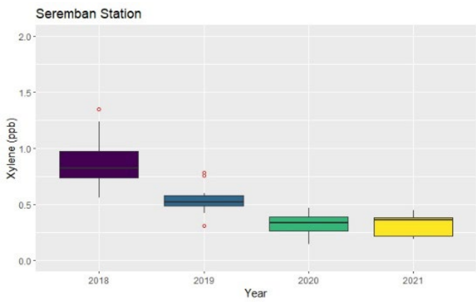

(h)

Fig. 3 *The Boxplot of ozone precursor in Cheras station, Kuala Lumpur and Seremban station, Negeri Sembilan*

Fig. 4 shows that by using Spearman correlation, toluene and ethylbenzene give a 0.76 strong positive correlation between each other. Toluene and benzene give a strong positive correlation which is 0.71. Some studies considered Toluene and Benzene as indicators to non-traffic-originated emissions [6], [34] and industrial pollution [6], [35]. Toluene shows that in Kuala Lumpur, Malaysia, the most polluted times of day were during rush hour, with contaminated areas near petrol stations, roadside, petrochemical businesses, and airports [36]. There is a very weak correlation between ozone and xylene, ethylbenzene, toluene, and benzene and which are -0.18, -0.02, -0.08, -0.09, respectively. The correlation between xylene and ethylbenzene is relatively weak (0.11). There is a weak positive correlation (0.31) between benzene and ethylbenzene. The correlation between benzene and xylene is a moderate positive correlation (0.42). There is a slight positive correlation (0.37) between xylene and toluene. Even though there is a weak correlation between the pollutants, overall, the emissions of these pollutants contribute to ozone formation [37].

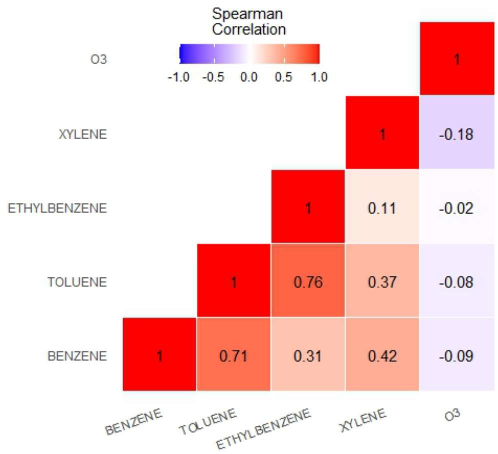

Fig. 4 *Spearman correlation between variables in Cheras*

Fig. 5 depicts the ozone precursor in Seremban station shows a strong positive correlation between toluene to benzene (0.91), xylene and toluene (0.83) and xylene to benzene (0.79). However, the relationship between ozone and xylene shows a positive weak correlation with value of 0.04. There is a very weak negative correlation between ozone and four ozone precursors – benzene, toluene, ethylbenzene, and xylene which are -0.01, -0.12, -0.18 and -0.04, respectively. In urban areas, road traffic pollution is reflected in BTEX. Apart from that, one of the sources of BTEX emissions is automobile exhaust [38], industrial processes [39], gasoline evaporates, natural gas and LPG leaks and cigarette smoke [40]–[42].

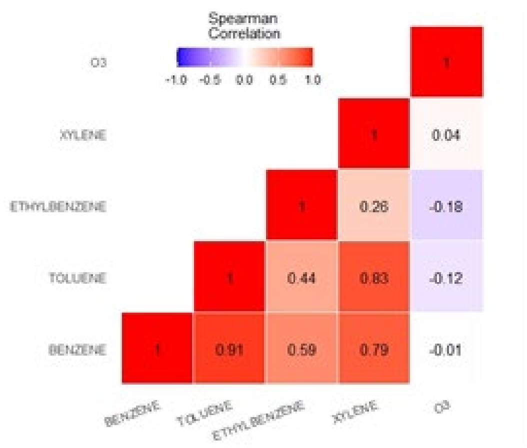

Fig. 5 *Spearman correlation between variables in Seremban*

Based on Fig. 4 and 5, toluene and benzene have a strong positive monotonic relationship at both stations and show that both pollutants have a high maximum value (Table 2) compared to others pollutants in those urban areas. The high concentrations of toluene and benzene indicated the presence of industrial and traffic emissions as sources of pollution [43].

5. Conclusion

Benzene, Toluene, Ethylbenzene, and Xylene (BTEX) compounds are important because they are common in urban areas and can cause adverse health effects, such as cancer and respiratory problems. This study aims to investigate and evaluate ozone precursors in Cheras and Seremban in the central zone of Peninsular Malaysia from 2018 to 2021. Each data set shows a non-normal distribution with a p value below 0.05, indicating statistical significance. These results lead to the rejection of the null hypothesis of normal distribution when analyzed using the Kolmogorov-Smirnov test. Based on the exploratory plot, Cheras exhibits higher concentrations of ozone precursors than Seremban even though both are urban cities. Cheras Station, located in Kuala Lumpur, is significantly affected by anthropogenic urban activities, including increased emissions of volatile organic compounds from industry, cars, and chemicals [44]. From 2018 to 2021, the maximum dispersion value of toluene is 5,738 ppb in Cheras, which is much higher than Seremban's 2,228 ppb and much larger than other ozone precursors. Furthermore, toluene is the main contributor to ozone generation in ambient air, with xylene, ethylbenzene, and benzene following closely behind [45]. Ozone and ozone precursor concentrations show lower concentrations in 2020 due to the COVID-19 outbreak. They are restricted due to minimal economic and human activity, as well as the implementation of movement control orders by the authorities [46]. A Spearman correlation analysis of ozone with BTEX was conducted, revealing a strong positive monotonic relationship between benzene and toluene in Cheras (0.72) and Seremban (0.91). After comparing the locations, Cheras showed more concentration pollutants than Seremban. Limitations of this study include the period of data collection and coverage area. The results are limited to specific locations and are not representative of the entire area. Despite these limitations, this study provides information about the pollution, which will help in implementing safety measures and projecting ozone pollution in the future.

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Conflict of Interest

Authors declare that there is no conflict of interests regarding the publication of the paper.

Author Contribution

The authors confirm contribution to the paper as follows: ***study conception and design:*** *Siti Hasliza Ahmad Rusmili, Firdaus Mohamad Hamzah;* ***data collection:*** *Siti Hasliza Ahmad Rusmili, Firdaus Mohamad Hamzah;* ***analysis and interpretation of results:*** *Siti Hasliza Ahmad Rusmili, Firdaus Mohamad Hamzah;* ***draft manuscript preparation:*** *Siti Hasliza Ahmad Rusmili, Firdaus Mohamad Hamzah. All authors reviewed the results and approved the final version of the manuscript.*

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