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Regression Study on the Impact of Vehicular Emission Pollutants on Ozone Level: Chemical and Material Perspectives

Patricia Adamma Ekwumemgbo[1,*], *Idongesit Edem Okon*[1, 2]

[1] Department of Chemistry, Ahmadu Bello University, Zaria

[2] Transport Technology Centre, Nigerian Institute of Transport Technology (NITT), Zaria, Kaduna State, Nigeria

*Correspondence: E-mail: pat_adamma@yahoo.com

ABSTRACT

This study verified the impact of vehicular emission pollutants and meteorological factors on the variability of ground-level ozone in Port Harcourt, Nigeria using multiple linear regression (MLR) analysis (p=0.05). Data were collected at traffic hot spots over twelve calendar months (December 2017 and November 2018). The explanatory variables were precursor pollutants (NO_2, CO, and VOCs) and meteorological factors (temperature, relative humidity, and wind speed). Data collected were subjected to correlation analyses, and O_3 concentrations showed a significant positive correlation with NO_2, CO, VOCs, and traffic density (p= 0.05). O_3 levels also correlated positively with temperature and negatively with wind speed and relative humidity across traffic periods. Three Models: Model 1, Model 2, and Model 3 were generated from MLR analyses for the estimation of O_3 variation in the morning peak traffic period, off-peak traffic period, and evening peak traffic period respectively. Validation of performance for each Model was achieved using performance statistics including adjusted R2, mean absolute error (MAE), mean biased error (MBE), mean square error (MSE), and root mean square error (RMSE).

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1. INTRODUCTION

Vehicular emissions from road transportation have been a major contributor to the high concentration of pollutants leading to pollution of our air environment (Singgih, 2020; Oderinde *et al*., 2016). These emissions are a significant source of pollution in Port Harcourt and other cities (Asif *et al*., 2021; Tiandho, 2017; Ugbebor & Longjohn, 2018). Vehicular emission contains some pollutants such as VOCs, NO_2, and CO, which are ozone (O_3) precursors (Suryadjaja *et al.,* 2020). Hence, enhances the formation of ground-level ozone (Wałaszek *et al*., 2018). Ozone is largely found in the strato¬sphere, at that height, it shields us from the harmful ultraviolet (UV) radiation from the sun, nevertheless at the top of the troposphere, ozone acts as a greenhouse gas and adds to global warming (Sharma *et al*., 2017). Ground-level ozone can cause respiratory disease in man (Karthik *et al*., 2017), and reduction in the photosynthetic process in plants (Chen *et al*., 2018). The precursors are also harmful: CO causes blood poisoning by forming COHb while reducing the O_2Hb level in blood at high exposure (Olusola *et al*., 2018). NO_2 causes asthma exacerbation (USEPA, 2015) and reduces plant chlorophyll (Sheng & Zhu, 2019). Ground-level ozone does not emanate directly from vehicle engine combustion processes; rather it is produced through a photochemical process from sunlight-initiated oxidation of precursor pollutants in the emissions that resulted from the combustion processes (Air Quality Expert Group (AQEG), 2009). Photochemical formation of ozone, which is the major cause of ground-level ozone, is thrived by the concentration of precursors (NO_2, CO, and VOCs) and is influenced by meteorological factors including temperature, wind speed, and relative humidity (Strömberg, 2022; Nidhi *et al*., 2015). Equations (1-4) present simple formation processes for the formation of ground-level ozone (O_3) from the precursor pollutants (Warmiński & Bęś, 2018).

From *photolysis* of *NO_2*

$$\mathrm{NO_2 + uv\ radiation\ (400 - 430\ nm) \rightarrow O + NO} \tag{1}$$

$$\mathrm{O + O_2 \rightarrow O_3} \tag{2}$$

From oxidation of CO

$$\mathrm{CO + 2O_2} \xrightarrow{NO_x,\ \mathrm{OH^{\cdot}},\ uv\ (400-430\,nm)} \mathrm{CO_2 + O_3} \tag{3}$$

From *oxidation* of *VOCs (RH):*

$$\mathrm{RH + 2O_2 + uv\ (400 - 430\ nm)} \xrightarrow{\mathrm{NOx,\ OH^{\cdot}}} \rightarrow\rightarrow \mathrm{RCHO + H_2O + 2O_3} \tag{4}$$

The relationship between ozone concentrations and the volume of pollutants (Precursors) from vehicular emissions, wind speed, relative humidity, and the temperature has been established by (Saxena & Ghosh, 2011; Henshaw & Nwaogazie, 2016).

This relationship has been studied using various modeling tools; the multiple linear regression (MLR) tools have shown fruitful results in the modeling of ground-level O_3 variation (Nidhi *et al*., 2015). This study, therefore, aims at generating model equations for the estimation of the concentration of traffic-related ozone in the air of the city using MLR analysis of data collected from the field.

2. METHODS

2.1. Study area

This study was conducted in Port Harcourt City, the capital of Rivers State, Nigeria. The city is found in the coastal region of the southern part of Nigeria. The city is located within latitudes 4o44’ 58.8’’N and 4o56’ 4.6’’N and within longitudes 6o52’ 7.2’’E and 7o7’ 37.7’’E (Robert, 2015; Emenike & Orjimo, 2017). Three major corridors take traffic in and out of the city: Port Harcourt- Aba Express Road, East-West Road, and Ikwerre Road. These three

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corridors are the main connectors to many feeder roads that lead to almost all parts of Port Harcourt city (Kio-Lawson & Dekor, 2014). Economic activities in the city have resulted in high population density and consequently a high volume of pollutants from vehicular traffic emissions (Robert, 2015).

2.2. Sampling sites

The sampling sites comprised eight (8) high-traffic junctions located along the three major corridors. These Junctions are Water Lines, Air Force, Rumukwurushi, Eliogbolo, Rumuokoro, Nkpolu, Rumukwuta, and Rumuola as shown in **Figure 1**.

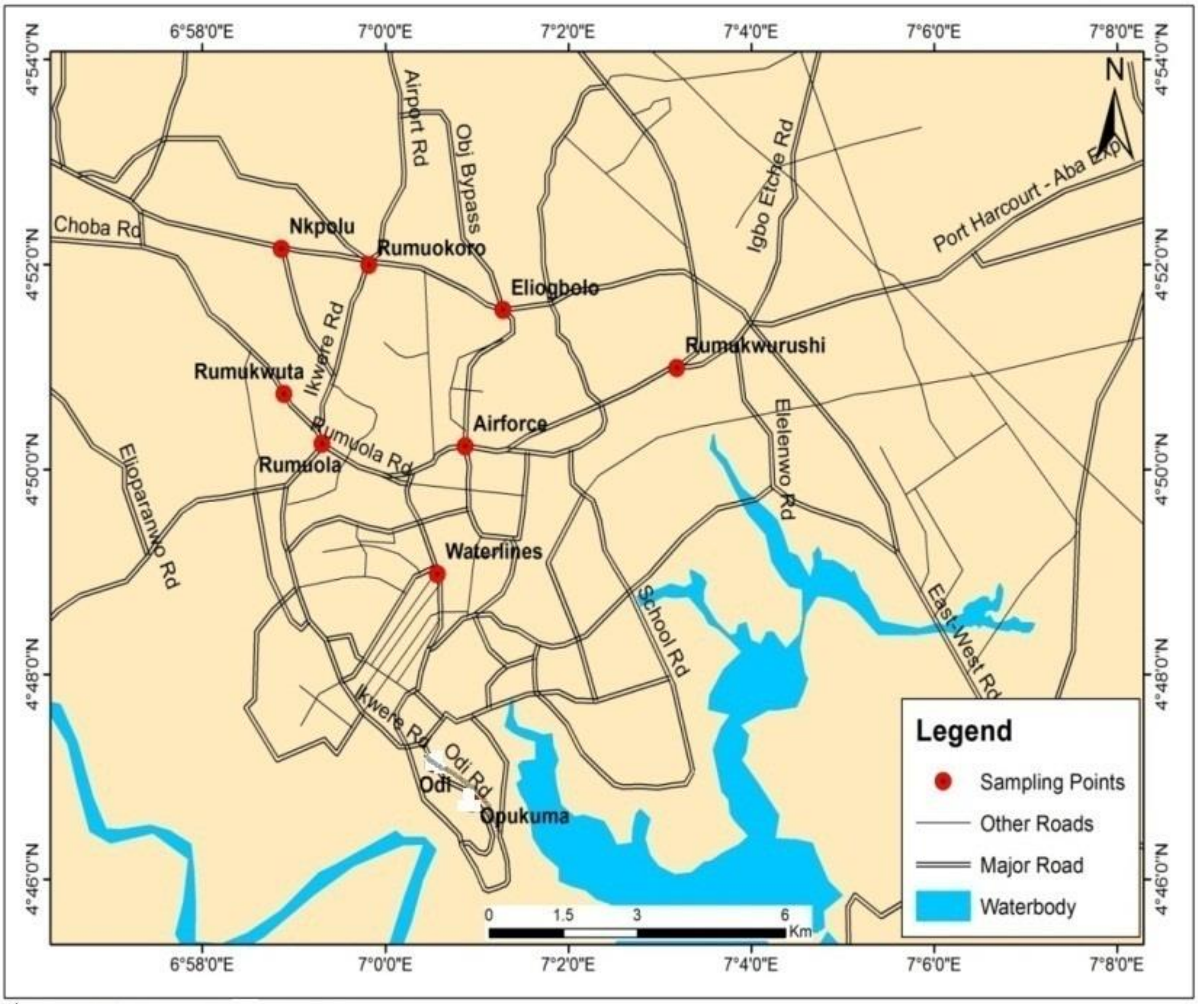

Figure 1. Map of the study area.

2.3. Data collection and statistical data analyses

Data used in the study were collected between December 2017 and November 2018. Data on the concentration of O_3 and its precursor pollutants (NO_2, CO, and VOCs), meteorological factors, and vehicular traffic density were collected. The gaseous pollutants were measured in situ using AeroQUAL 500 series (Aeroqual, New Zealand) hand-held ambient air analyzer. EXTECH 45170 (EXTECH Instruments, USA) weather station was used for measuring temperature, relative humidity, and wind speed. The traffic flow survey was achieved through the direct counting method. The time range for carrying out measurements covered periods of high and low traffic (Utang & Peterside, 2011; Emenike & Ojime, 2017). The "rush hours" of 7:00 – 9:00 am and 4:00 – 6:00 pm, served as the morning peak traffic period and evening peak traffic period respectively. The time range (12:00 am - 2:00 pm) for low traffic served as an off-peak traffic period. Measurements were carried out at 1.5 meters above the ground as this height represented the breathing zone for people (Nandiyanto, 2020). The measurements were made with consideration to the wind direction to avoid taking the reading at up-wind positions. Measurements were made in triplicates for each of the parameters and the mean was taken as the measured value. Data were presented in Tables and graphs, and descriptive and inferential statistics were used for analysis. The Inferential analysis was performed using monthly levels of parameters across sampling sites. The relationship among traffic flow, meteorological factors, and gaseous pollutants was analyzed using Pearson's product-moment correlation tool (Nidhi *et al*., 2015). Multiple linear regression (MLR) analysis was further carried out to determine the variability in ground-level O_3 with precursors and meteorological parameters (Nidhi *et al*., 2015; Capilla, 2016).

2.4. Quality assurance of analytical data

For analytical data quality assurance, the AeroQUAL 500 analyzer was subjected to zero calibration for each sensor, and a bump test on the analyzer was carried out before being deployed for the measurement of the gaseous pollutants for each month.

2.5. Multiple linear regression (MLR)

For the fact that the data has to be transformed to a normal distribution by taking the natural logarithm of the dependent and the explanatory variables, the model equation for ozone estimation is as given in Equation 5.

$$\ln(O_3) = A + B_1\ln(NO_2) + B_2\ln(CO) + B_3\ln(VOCs) + B_4\ln(Temp) + B_5\ln(RH) + B_6\ln(WS) + E \quad (5)$$

Where: O_3 is the dependent variable; A is the constant of regression; NO_2, CO, VOCs, Temp (temperature); RH (Relative Humidity) and WS (Wind Speed) are explanatory variables; B_1, B_2, B_3, B_4, B_5, B_6 are coefficients of the explanatory variables.

The regression method was subjected to performance test using statistics such as coefficient of determination (R2), standard error of estimate (E), and error metrics including mean absolute error (MAE), mean biased error (MBE), mean square error (MSE) and root mean square error (RMSE) to find out the performance of the different model equations derived from the MLR analysis. The variance inflation factor was used to check for multicollinearity.

The error metrics were calculated as expressed in Equations 6 – 9.

$$MAE = \frac{1}{n}\sum_{i=1}^{n}|Oi - Ei| \quad (6)$$

$$MBE = \frac{1}{n}\sum_{i=1}^{n}(Oi - Ei) \quad (7)$$

$$MSE = \frac{1}{n}\sum_{i=1}^{n}(Oi - Ei)^2 \quad (8)$$

$$RMSE = \sqrt{\frac{1}{n}\sum_{i=1}^{n}(Oi - Ei)^2} \quad (9)$$

Where Oἱ is the observed value of O_3 and Eἱ is the corresponding estimated value of O_3 given by the model Equation.

3. RESULTS AND DISCUSSION

3.1. Pollutants and traffic levels

Figures 2 – 5 show monthly levels of vehicular emission pollutants. Average concentration (ppm) for each of the pollutants during the morning peak traffic period were 0.074 ± 0.007, 15.186 ± 0.694, 1.756 ± 0.078, and 0.046 ± 0.006 for NO_2, CO, VOC, and O_3 respectively. At off-peak, average concentrations (ppm) were 0.049 ± 0.004, 12.272 ± 0.429, 1.444 ± 0.166, and 0.051 ± 0.006 for NO_2, CO, VOC, and O_3 respectively. During the evening peak traffic period, the average (ppm) was 0.077 ± 0.007, 15.544 ± 0.556, 1.767 ± 0.124, and 0.050 ± 0.007 for NO_2, CO, VOC, and O_3 respectively. The high level of CO compared to other pollutants could be attributed to the fact that CO is the predominant pollutant emitted by vehicles, especially gasoline engine vehicles (Aneri, 2018).

The average concentrations for each of NO_2, CO, and VOCs were significantly higher ($p = 0.05$) in the evening followed by morning and then afternoon (off-peak) as adjudged in **Table 1**. Higher concentrations observed for NO_2, CO, and VOC in the evening could be a result of more traffic flow and residual buildup from other periods (Ucheje & Chidozie, 2015).

Table 1. T-test values for comparison between concentrations of pollutants at peak period with off-peak period (two tail; p = 0.05).

Pollutants	**Off-peak versus Morning Peak**		**Off-Peak versus Evening peak**		**Evening Peak versus Morning peak**	
	t cal.	*t crit.*	*t cal.*	*t crit.*	*t cal.*	*t crit.*
NO_2	23.616	2.201	26.911	2.201	9.753	2.201
CO	15.651	2.201	23.346	2.201	6.588	2.201
VOC	8.035	2.201	7.835	2.201	0.637	2.201
O_3	7.817	2.201	0.553	2.201	6.298	2.201

t cal. = t calculated; t crit. = t critical

For O_3, the average value at off-peak (0.051 ± 0.006 ppm) was higher than the evening value (0.050 ± 0.007 ppm) and the morning value (0.046 ± 0.006 ppm), however, the difference in value at off-peak was significant ($p = 0.005$) compared to the morning but was not significant when compared to evening as revealed in **Table 1**. The higher concentration of O_3 at off-peak (afternoon) than at morning peak despite the lower number of precursors observed at off-peak could result from the fact that high temperature in the afternoon can initiate more photochemical reactions leading to higher yield in ozone production from the precursors (Muspita *et al*., 2021; Melkonyan & Wagner, 2013).

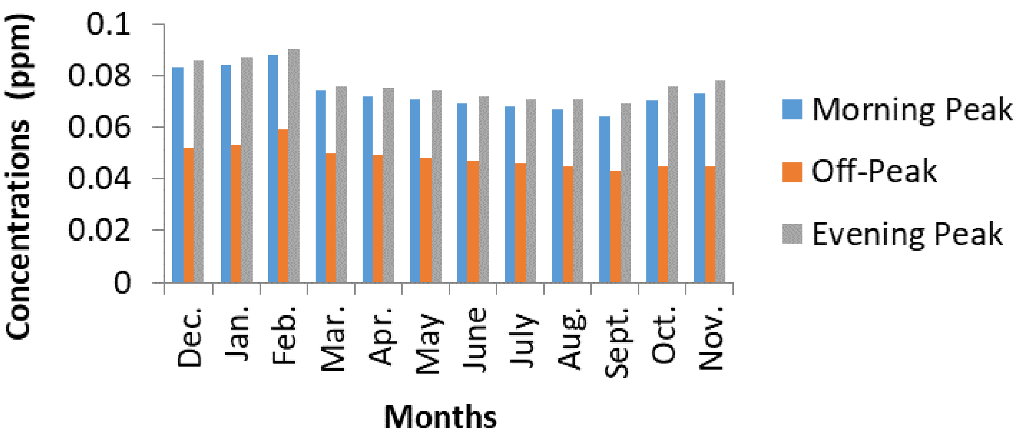

Figure 2. Monthly concentration of NO_2.

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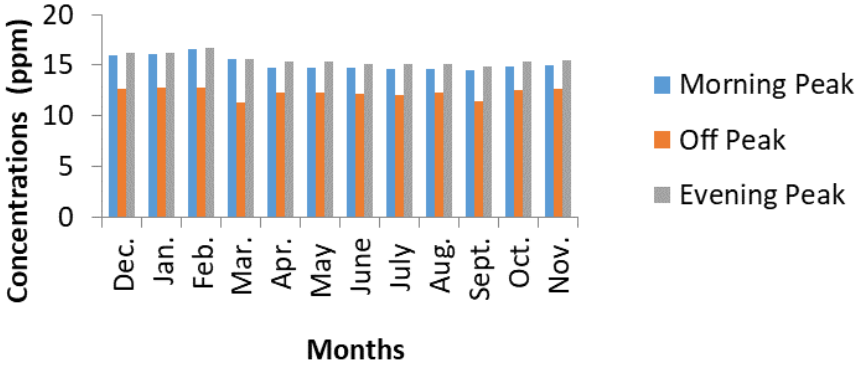

Figure 3. Monthly concentration of CO.

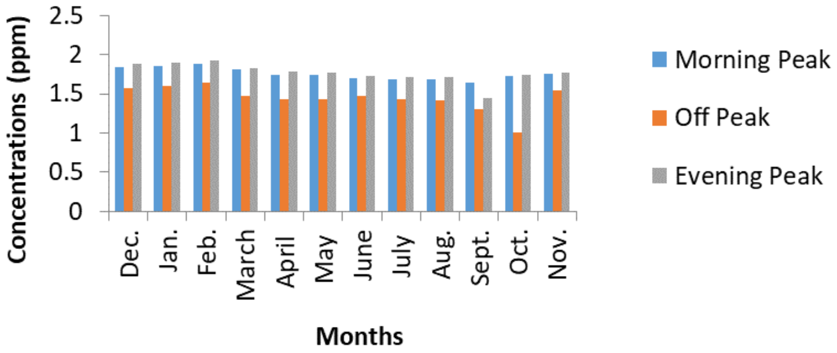

Figure 4. Monthly concentrations of VOCs.

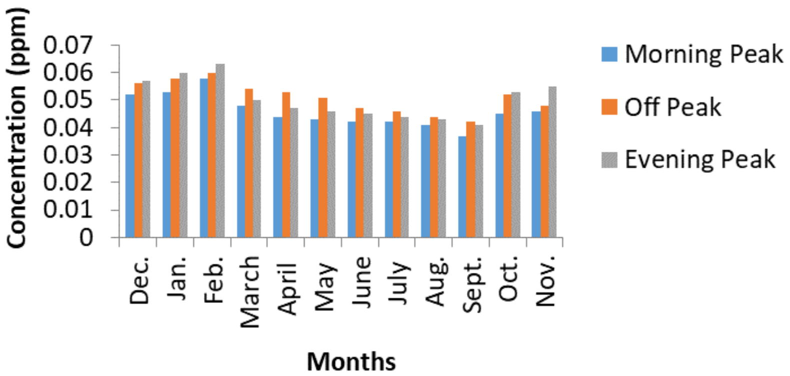

Figure 5. Monthly concentrations of O_3.

Figures 6 – 8 show the levels of meteorological factors. The maximum level of temperature was observed during the off-peak traffic period (afternoon), followed by the evening peak and then the morning peak. The highest level of temperature (37.47 ± 0.83 ^oC) was observed in February while the lowest (20.02± 0.60 ^oC) was observed in September as shown in Figure 6. Relative humidity level was observed in the order morning peak > evening peak > off-peak, this could be attributed to very low temperature in the morning. The maximum level of humidity (65.59 ± 0.38 %) was observed in August while the minimum (43.10 ± 0.60 %) was observed in February as presented **in Figure 7**. For wind speed, the maximum level (3.58 ± 0.35 m/s) was observed in September (at evening peak) while the minimum (2.00 ± 0.14 m/s) was in February (at off-peak) as presented in **Figure 8**.

Figure 9 shows the monthly traffic flow in vehicles per hour (v/h). The maximum value (1591 ± 17 v/h) was observed in January at the evening peak while the lowest (711 ± 95 v/h) was observed in July at off-peak. The overall average for traffic flow across traffic periods was 1270 ± 189 v/h, 847 ± 92 v/h, and 1364 ± 169 v/h for morning peak, off-peak, and evening

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peak respectively. Higher traffic flow observed in the evening is attributed to the smaller travel time (rush) that led to the higher density of vehicles.

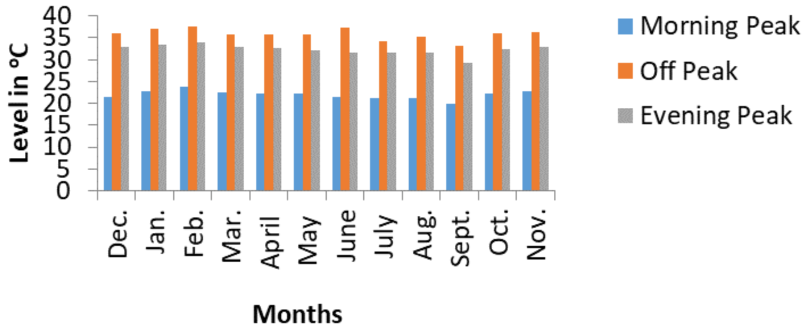

Figure 6. Monthly temperature level.

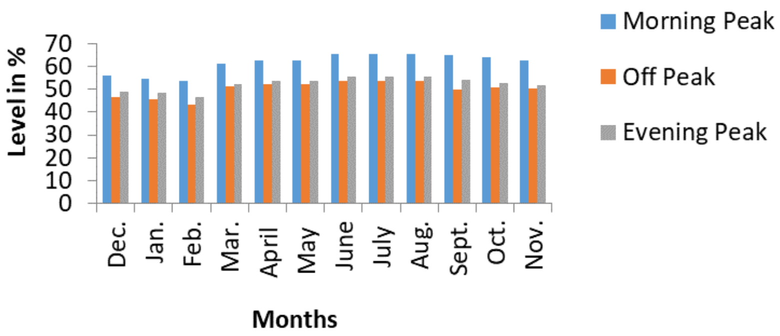

Figure 7. Monthly relative humidity level.

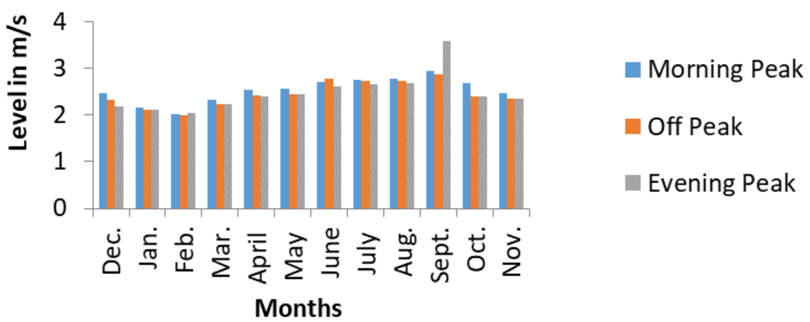

Figure 8. Monthly wind speed level.

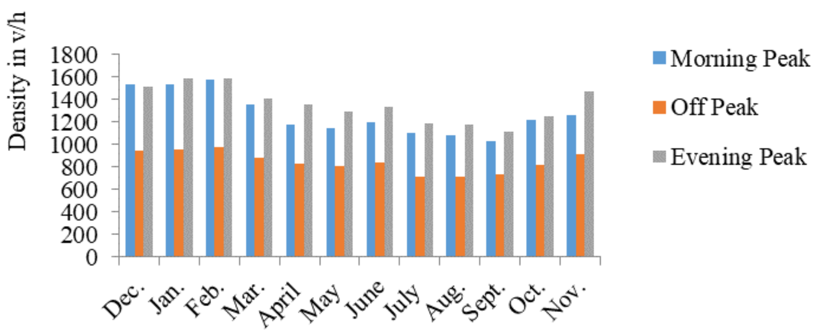

Figure 9. Monthly traffic flow.

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3.2. Correlation

There was a significant correlation between ozone and other variables as shown in **Table 2**. O3 correlated with the precursors across traffic periods with a coefficient of correlation (r) ranging from 0.89 – 0.98, 0.51 – 0.97, and 0.42 – 0.98 for NO_2, CO, and VOCs respectively. O_3 correlated with meteorological factors and traffic density at r ranges of 0.70 – 0.83, -0.75 – -0.95, -0.78 – -0.94, and 0.85 – 0.97 for temperature, relative humidity, wind speed, and traffic density respectively. The strong correlation reveals a linear relationship between ozone and other variables; hence, the possibility of MLR estimating ozone levels with variability in the other variable levels (Nidhi et al., 2015; Marathe et al., 2017). There was also a significant relationship between each of the precursor pollutants and traffic flow where the ranges for r were 0.77 – 0.97, 0.51 – 0.97, and 0.58 – 0.96 for NO_2, CO, and VOCs respectively. This significant relationship reveals that the emission sources are similar and that the emissions from traffic flow contribute to the concentration of these pollutants in the air (Sharma *et al*., 2009; Kolakoti *et al*., 2022).

Table 2. Correlation analysis.

				Morning Peak				
	NO_2	CO	VOCs	O_3	Temp (°C)	RH (%)	WS (m/s)	TD (v/h)
NO_2	1.00							
CO	0.97	1.00						
VOC	0.97	0.95	1.00					
O_3	0.98	0.97	0.98	1.00				
Temp (°C)	0.74	0.68	0.81	0.81	1.00			
RH (%)	-0.98	-0.97	-0.95	-0.95	-0.67	1.00		
WS (m/s)	-0.92	-0.91	-0.96	-0.94	-0.90	0.89	1.00	
TD (v/h)	0.97	0.97	0.96	0.97	0.69	-0.95	-0.89	1.00
				Off-peak (Afternoon)				
	NO_2	CO	VOCs	O_3	Temp (°C)	RH (%)	WS (m/s)	TD (v/h)
NO_2	1.00							
CO	0.44	1.00						
VOC	0.66	0.27	1.00					
O_3	0.89	0.51	0.42	1.00				
Temp (°C)	0.65	0.62	0.40	0.70	1.00			
RH (%)	-0.79	-0.49	-0.49	-0.75	-0.45	1.00		
WS (m/s)	-0.81	-0.50	-0.43	-0.94	-0.67	0.73	1.00	
TD (v/h)	0.77	0.51	0.58	0.85	0.76	-0.81	-0.86	1.00
				Evening Peak				
	NO_2	CO	VOCs	O_3	Temp (°C)	RH (%)	WS (m/s)	TD (v/h)
NO_2	1.00							
CO	0.98	1.00						
VOC	0.81	0.81	1.00					
O_3	0.96	0.93	0.79	1.00				
Temp (°C)	0.79	0.78	0.97	0.83	1.00			
RH (%)	-0.97	-0.96	-0.69	-0.94	-0.69	1.00		
WS (m/s)	-0.76	-0.75	-0.98	-0.78	-0.99	0.64	1.00	
TD (v/h)	0.92	0.89	0.85	0.91	0.86	-0.88	-0.82	1.00

3.3. Multiple Linear Regression (MLR) analysis

A regressional study on the O_3 level aims at creating an equation for its estimation or prediction. From the MRL analysis, three equations were created for Model 1, Model 2, and

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Model 3 respectively. Model 1 equation was created from data collected during the morning peak traffic period; Model 2 equation was created from data collected during the off-peak traffic period, while Model 3 equation was created from evening peak traffic data as shown in **Tables 3 and 4**.

Table 3. Summary of each model.

Models	R^2	Adjusted R^2	Standard error of Estimation (SEE)
1 (for morning peak data)	0.997	0.994	0.010
2 (for off-peak data)	0.950	0.890	0.037
3 (for evening peak data)	0.982	0.961	0.028

Table 4. Multiple linear regression models for $\ln o_3$ estimation.

Models	Traffic periods	Equation of model
1	Morning peak	$\ln O_3 = -13.202 + 0.804\ln NO_2 + 2.089\ln CO + 0.283\ln VOCs + 1.054\ln Temp + 0.652\ln RH + 0.470\ln WS + 0.010$
2	Off-Peak	$\ln O_3 = -1.637 + 0.785\ln NO_2 + 0.145\ln CO - 0.184\ln VOCs + 0.0981\ln Temp + 0.222\ln RH - 0.547\ln WS + 0.037$
3	Evening Peak	$\ln O_3 = -4.273 + 2.197\ln NO_2 - 0.048\ln CO - 2.780\ln VOCs + 1.431\ln Temp + 1.161\ln RH - 1.059\ln WS + 0.028$

The summary of model parameters including coefficient of determination (R^2), adjusted R^2, and standard error of estimate (E) are presented in **Table 3**. R^2 describes the amount or proportion of variability in the dependent variable (O_3) that the model equations account for (Antai *et al*., 2018). This implies that the higher the value of R^2, the better the model fits the data (Nidhi *et al*., 2015). Adjusted R^2 is a measure of decrease or loss in the predictive power of the regression model equations.

Traffic density is excluded in the MLR model equations as an explanatory variable since the precursor pollutants (NO_2, CO, and VOCs) emanated from it, this is to avoid double counting.

Model 1 denotes MLR analysis of $\ln O_3$ at the morning peak traffic period, with an adjusted R^2 value of 0.994, signifying that a 99.4% variation in O_3 concentration was accounted for by the explanatory variables. Model 2 denotes $\ln O_3$ estimation at off-peak traffic periods, the adjusted R^2 (0.890) shows that 89% variation in $\ln O_3$ emanated from the explanatory variables.

Model 3 with adjusted R^2 of 0.961 explains 96.1% variance in $\ln O_3$ at evening peak traffic period. The three models were evaluated for accuracy by comparing their standard error of estimate (SEE) and R^2. As adjudged in **Table 3**, Model 1 displays the highest accuracy (goodness-of-fit) as its R^2 is highest (0.997) and with the lowest SEE of 0.010.

3.4. Validation of model accuracy

Model accuracy was validated using different model performance indicators. The indicators used were the error metrics (MAE, MBE, MSE, and RMSE) as presented in **Table 5**. All error terms for the three models were very close to zero, an indication that the residuals clusters are very close to the regression line or that the distances between the data points and the fitted values are very small making the models have high estimation accuracy. Model

1 showed the lowest value for all the error terms (MAE, MBE, MSE, and RMSE), this further reveals that model 1 has a higher accuracy of estimation compared to the other two.

Table 5. Statistics for validation of models performance.

Models	Adjusted R^2	MBE	MAE	MSE	RMSE
1	0.994	1.59×10^{-15}	0.00495	0.00004	0.00620
2	0.890	-3.70×10^{-16}	0.01706	0.00057	0.02387
3	0.961	-1.18×10^{-15}	0.01390	0.00076	0.01797

The model equations generated explains the influence of the explanatory variables on ozone level, however, multicollinearity between explanatory variable may affect the reliability of the result or information gotten, hence the multicollinearity between the explanatory variables was scrutinized by subjecting the variables to variance inflation factor (VIF) analysis as presented in **Table 6**. From the analysis, all the VIF values in Model 2 were less than 10. VIF for explanatory variables in model 1 and model 3 were far above 10 which is the acceptable range for the reliability of an MLR model given as $1 \leq VIF \leq 10$ (Dalson *et al*., 2016). Hence, model 2 with R^2 (0.950) is the most reliable despite higher R^2 values of 0.997 and 0.982 given by models 1 and 3 respectively. **Figures 10 – 12** illustrate a variation of the mean values of the observed and estimated level of O_3 in ppm. It is observed that at every data point, the estimated values of O_3 are very close to the observed values. The closeness could have resulted from the low SEE and high R^2 (0.950 – 0.997) as this implies that the distances between the data points and the fitted values are smaller.

Table 6. Collinearity analysis.

Explanatory variables	Model 1	Model 2	Model 3
	VIF	VIF	VIF
NO_2	50.824	5.952	76.923
CO	30.303	1.862	111.111
VOC	32.258	1.873	250.000
Temperature	14.286	2.742	66.667
Relative humidity	38.462	3.425	125.000
Wind Speed	48.000	3.802	250.000

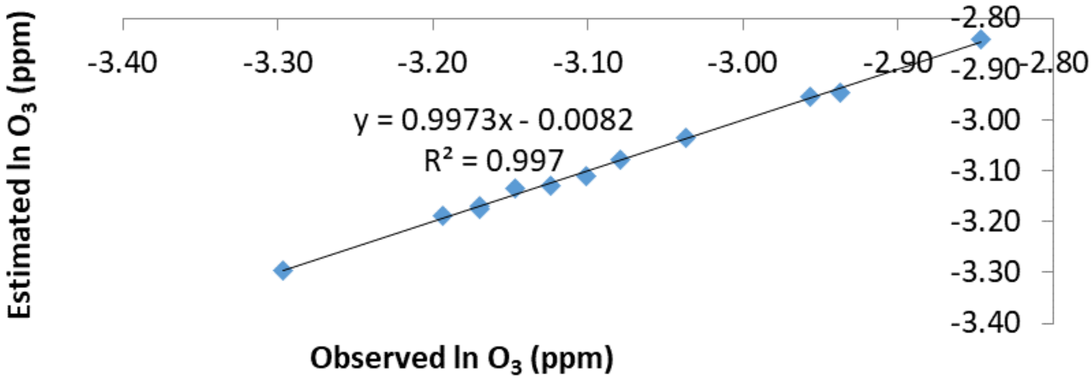

Figure 10. Plot of estimated in O_3 against observed in O_3 (Model 1).

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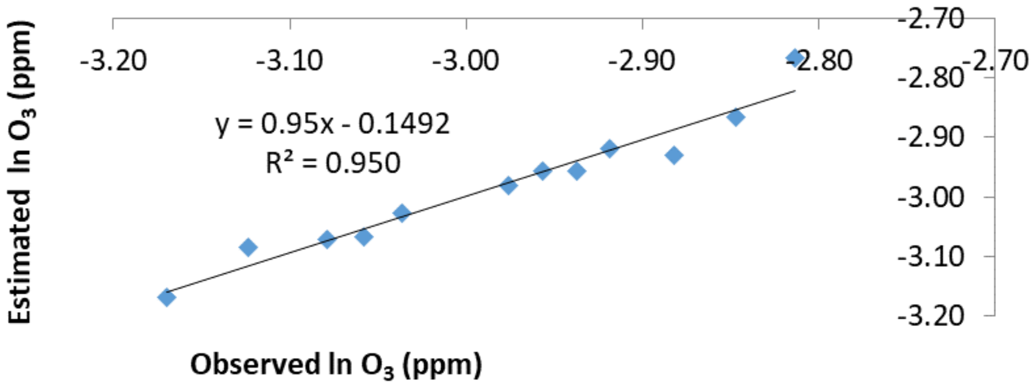

Figure 11. Plot of estimated in O_3 against observed in O_3 (Model 2).

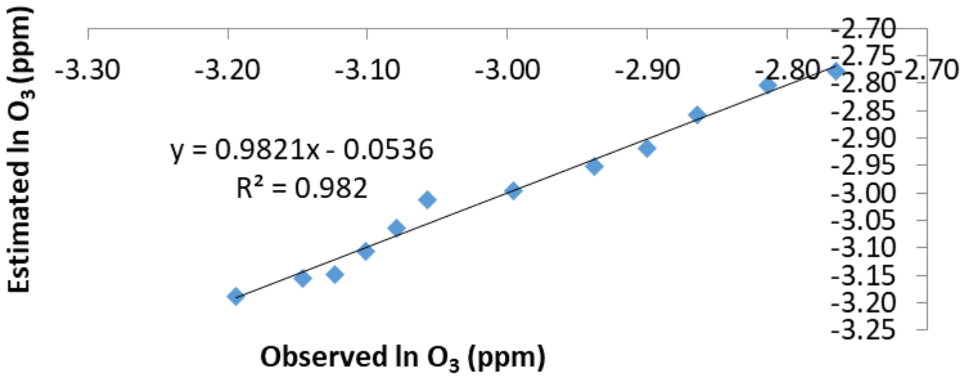

Figure 12. Plot of estimated in O_3 against observed in O_3 (Model 3).

4. CONCLUSION

From the results obtained, the concentration of pollutants was highest during the evening peak traffic period followed by morning and then off-peak except for O_3 where the off-peak range (0.051 ± 0.006 ppm) was higher than that of the morning (0.046 ± 0.006 ppm). Concentrations of NO_2, CO, VOC, and O_3 increased with temperature and vehicular traffic. Variation of observed and estimated concentrations of O_3 given by each of the models at every data point was very close (R2 = 0.950 – 0 .997). MLR showed high accuracy for ozone estimation and was more reliable for ozone estimation during off-peak traffic periods.

5. AUTHORS' NOTE

The authors declare that there is no conflict of interest regarding the publication of this article. Authors confirmed that the paper was free of plagiarism.

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