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EXPERIMENTAL STUDY ON MONITORING AND MATHEMATICAL MODELLING OF GASEOUS POLLUTANTS CONCENTRATIONS

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Abstract

This study carried out the monitoring and mathematical modelling of gaseous pollutants concentrations at Utorogu flow station in Delta State of Nigeria. Modelling the relationship between pollutants concentrations and flare distance helps in evaluating the impact of distance from the flow station on pollutants concentrations and aid in sustainable development and pollution control. The gaseous pollutants, viz: volatile organic compounds (VOCs), ozone (O_3) and nitrogen dioxide (NO_2)were monitored using Multi-parameter gas monitor while the particulate matter ($PM_{2.5}$) was monitored with SPM meter for twelve weeks and their concentration data were obtained. The important climatic variables such wind speed, atmospheric pressure, ambient temperature and relative humidity were obtained using sky-master thermo anemometer. The maximum concentration of each monitored gaseous pollutant was selected and recorded for data processing. The curve fitting tool in Matrix Laboratory (MATLAB) software was employed to select models and simulate the exact mathematical relationship between the pollutants concentrations and the flare distance. The gaseous pollutants concentrations were predicted beyond the experimental distance of 500m from the flare point. The results show that the best mathematical relationship between sampling distance for the prediction of VOCs concentration was the quadratic polynomial model with the lowest root mean square error (RMSE) value of 0.2123 and coefficient of determination (R^2) value of 0.9952, that of particulate matter was a fourier function model with the lowest RMSE value of 0.7694 and R^2 value of 0.9927,for ozone was Gaussian model with the lowest RMSE value of 0.00341 and R^2 value of 0.9617 and that of nitrogen dioxide was exponential function model with the lowest RMSE value of 0.0006134 and R^2 value of 0.9928.The study has revealed that at a distance of 1100m and above, the concentration of VOCs approaches zero. The Gaussian model revealed that the concentrationof ozone gradually increases beyond the sampling distance of 500m. At 1100m and above, the concentration of NO_2 approached zero. The study also revealed that variation in wind speed of the the climatic variables has significant effect on the four gaseous pollutants studied.

***Keywords*:** Gaseous pollutants Concentration, Monitoring, Mathematical modelling, Matrix Laboratory, Mathematical models

1.0 Introduction

Gaseous Pollutants are the gases released into the atmosphere which act as primary or secondary pollutants. Gaseous pollutants are mainly produced as a result of human activity and are vital components in the formation of photochemical smog and acid deposition, both of which can have a range of harmful effects including the deterioration of building materials, the degeneration of trees and other plants, and respiratory ailments in humans and animals [1, 2].

Utorogu gas plant, which is the study area for this research work, involves large scale combustion of gas by means of horizontal and vertical flares. The consequential gaseous pollutants, namely: volatile organic compounds (VOCs), particulate matters ($PM_{2.5}$), ozone (O_3) and oxides of nitrogen (NO_2) which are emitted from the flare site are hazardous to man, animals

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and the total environment. Gas flaring is one of the most challenging energy and environmental problems facing the world today with local environmental catastrophe and a global energy and environmental problem which has persisted for decades [3]. Gas flaring degrades soil, makes it poor and infertile for crop production; excessive heat from the flare kills or scares away most of the micro- and macro-organisms that would have helped to improve the soil fertility through further breaking down of the soil particles, further decaying and decomposition of the soil organic matters [4].Gas flares damage vegetation, economic crops and the environment, contaminate surface and ground water, corrode roofing sheets, monuments and structures through acidification of rain water [5,6,7].

Global flaring and venting of petroleum associated gas are significant sources of greenhouse gas emissions and airborne contaminants that have proven difficult to mitigate over the years. Poor efficiency in the flare systems from incomplete combustion produces a variety of volatile organic compounds (VOCs), polycyclic aromatic hydrocarbons (PAHs) and inorganic contaminants [8].Air pollution is a major problem with strong impact on the environment [9], economy [10] and human health [11].There is therefore a need to model and predict the concentration and the spread of gaseous pollutants from Utorogu gas plant so as to determine at what distance from the flare point the pollution effect will be minimal in order to proffer solutions to pollution problem.

The essence of mathematical modelling is to understand the relationship between sampling distance and pollutants concentrations and to be able to make predictions. Dispersion modelling is undertaken in order to predict the concentration and spread of pollutants [12]. Dispersion models are used to predict the fate of pollutants after they are released into the atmosphere[13].The goal of air quality dispersion modelling is to estimate a pollutant's concentration at a point downwind of one or more emission sources [14]. The first step in the modelling and prediction of ground level concentration of gaseous pollutants is to understand the exact mathematical relationship between the pollutants concentrations and the distance from flow station at normal environmental stability and wind speed. The objectives of this study are to identify the gaseous pollutants whose concentrations are being monitored in the study area; determine the best mathematical model most suited for the predictions of the concentration of the identified gaseous pollutant as well as ascertain the mathematical relationship between the pollutants concentrations and the flare distance in order to obtain the distance where the effect of the gaseous pollutants was minimal.

2.0 THEORETICAL ANALYSIS

2.1 Sources of Gaseous Pollutants

The sources of gaseous pollutants can be grouped according to the number and spatial distribution [15,16] which include:

a) Stationary (stable) Sources: It is further sub – divided into two categories: i) Point (single) sources, whose sources of gaseous emission are easily identifiable. Examples are pollutions from factories, oil refineries, power plants, etc ii) Multiple or non – point sources, which are pollutants are from diverse sources and are not easily identifiable. They include: - Domestic combustion of fuel in residential areas, apartments, hotels, hospitals, offices, utilities, waste disposal units and institutions inter alia.

b) Mobile Sources: - Mobile sources of gaseous pollutants are special categories of non – point emitters. These are mainly through transportation. Mobile sources of gaseous pollutants can also be sub – divided into two [17]: i) Line sources: This is when the gases are coming from a stream of moving sources such as highway vehicles, trains and channel vessels. A line source of pollution is a one – dimensional source of air pollutant emissions. ii) Area sources: here the pollutants are from different directions such as aircraft, light medium, heavy duty vehicles/equipment, rail yard locomotives and port vessels.

Other sources: gaseous pollutants can also come from natural sources, smoke and carbon monoxide (CO) from wildfires which may result from lightning. These sources produce mainly hydrocarbon, oxides of sulphur (SO_x), oxides of nitrogen (NO_x), oxides of carbon (CO_x) and smoke.

2.2Major air pollutants: Five primary (major) air pollutants are nitrogen oxides (NO_x), suphur oxides (SO_x), carbon monoxide (CO), volatile organic compounds (VOCs) and particulate matter (PM), and a secondary (minor) pollutant is ozone (0_3) [15].

i) Sulphur Oxides (SO_x): Oxides of sulphur are serious pollutants which are produced whenever a fuel containing sulphur is burnt, the main source is the combustion of fossil fuel. Sulphur dioxide (SO_2) is the most important and common gaseous pollutant produced in huge quantity in the combustion of coal and other fuels in industrial and domestic use. As opined by [15,16], the most important oxide of sulphur emitted by pollution sources is sulphur dioxide (SO_2) which is a colourless gas with a characteristic sharp, pungent (choking) odour. O_2 causes intense irritation to eyes and respiratory tract. Exposure to even as low (0.25 – 0.50ppm) concentration of SO_2 causes constriction in asthmatics. However, some SO_3 is found in the furnace and the atmosphere. SO_2 and SO_3 can form acid when hydrolyzed with water.

$$2SO_2 + 2H_20 + 0_2 \rightarrow 2H_2S0_4 \qquad (2.1)$$

where,
S= Sulphur
H= Hydrogen
O= Oxygen

ii) Nitrogen oxides: Nitrogen oxides are formed whenever any fuel is burnt under high temperature and high pressure [1, 16]. Nitrogen and oxygen combine to form nitric oxide (NO) which changes into nitrogen dioxide (NO_2) in the ambient air and contributes to photochemical smog and haze. NO is responsible for several photochemical reactions in the atmosphere particularly in the formation of secondary pollutants such as O_3 in the presence of other organic substances. NO_2 is highly injurious to plants. NO produced largely by fuel combustion is oxidized to NO_2 in polluted atmosphere through photochemical secondary reactions[15]. NO_2 is highly injurious to plants. It causes irritation to alveoli, leading to lung inflammation and finally death upon prolonged exposure to 1ppm level[16]. NO_X are oxidized into nitric acid which when dissolved in the water in the atmosphere fall to the ground as acid rain.

$$2NO_2 + H_2O \rightleftharpoons HNO_3 + HNO_2 \quad (2.2a)$$

$$3HNO_2 \longrightarrow HNO_3 + 2NO + H_2O \quad (2.2b)$$

$$3NO_2 + H_2O \longrightarrow 2HNO_3 + NO \quad (2.2c)$$

where,
N= Nitrogen
H= Hydrogen
O= Oxygen

(iii) Particulate matter (PM):

Particulate matter results from direct emission of particles as well as emission of gases that condense as particles or undergo transformation to form particles. Dust or smoke particles emitted from factory are called primary pollutants. Particulate matters when inhaled by man, causes respiratory diseases such as tuberculosis and cancer. Under high wind velocity PM acts as abrasive damaging exposed surfaces and can accelerate corrosion on metallic surfaces [14]. PM_{10} is particulate matter with diameter less or equal 10 micrometers while $PM_{2.5}$ are fine particles of 2.5 micrometers or less in diameter. The fine particles $PM_{2.5}$ are easily inhaled and more harmful to man.

(iv) Ozone(0_3): Ozone layer absorbs ultra violet (UV) light and thus protects all life on earth from harmful effect of radiation. By absorbing the UV radiations the ozone layer heats up the stratosphere causing temperature inversion which limits vertical mixing of pollutants thereby causing the dispersion of pollutants over larger areas near the earth's surface. This causes dense cloud of pollutants to hang over the atmosphere in highly industrialized areas causing several unpleasant effects. Increase in O_3 concentration near the earth's surface reduces crop yields significantly, affects young plants and their leaves. It has adverse effects on human health, causes smog and contributes to acidification and climate change. Ozone is an aggressive gas which can easily penetrate the respiratory tract. Exposure of humans to ozone causes eye irritation and that of the respiratory tract. Thus, while higher levels of ozone in the atmosphere protect man, it becomes harmful when it comes in direct contact with man and plants on the earth's surface[16].

2.3 Mathematical Models used to determine the pollutants concentration

The five mathematical models used in this study for ascertaining the gaseous pollutant concentration in the study area are linear polynomial, quadratic polynomial, exponential, Gaussian and Fourier. The mathematical expression for the pollutant concentration in the linear polynomial model is as follows:

$$F(x) = ax + b \quad (2.3)$$

where,
F(x) =pollutant concentration
X = sampling distance
a and b = real numbers.

In the quadratic polynomial model, the pollutant concentration is expressed as follows [18]:

$$F(x) = ax^2 + bx + c \quad (2.4)$$

where,
F(x) = pollutant concentration
a, b and c =constants (numerical coefficients)
x = sampling distance

For the exponential function (model), the concentration of the pollutant is expressed mathematically as:

$$F(x) = aexp(bx) \quad (2.5)$$

where,
F(x) = pollutant concentration
a = any value greater than 0
b = a positive real number
x = sampling distance
In the Gaussian function, the pollutant concentration is expressed mathematically as follows[19]:

$$F(x) = a^* exp^{\frac{(x-b)}{c2}} \quad (2.6)$$

where,
F(x) = pollutant concentration
a, b = arbitrary real constants
$c \neq 0$ [c = standard deviation, also called the Gaussian root mean square, (RMS) width]
The pollutant concentration for the Fourier Series model is represented mathematically as[20]:

$$F(x) = a_0 + b_n \cos(nx) + b_n \sin(nx) \quad (2.7)$$

where,
F(x) = pollutant concentration
a_n= Fourier cosine coefficient
b_n= Fourier sine coefficient
x = sampling distance
n = 1, 2, 3, --- etc

3.0 Research Methodology

3.1 The Study Area

The study area is situated at Utoroguoil and gas plant flow station of Delta State of Niger Delta Area of Nigeria. Utorogu facility supplies more than 80percent of gas used in Nigeria. It is one the gas processing plants in the whole of West Africa, which is located at the Oil Mining Lease (OML) 34 in Delta State of Niger Delta Region. The map of the OML 34 showing the location of Utorogu Gas Plant is shown in Figure1.

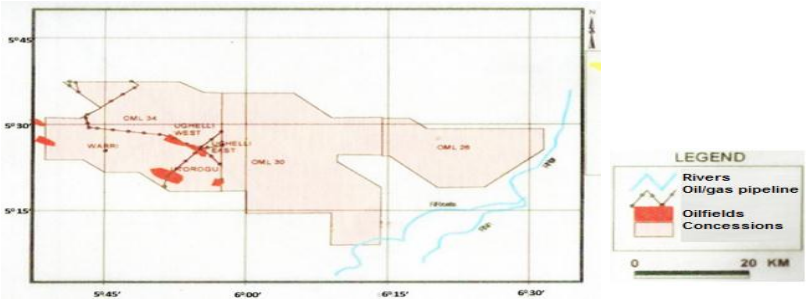


Figure1: Map of OML 34 showing location of Utorogu Gas Plant (Source: SPDC, 2000)
Figure1: Map of OML 34 showing location of Utorogu Gas Plant (Source: [21])

3.2 Data Acquisition and Processing

The monitoring points were established in the study area at the distance of 60m to 500m away from the flare point. The spacing distances of 60m, 80m, 100m, 150m, 200m, 250m, 300m, 350m, 400m, 450m and 500m from the flare point were used. Sky master thermo anemometer (SM-28) was used to obtain the important climatic variables such as wind speed, atmospheric pressure, ambient temperature and relative humidity, which affect the dispersion of gaseous pollutants. The geospatial coordinates of the flow station were obtained with GNSS receivers. The four gaseous pollutants which were identified, monitored and their concentration determined in this study, are volatile organic compounds (VOCs), particulate matter ($PM_{2.5}$), ozone (O_3) and nitrogen dioxide (NO_2). Aeroqual multi-parameter environmental monitor (series 500), with different gas sensors, was employed to monitor the concentrations of three of the gaseous pollutants, viz: volatile organic compounds (VOCs), ozone (O_3) and nitrogen dioxide (NO_2).The concentrations of these gases were obtained at each monitoring point on daily bases for a period of twelve weeks. Aerocet-531 SPM meter was used to monitor the concentration of particulate matter ($PM_{2.5}$) at each monitoring point also on daily bases for a period of twelve weeks. The maximum concentration of each monitored gaseous pollutant during the monitoring period was selected and recorded for data processing.
Five mathematical models, namely: linear polynomial, Quadratic polynomial, Exponential, Gaussian and Fourier were employed. The root square (R^2), which represents a linear criterion; the root mean square error (RMSE) and sum of square

error (SSE) which are non-linear criteria were also used to select the adequacy of a mathematical model. The model with the lowest root mean square error or sum of square error value was considered the best model. The pollutant concentration which form the dependent variable and the distance from flare point which form the independent variable were imported into MATLAB environment and thereafter, "cftool" command was used in the MATLAB command window to activate the curve fitting tool. Different mathematical models exist in the curve fitting environment ranging from polynomial of order 1 to 8, exponential, inverse, fourier, etc. In order to validate the selected models, several goodness of fit statistics such as error sum of square (SSE), R-square, Adj. R-square and RMSE were employed.

4.0 Results and Discussion

4.1 Input and Output parameters used for the mathematical modelling

Tables 1 and 2 show the input and output parameters obtained from the field and used for the mathematical modelling.

Table 1: Input parameters for Utorogugas station

Sampling Distance (m)	Wind Speed (m/s)	Atm. Pressure (mmHg)	Ambient Temperature (deg C)	Relative Humidity (%)
60	1.85	1011	39.8	88.1
80	2.33	1011	37.6	90.2
100	2.56	1011	37.2	87.2
150	2.59	1011	35.7	92.3
200	2.66	1011	34.5	82.7
250	2.67	1011	30.5	87.4
300	2.78	1011	32.5	91.4
350	2.83	1011	31.4	83.6
400	2.91	1011	30.5	81.5
450	2.92	1011	32.1	72.8
500	3.34	1011	29.7	73.9

Table 2: Output parameters for Utorogugas station

Sampling Distance (m)	Maximum VOCs (μg/m³)	Maximum CH_4 (μg/m³)	Maximum NO_2 (μg/m³)	Maximum $PM_{2.5}$ (μg/m³)	Naximum Ozone (μg/m³)	Maximum SO_2 (μg/m³)
60	19.01	10.23	0.37	46.83	0.052	0.05
80	18.23	9.71	0.32	45.78	0.051	0.046
100	17.78	8.37	0.32	44.23	0.043	0.044
150	17.14	8.01	0.27	43.27	0.041	0.041
200	16.41	7.44	0.23	40.81	0.041	0.037
250	15.27	7.18	0.2	35.69	0.038	0.031
300	14.37	6.19	0.18	33.44	0.031	0.028
350	13.97	5.26	0.16	31.23	0.031	0.023
400	12.67	4.83	0.13	29.74	0.026	0.021
450	11.69	4.19	0.11	28.03	0.024	0.017
500	10.88	3.33	0.1	26.8	0.065	0.015

4.2Sampling distance and concentration of VOCs in Utorogu gas plant

To determine the exact mathematical relationship between sampling distance against the concentration of volatile organic compounds (VOCs) at Utorogu gas station, five (5) mathematical models were tested and the calculated parameters of the models are presented in Table 3.

Table 3: Calculated model parameters for determining the mathematical relationship between sampling distance and VOC

Model	R-Square	Adj. R-Square	SSE	RMSE
Linear polynomial	0.9951	0.9946	0.3674	0.223
Quadratic Polynomial	0.9952	0.9946	0.3606	0.2123
Exponential	0.9892	0.9880	0.814	0.3007
Gaussian	0.9948	0.9931	0.3606	0.227
Fourier	0.9952	0.9931	0.3606	0.227

Based on the parameters in Table 3, it was observed that the quadratic polynomial model had the lowest root mean square error value of 0.2123 and coefficient of determination (R^2) value of 0.9952. It was concluded that the best mathematical relationship between sampling distance and VOCs concentration at Utorogu gas station was a quadratic polynomial equation as presented in Table 4.

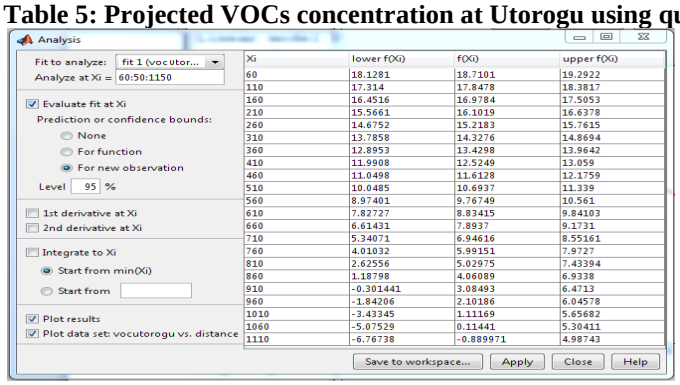
Table 4: Quadratic polynomial function for VOCs and the sampling distance

```
Linear model Poly2:
       f(x) = p1*x^2 + p2*x + p3
Coefficients (with 95% confidence bounds):
       p1 = -1.421e-006  (-9.909e-006, 7.067e-006)
       p2 =      -0.017  (-0.02171, -0.0123)
       p3 =       19.74  (19.2, 20.27)
```

where;
f(x): VOCs concentration (µg/m^3)
x: Sampling distance (m)

Using the quadratic polynomial function of Table 4, the concentration of VOCs was projected to a sampling distance above the initial 500m at 95% confidence level as presented in Table 5 and Figure 2.

Table 5: Projected VOCs concentration at Utorogu using quadratic polynomial function



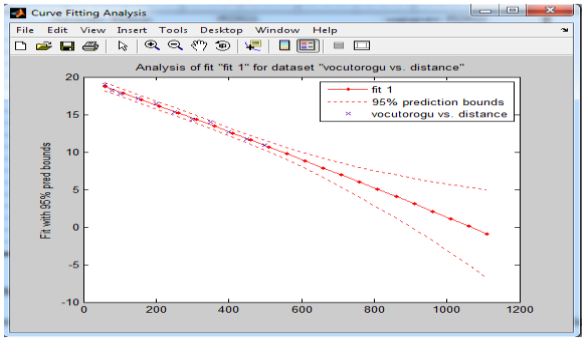


Figure 2: Model validation plot using 95% prediction bounds

The result in Figure 2 revealed that at 95% confidence level (prediction bounds), the quadratic polynomial function could be used to accurately determine the sampling distance at which zero concentration of volatile organic content (VOCs)would be obtained. From the result in Table 5, it was observed that at a distance of 1100m and above, the concentration of VOCs approaches zero. To test the accuracy of the quadratic polynomial function in predicting the concentration of VOCs, a reliability plot of the observed VOCs concentration and the predicted VOCs concentration was obtained and presented in Figure 3.

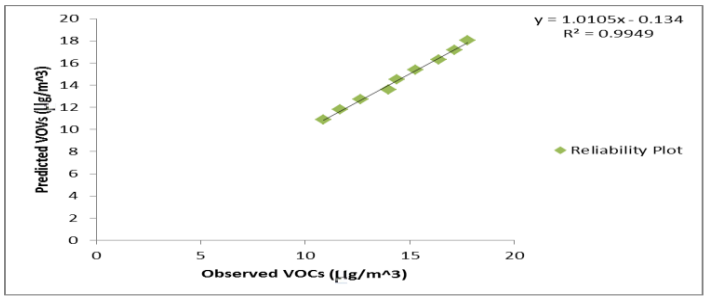


Figure 3: Reliability of quadratic polynomial model

The high coefficient of determination (0.9949) as observed in Figure 3, has revealed that the mathematical model developed is adequate and reliable.

3.3Sampling distance and concentration of particulate matter ($PM_{2.5}$)

In order to determine the exact mathematical relationship between sampling distance and the concentration of particulate matter at Utorogu gas station, five (5) mathematical models were also tested and the calculated parameters of the models are presented in Table 6.

Table 6: Calculated model parameters for determining the mathematical relationship between sampling distance and particulate matter ($PM_{2.5}$)

Model	R-Square	Adj. R-Square	SSE	RMSE
Linear polynomial	0.9792	0.9769	11.74	1.142
Quadratic Polynomial	0.9870	0.9837	7.347	0.9583
Exponential	0.9863	0.9848	7.745	0.9276
Gaussian	0.9863	0.9829	7.743	0.9838
Fourier	0.9927	0.9895	4.144	0.7694

Based on the parameters of Table 6, it was observed that the Fourier function model had the lowest root mean square error value of 0.7694 and coefficient of determination (R^2)value of 0.9927. It was therefore inferred that the best mathematical relationship between sampling distance and the concentration of particulate matter was a Fourier function equation as presented in Table 7.

Table 7: Fourier function model for $PM_{2.5}$and sampling distance

```
General model Fourier1:
       f(x) =  a0 + a1*cos(x*w) + b1*sin(x*w)
Coefficients (with 95% confidence bounds):
       a0 =         37.75   (35.1, 40.41)
       a1 =          10.3   (9.049, 11.56)
       b1 =        -2.663   (-12.4, 7.071)
       w =      0.005637   (0.003057, 0.008217)
```

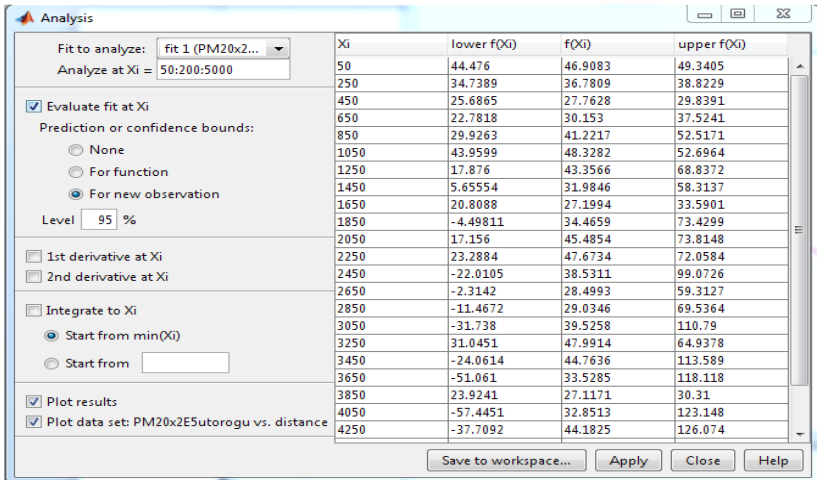
where;

f(x): Particulate matter concentration ($\mu g/m^3$)

x: Sampling distance (m)

Using the Fourier function model of Table 7, the concentration of particulate matter was projected to a sampling distance above the initial 500m at 95% confidence level as presented in Table 8 and Figure3.

Table 8: Projected $PM_{2.5}$ concentration at Utoroguusing Fourier function model



Xi	lower f(Xi)	f(Xi)	upper f(Xi)
50	44.476	46.9083	49.3405
250	34.7389	36.7809	38.8229
450	25.6865	27.7628	29.8391
650	22.7818	30.153	37.5241
850	29.9263	41.2217	52.5171
1050	43.9599	48.3282	52.6964
1250	17.876	43.3566	68.8372
1450	5.65554	31.9846	58.3137
1650	20.8088	27.1994	33.5901
1850	-4.49811	34.4659	73.4299
2050	17.156	45.4854	73.8148
2250	23.2884	47.6734	72.0584
2450	-22.0105	38.5311	99.0726
2650	-2.3142	28.4993	59.3127
2850	-11.4672	29.0346	69.5364
3050	-31.738	39.5258	110.79
3250	31.0451	47.9914	64.9378
3450	-24.0614	44.7636	113.589
3650	-51.061	33.5285	118.118
3850	23.9241	27.1171	30.31
4050	-57.4451	32.8513	123.148
4250	-37.7092	44.1825	126.074

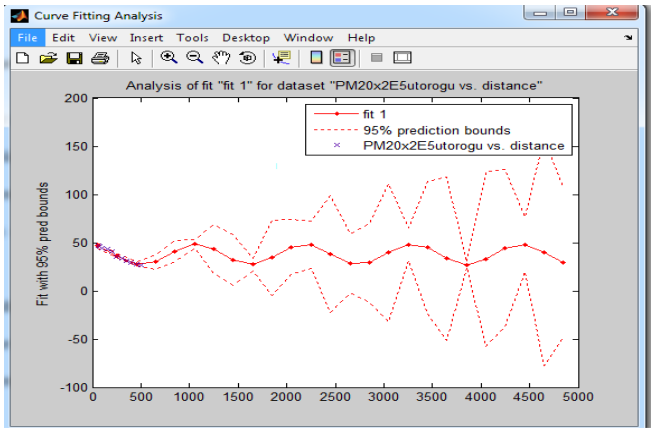


Figure 4: Model validation plot using 95% prediction bounds

The result of Figure 4revealed that at 95% confidence level (prediction bounds), the Fourier function model can be utilized to accurately determine the concentration of particulate matter at varied sampling distance. From the result of Table 8, it was observed that wind speed has pronounced effect on the concentration of particulate matter at each point. The high surface area of the particulate matter would have also contributed to the result.

To test the accuracy of the Fourier function model in predicting the concentration of particulate matter, a reliability plot of the observed $PM_{2.5}$ concentration and the predicted $PM_{2.5}$ concentration was also obtained as presented in Figure 5.

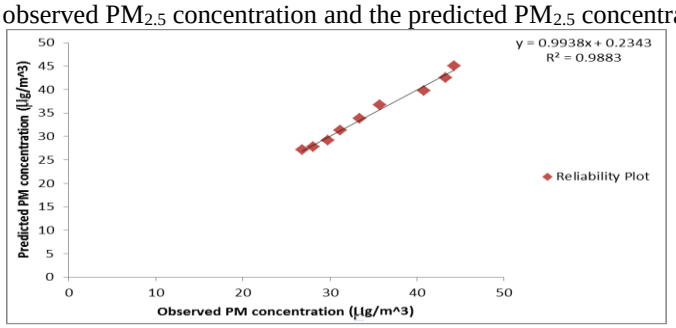


Figure 5: Reliability of Fourier function model

The high coefficient of determination (0.9883),as observed in Figure 5,has shown that the mathematical model developed is adequate and reliable.

3.4 Sampling distance and concentration of ozone

Table 9: Calculated model parameters for determining the mathematical relationship between sampling distance and the concentration of ozone

Model	R-Square	Adj. R-Square	SSE	RMSE
Linear polynomial (poly 5)	0.9588	0.9176	6.251E-005	0.003536
Quadratic Polynomial	0.5069	0.3836	0.0007486	0.009673
Exponential	0.0878	-0.01355	0.000385	0.0124
Gaussian(Gaus 2)	0.9617	0.9234	5.813E-005	0.00341
Fourier	0.5015	0.2879	0.0007568	0.0104

Based on the parameters in Table 9, it was observed that the Gaussian model had the lowest root mean square error value of 0.00341 and coefficient of determination (R^2) value of 0.9617. It was concluded therefore that the best mathematical relationship between sampling distance and the concentration of ozone was Gaussian model equation as presented in Table 10.

Table 10: Gaussian model for ozone and the sampling distance

```
General model Gauss2:
       f(x) =  a1*exp(-((x-b1)/c1)^2) + a2*exp(-((x-b2)/c2)^2)
Coefficients (with 95% confidence bounds):
       a1 =  3.629e+012  (-6.389e+016, 6.389e+016)
       b1 =        1804  (-7.051e+005, 7.087e+005)
       c1 =       230.8  (-6.126e+004, 6.172e+004)
       a2 =     0.05145  (0.02209, 0.0808)
       b2 =      -48.55  (-801.8, 704.7)
       c2 =       517.4  (-323.1, 1358)
```

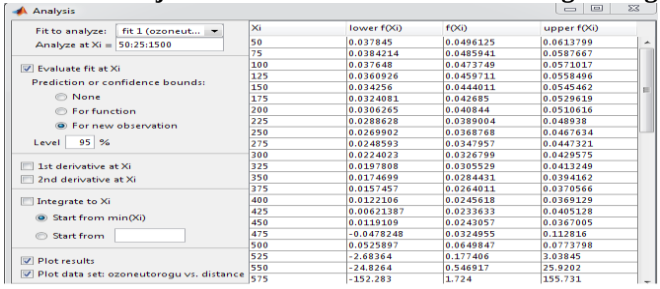
where;

f(x): Ozone concentration ($\mu g/m^3$)

x: Sampling distance (m)

Using the Gaussian model of Table 10, the concentration of ozone was projected to a sampling distance above the initial 500m at 95% confidence level as presented in Table 11 and Figure 6.

Table 11: Projected ozone concentration at Utorogu using Gaussian model



The results of Table 11 revealed a gradual decrease in the concentration of ozone with increasing sampling distance up to a distance of 425m. It was also observed from the Gaussian model predicton that the concentration of ozone gradually increases beyond the sampling distance of 500m. This could be attributed to wind effect. Variation in wind speed have significant influence on pollutants dispersion especially for point source pollution. Projected pollutants monitoring beyond a predetermined location can be used as base data for urban planning and environmental sustainability assessment studies.

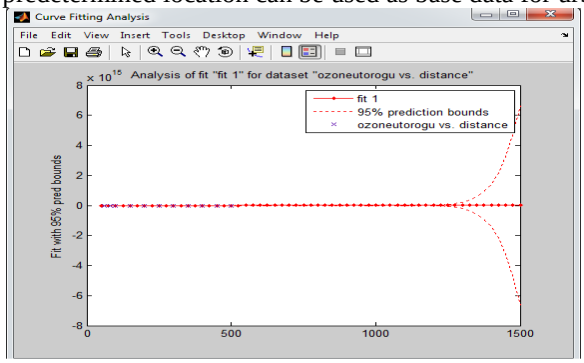


Figure 6: Model validation plot using 95% prediction bounds

The results in Figure 6 revealed that at 95% confidence level (prediction bounds) the Gaussian model can be used to accurately determine the concentration of ozone at varied sampling distances.

To test the accuracy of the Gaussian model in predicting the concentration of ozone, a reliability plot of the observed ozone concentration and the predicted ozone concentration was obtained as presented in Figure 7.

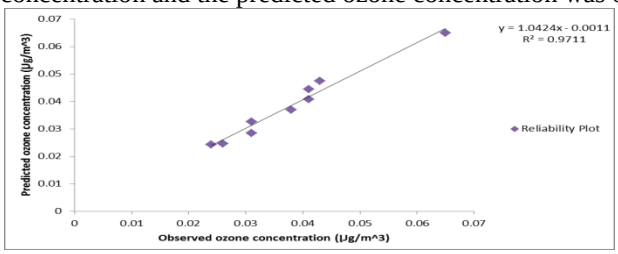


Figure 7: Reliability of Gaussian model

The high coefficient of determination (0.9711) as observed in Figure 7 was employed to conclude that the mathematical model developed is adequate and reliable.

3.5 Sampling distance against concentration of Nitrogen dioxide (NO_2)

Table 12: Calculated model parameters for determining the mathematical relationship between sampling distance and Nitrogen dioxide (NO_2)

Model	R-Square	Adj. R-Square	SSE	RMSE
Linear polynomial	0.9611	0.9568	0.0033140	0.019190
Quadratic Polynomial	0.9914	0.9893	0.0007319	0.009565
Exponential	0.9928	0.9920	0.0006134	0.008255
Gaussian	0.9927	0.9909	0.0006233	0.008827
Fourier	0.9140	0.9877	0.0007319	0.010230

Based on the parameters in Table 12, it was observed that the Exponential function model had the lowest sum of error square value of 0.0006134 and coefficient of determination (R^2) value of 0.9928. It was therefore deduced that the best mathematical relationship between sampling distance and the concentration of nitrogen dioxide was Exponential function model equation as presented in Table 13.

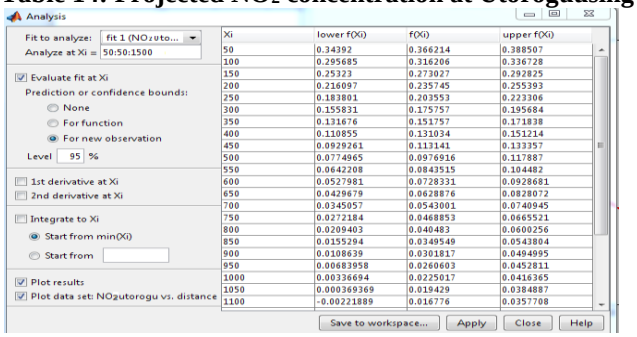
Table 13: Exponential function model for $NO_2$and sampling distance

```
General model Exp1:
      f(x) = a*exp(b*x)
Coefficients (with 95% confidence bounds):
      a =      0.4241  (0.4065, 0.4417)
      b =   -0.002936  (-0.003154, -0.002719)
```

where;
f(x): NO_2 concentration ($\mu g/m^3$)
x: Sampling distance (m)

Using the Exponential function model of Table 13, the concentration of nitrogen dioxide was projected to a sampling distance above the initial 500m at 95% confidence level as presented in Table 14 and Figure 8.

Table 14: Projected NO_2 concentration at Utoroguusing Exponential function model



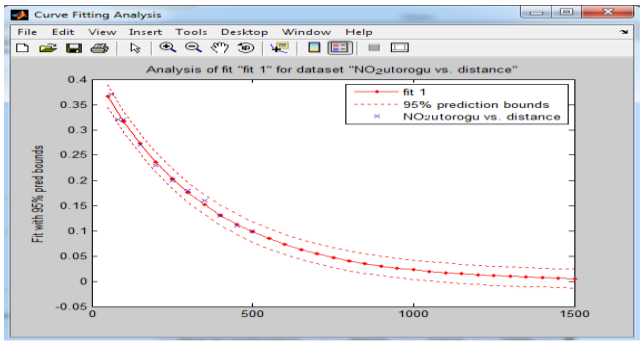


Figure 9: Model validation plot using 95% prediction bounds

The result of Figure 9 revealed that at 95% confidence level (prediction bounds) the Exponential function model can be employed to accurately determine the concentration of nitrogen dioxide at varied sampling distances.

To test the accuracy of the Exponential function model in predicting the concentration of NO_2, a reliability plot of the observed NO_2 concentration and the predicted NO_2 concentration was obtained as presented in Figure 10.

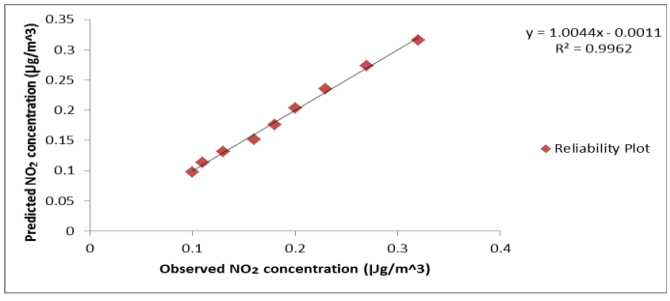


Figure 10 : Reliability of Exponential function model

The high coefficient of determination (0.9962) as observed in Figure 10 was employed to conclude that the mathematical model developed is adequate and reliable.

Conclusion

The monitoring and mathematical modelling of gaseous pollutants concentrations in the study area was examined. Four gaseous pollutants, together with their concentrations, that were determined in the study area, included VOCs, $PM_{2.5}$, $O_3$and NO_2.The mathematical modelling of the relationship between gaseous pollutants concentrations and flare distance was carried out using Matlab software and five mathematical models, viz: linear polynomial, Quadratic polynomial, Exponential, Gaussian and Fourier models. The accuracy and adequacy of the mathematical models in determining the concentration of the gaseous pollutants was also carried out.

The study has shown the mathematical models that have the best mathematical relationship with the flare distance for predicting the concentration of gaseous pollutants monitored in the study area. The mathematical model that has the lowest root mean square error or sum of square error value was considered the best model for each gaseous pollutant. The study has also revealed that variation in wind speed have significant influence on pollutants dispersion especially for point source pollution.The use of these mathematical models will help environmental engineers and scientists to ascertain at what points from the flare point the concentrations of the gaseous pollutants will be minimal and this will aid in sustainable development and pollution control.

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