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Assessment of Heavy Metals in Rainwater from Metropolis and Suburbs, Lagos State, Nigeria

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Authors' contributions

This work was carried out in collaboration among all authors. All authors read and approved the final manuscript.

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ABSTRACT

Heavy metal pollution poses a threat to rainwater which serves as a major alternative source for water for developing cities like Lagos. In the investigated of heavy metal in rainwater, 176 rainwater samples collected directly from the sky were analyzed from 2018 to 2019 during periods of light rainfall (Oct-Nov) and heavy rainfall (April-July). The pH> 5.6 indicated alkalinity. Light rainfall period average value 7.33 and heavy rainfall period 7.4.The MATLAB 7^{th} degree polynomial regression described the relationship between dependent and independent variables for the pollutants. The correlation coefficient, R^2 verified that the MATLAB models could accurately predict and forecast. Analysis of Variance (ANOVA) showed $p<0.05$ for Cadmium (Cd), Copper (Cu), Zinc (Zn), Iron (Fe) and Nickel (Ni), indicating that the probability that rainfall affected their concentration levels was high. The GIS Inverse Distance Weighted (IDW) pollution models revealed that the

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pollutants were present in the atmosphere throughout the year. It portrayed industrialized areas as the more affected areas thereby identifying anthropogenic activities as the main cause of these pollutants. During heavy rainfall periods hot spots appeared for Cd, Cu, Zn and Ni. In addition, Cd, Cu, Zn, Pb, and Ni were present in high concentration in the rainwater from suburb areas during periods of heavy rainfall. The concentration of heavy metals found in the rainwater follows the order: Fe>Zn>Ni>Cu>Cd>Pb. Cd and Pb exceeded WHO standards. Therefore there is need for rainwater treatment and monitoring by Government Agencies and parastatals to ensure public health and safety.

Keywords: Rainwater; heavy metals; GIS model; MATLAB model; polynomial regression.

1. INTRODUCTION

Water is an essential commodity for life. No living thing can survive without it [1]. Over 1 billion people in developing countries are facing water scarcity [2,3]. They depend on rainwater as a reliable and sustainable alternative source of water [4]. For some tropical regions it is their main source of drinking water [5]. According to UN-Water, by 2025, 1.8 billion people in the world will be living in areas with complete water scarcity. The dependence on rainwater as a vital ecological factor cannot be over emphasized [6]. In Lagos, Nigeria, production of water by the Lagos State Water Corporation (LSWC) is at 210 Millions of Gallon per Day (MGD) is far below the 540 MGD needed. The public water corporation only serves 10% of the populace [7]. In the State, rainwater is considered a major alternative source of water for the populace. Rainwater is rainfall precipitation with pH 5.6 due to the dissolution of CO_2 in rain droplets and it is supposed to be a clean water source and safe for potable consumption [1]. Unfortunately, in recent times, according to reports rainwater is no longer safe to drink due to chemical contamination by pollutants such as heavy metals [8,3]. 3.4 million People die annually from water-related causes, 99% live in the developing countries [2].

Rainfall which is an instrument of wet deposition can remove vapours or particles from the atmosphere. Heavy metals are emitted into the air as vapours or particles by both natural and man-made sources [9,10]. The quantities may range from hundreds to millions of tonnes annually. Rainfall can remove these vapours or particles of heavy metals from the atmosphere depending on its scavenging efficiency [5,11]. This wet deposition is a major pathway of accumulation of heavy metals in the aquatic ecosystem (surface and ground water). The scavenging of heavy metal pollutants by rain alters the chemical composition of the rainwater thereby leading to detrimental consequences for humans, animals and pollution of the soil and vegetation. Industrialization and urbanization are termed the two major culprits for the recent increasing levels of heavy metal in rainwater [12,13]. Some of the heavy metal pollutants include Cadium (Cd), Copper (Cu), Lead (Pd), Iron (Fe), Zinc (Zn), and Nickel (Ni). Therefore, a good knowledge of the chemical quality of rainwater is imperative in order ascertain its suitability.

Heavy Metals are elements with high atomic weight (>20) and relatively high density (> 5g/cm3), a high degree of toxicity. They are persistent, non-degradable and have a bioaccumulative nature in the food chain [14]. They also affect the biodegradability of organic pollutants thereby making the organic pollutants less degradable [15]. They are naturally occurring elements but because of their multiple industrial applications it has led to their wide spread distribution in the environment [16,17]. Some anthropogenic activities that introduce them into the environment include use of pesticides and phosphate fertilizers, waste incineration, car exhausts, combustion of fossil fuels, industrial emissions from oil refineries, petrochemical plants, foundries, smelters, chemical industry etc. Cadmium has been known to cause liver disease and nerve or brain damage, kidney damage, nervous system damage, immune system damage, psychological disorders and cancer [18]. Long-term exposure to copper can cause copper poisoning which results in Wilson's disease. Chronic inhalation of excessive concentrations of iron oxide fumes or dusts may result in development of benign pneumoconiosis, called siderosis [15,19]. Lead is one out of four metals that have the most damaging effects on human health. It can cause several unwanted effects such as, anemia, a rise in blood pressure, kidney damage, miscarriages, disruption of nervous systems, brain damage, declined fertility in men, diminished learning abilities in children and behavourial disruptions in children. It can enter a fetus through the placenta of the mother. Because of this it can cause serious damage to the nervous system and the brains of unborn children [20]. Zinc imparts an undesirable astringent taste to water causing vomiting. Nickel fumes are respiratory irritants and may cause chronic bronchitis, reduced lung function and cancer of the lung, nose cancer, larynx cancer and prostate cancer. High level of nickel concentrations on sandy soil can damage plants and it can diminish the growth rate of algae in surface water. Heavy metal pollutants in rainwater have become one of the major environmental problem of public health concern today.

Recent studies on rainwater show that investigating rainwater pollution is a good medium to study the extent of pollutants in an environment [11]. Several scientists used the Atomic Absorption Spectrophotometer (AAS) method to measure heavy metal concentrations in liquids. It is adjudged the best way for doing so as it has the benefit of permitting low detection limits thresholds [11]. Some authors recorded high readings of heavy metals in rainwater. For instance, in their analysis of harvested rain water in Hebron they reported Pb with a range of 12.94–486.4mg/L as above the WHO limit. Also, it is reported that the levels of Ni, Cd, Pb, Fe, and Mn in rainwater and groundwater at all sites exceeded WHO quality guidelines while Cu and Zn were below in their study on rain water in Eket, Nigeria. Study on assessment of natural rain in Yola metropolis recorded maximum readings for Fe and Zn as 0.30 mg/L and 0.12 mg/L respectively as below WHO limits. Wet deposition accounts for the bulk of metal deposition in the urban and industrial areas. According to [4] rainwater due to its insignificant hardness, low alkalinity and pH < 7, is considered to be water with increased corrosive aggressiveness regardless of the method of rainwater collection. Furthermore, they found that for rainwater collected directly from precipitation, the ones collected in spring showed the highest concentrations of heavy metals.While for harvested rainwater no significant correlation was observed. From research it was observed that most of the works done on rainwater obtained there result from harvested rainwater [21,4,22]. In order to investigate without interference the effect of rain on the concentration of heavy metals this work therefore studied rainwater collected directly from the sky in Lagos State to ascertain pollution levels.

Lagos State a coastal region in the Southwest of Nigeria is the most populated state and economic hub of the country. It is a barrier Island being surrounded by ocean and a lagoon. It has a tropical rainy and dry season [23]. Most months of the year are marked by significant rainfall.It actually experiences two rainy seasons, the heaviest rain falls from April to July while the weaker rainy season falls from October to November .The short dry season which is accompanied by harmattan winds from the Sahara desert has little impact. The annual rainfall is 1783mm/70.2 inch. The month with the highest number of rainy days is June (27.50 days). The month with the lowest number of rainy days is January (3 days). The rainy season being the more predominant season makes it imperative to study as rainwater serves as a good medium for wet deposition of heavy metals from the atmosphere.

So far, there is paucity of information of studies on rainwater collected directly from the open sky especially in the state. In addition, there is little or no information on the use of predictive models for analysis of rainwater data in the state. Therefore, in this study, we have carried out comprehensive analysis on rainwater collected directly from the open sky, and used chemometrics methods such as multivariate statistical analysis and geostatistical technique for data analysis. This study therefore, applied GIS and MATLAB to integrate the measure data and the spatial data of heavy metal concentrations of rainwater samples taken in 16 locations in Lagos State. This study contributes to knowledge in showcasing the mappings of the spatial cluster of heavy metal pollutants in rainwater in the state. It identified the major areas prone to the pollutants and the sources of these pollutants. It also provides mathematical tool for predictive proactive simulations. The generated information will assist in environmental pollution mitigation and effective environmental pollution management [24,10].

2. MATERIALS AND METHODS

2.1 Study Area

Lagos State is a port city situated on the Gulf of Guinea in the Southwestern region of Nigeria. It lies on latitude 6.455027 ^{o}N and longitude 3.384082 ^{o}E making it the smallest state in Nigeria. It is boarded on the North and East by Ogun State, in the West by Republic of Benin and the south by the Atlantic Ocean. 22% of its

3,577 km^2 are lagoons and creeks. Lagos has two seasons, the tropical wet and dry seasons. The maximum temperature recorded in Lagos was 37.3 °C, and the minimum was 13.9°C. The average temperature in Lagos is 27°C, and the annual average rainfall is 1657 mm [25].

2.2 Sample Collection

Data acquisitions for heavy metals were performed within the 16 sampling locations (as shown in Fig. 1 and Table 1). The selected locations were geo-referenced using a GPS (Global Positioning System) device. Research activities lasted for 63 days in the heavy rain period (May –July) and 25 days in the lighter rainy days (Oct – Nov) from 2018 to 2019. To collect the rainwater a new plastic bowl was placed 1.5 m from the ground in open space as recommended by [26]. The sample bottles were labeled and covered with black nylon bags to prevent sunlight before transportation to the laboratory.

2.3 Measurement of Heavy Metals Concentrations

Agilent Technologies 200 series AA Atomic Absorption Spectrophotometer (AAS) was used for the quantitative determination of the heavy metals (Zn, Pb, Ni, Cd, Fe, Cu). The specific hollow cathode lamp of the element under investigation was fixed in the turret assembly of the AAS. The burner was lit and a flame established from the use of acetylene/ compressed air as fuel/ oxidant. The calibration curve was created by aspirating the standard solution of each element under investigation into the nebulizer-burner assembly and the corresponding absorbance readings obtained from the digital readout of the AAS at the wavelength of the element under investigation. This was followed by the aspiration of each of the rain water sample solution and the absorbance reading obtained from the digital readout. The concentration of each element in the rain water sample was obtained by extrapolation from its calibration curve. The detection limits of the chemical analysis for Cu, Zn, Fe, Pb were less than 0.03 mg/L, each measurement was performed thrice and the calculated difference between the three determinants was less than 5%.

2.4 Air Pollution Modeling

MATLAB Simple linear regression technique was used to provide a means to model a straight-line relationship between an independent variable and a dependent variable. The regression model is given by: $y = mx + c$, where y is the output dependent variable, x is the independent input variable, m is the slope, and c is the y-intercept.

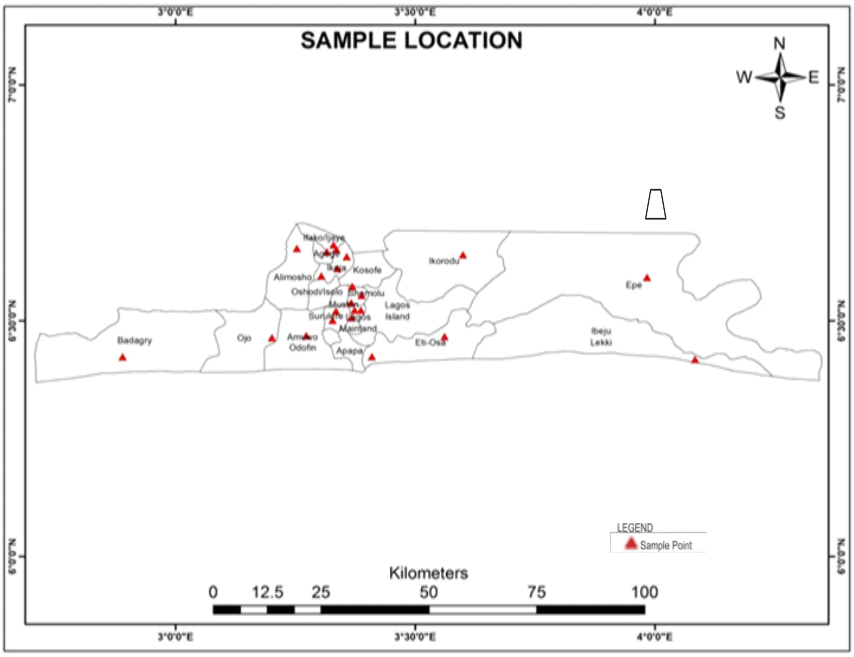


Fig. 1. GIS map of the study area showing sampling locations

Table 1. The GPS and the description of sample locations [17]

Sampling Site	Population	Lat/ Long	Altitude (ft)	Description
Agege	1,326,371	6.62, 3.33	137	Commercial, Residential
Egbeda	1,102,565	6.59,3.30	137	Commercial, Residential
Festac	542,317	6.47, 3.28	118	Residential
Ilasamanja	1,382,126	6.52, 3.33	121	Commercial Industrial
Badagry	8,801	6.42, 2.88	118	Residential
Ajah	276,824	6.47, 3.56	124	Residential
Victoria Island	138,885	6.43, 3.44	118	Commercial, Residential
EbuteLekki	3,355	6.42, 4.10	154	Residential
Ogba	1,040,471	6.64, 3.36	137	Residential
Ikeja	1,578,176	6.60, 3.34	134	Commercial, Industrial
Ikorodu	579,480	6.62, 3.51	137	Residential, Industrial
Ojodu	966,367	6.64, 3.36	134	Commercial, Residential
Obalende	197,340	6.45, 3.42	114	Commercial, Residential
Yaba	1,027,813	6.51, 3.37	118	Residential, Commercial
Palmgrove	1,742,048	6.53,3.34	124	Commercial, Residential
Ojo	422,952	6.46, 3.16	118	Commercial, Residential

For this study the best suited simple linear regression formula (Eq.1) notation used was,

$$y = a_7x^7 + a_6x^6 + a_5x^5 + a_4 x^4 + a_3x^3 + a_2x^2 + a_1x^1 + a_o \quad (1)$$

Where, y = output dependent variable (conc. levels of pollutant)

x = input independent variable (locations)
a_o = factor
a = regression coefficient

2.5 MATLAB Models

To plot the MATLAB graphs, the measure database was imported from excel to the software. Data was inputted in the form of a matrix. The command window x and y were defined as stated in the database. The plot command (x, y, 'o') was used to plot the points on the graph. The plot fit function (x, y, 7) was used to generate the best fit line. In plotting the best fit line, the Least Square method (Eqs. 2 and 3) was used to determine a and a_0, thus generating the MATLAB Mathematical models,

$$a = \frac{N\,\Sigma(xy) - \Sigma x \Sigma y}{N\,\Sigma(x^2) - (\Sigma x)^2} \quad (2)$$

$$a_o = \frac{\Sigma y - a\,\Sigma x}{N} \quad (3)$$

2.6 MATLAB Correlations Methods

Coefficient of determination R^2 (goodness of fit).

Coefficient of determination R^2 (Eq. 4) was calculated to determine how well the regression model fits the observed data. R^2 can measure the degree of fit of the model. The closer it is to 1, the better the degree of model fit.

$$R^2 = 1 - \frac{SSE}{SST} \quad (4)$$

Where,

SST (total sum of square) (Eq. 5);

$$SST = SSE + SSR \quad (5)$$

SSE (sum of square error) (Eq. 6);

$$SSE = \sum_{i=1}^{n} (Y_a - Y_p)^2 \quad (6)$$

SSR (residual sum of square) (Eq. 7);

$$SSR = \sum_{i=1}^{n} (Y_p - Y_{am})^2 \quad (7)$$

Where,

Y_a = actual response
Y_p= predicted response
Y_{am}= mean of the actual response

2.7 Root Mean Square Error (RMSE)

RMSE (Eq. 8) was used to evaluate the quality of predictions and give the spread of the residuals. Residuals show how robust the data is around the line of best fit. The closer it is to 0, the smaller the error between the predicted and true values.

$$RMSE = \sqrt{[\Sigma(\hat{y} - y)^2 / n - 2]} \quad (8)$$

Where, $\hat{y}$ = mean value of y

2.8 Adjusted R-square

Adjusted R-square (Eq. 9) is a modified version of R^2 that has been adjusted for the number of predictors in the model. It was used to determine how reliable the correlation is and how much the addition of more independent variables determines this. Typically, the adjusted R^2 is positive, not negative. It is always lower than the R^2.

$$Adj\ R^2 = 1 - \left[\frac{(1-R^2)(N-1)}{N-p-1}\right] \quad (9)$$

Where N is the sample size, p is the number of predictions.

2.9 GIS Modeling

The GIS IDW technique applied in this study is a multivariate interpolation technique that obeys the Tobler's 1^{st} law of geography. It makes the assumption that things that are close to one another are more alike than those that are farther apart. The measured values closest to the prediction location had more influence on the predicted value than those farther away. The average value for unsampled locations were generated using values from nearby weighted locations. The weights were proportional to the proximity of the sampled points to the unsampled location and were specified by the IDW power coefficient of 2. Thus (Eq. 10),

$$\hat{Z}j = \frac{\sum_i Zi/đ_i^{n} j}{\sum_i 1/đ_i^{n} j} \quad (10)$$

Where;

Z = sampled cell value
n = power coefficient
$\hat{Z}$ = unsampled cell value at *j*
$đ_i^{n} j$ = distance from unsampled location

3. RESULTS

Two years of Heavy Metals pollutant levels taken during light rain periods (October -November) and the heavy rain period (May, June, and July) in the selected locations in Lagos State are summarized in Table 2 – Table 5. Table 6 – Table 11 captured the average mean values of the heavy metal pollutants for both years and shows their histogram. MATLAB mathematical models for both years were summarized in Table 12. Table 13 shows the MATLAB model plots. Also, Figs. 2-7 displays the GIS mappings for the pollutants in both years. Fig. 8 portrays the pollutants trends in the MATLAB comparison graphs. Fig. 9 shows the pollutants MATLAB Box and whiskers plots.

Table 2. Light rain period (Year 1) mean value data for heavy metals

Sample area	pH	Cd (ppm)	Cu (ppm)	Zn (ppm)	Fe (ppm)	Pd (ppm)	Ni (ppm)
Festac	6.84	0.039	0.054	0.0053	0.265	0.11	0.047
Agege	7.6	0.04	0.05	<0.001	0.249	0.12	0.044
Ojo	7.85	0.041	0.041	<0.001	0.237	0.11	0.045
Ojodu	7.65	0.04	0.047	0.0746	0.06	0.11	0.049
Egbeda	7.56	0.04	0.046	<0.001	0.382	0.13	0.037
Yaba	7.85	0.038	0.034	<0.001	0.049	0.13	0.046
maryland	6.7	0.038	0.048	0.0352	0.082	0.12	0.048
Surulere	6.76	0.037	0.041	<0.001	0.065	0.12	0.039
Gbagada	7.85	0.037	0.032	<0.001	0.056	0.1	0.039
obalende	7.3	0.037	0.029	<0.001	0.088	0.12	0.039
Palmgrove	6.51	0.037	0.031	<0.001	0.062	0.1	0.039
Ilesamanja	7.62	0.038	0.029	0.2774	0.041	0.13	0.041
Ikeja	6.02	0.037	0.031	<0.001	0.06	0.19	0.036
Bariga	7.23	0.034	0.051	<0.001	0.105	0.14	0.037
Ogba	7.55	0.034	0.035	<0.001	0.166	0.17	0.034
Victoria island	7.68	0.037	0.029	<0.001	0.089	0.13	0.031

Table 3. Heavy Rainy period (Year 1) mean value for heavy metals

Sample area	pH	Cd (ppm)	Cu (ppm)	Zn (ppm)	Fe (ppm)	Pd (ppm)	Ni (ppm)
Festac	7.67	0.047	0.046	<0.001	0.184	0.11	0.073
Agege	7.6	0.049	0.057	0.1661	0.124	0.14	0.074
Ojo	7.86	0.049	0.053	0.0016	0.058	0.16	0.076
Ojodu	6.67	0.048	0.042	< 0.001	0.068	0.14	0.07
Egbeda	7.6	0.049	0.042	< 0.001	0.034	0.12	0.074
Yaba	7.67	0.048	0.045	< 0.001	0.097	0.1	0.068
Maryland	6.7	0.046	0.045	0.026	0.102	0.11	0.075
Surulere	6.86	0.046	0.051	0.0295	0.076	0.14	0.07
Gbagada	7.65	0.044	0.048	0.0906	0.063	0.13	0.071
Obalende	7.65	0.045	0.046	0.061	0.053	0.11	0.06
Palmgrove	6.8	0.045	0.051	0.0102	0.109	0.12	0.068
Ilesamanja	7.63	0.048	0.046	0.0626	0.129	0.15	0.072
Ikeja	6.42	0.046	0.047	0.1792	0.109	0.13	0.067
Bariga	7.33	0.045	0.048	0.0215	0.084	0.12	0.061
Ogba	7.75	0.045	0.054	0.0046	0.018	0.12	0.066
Victoria island	7.56	0.041	0.042	< 0.001	0.049	0.13	0.064

Table 4. Light rain period (Year 2) mean value for heavy metals

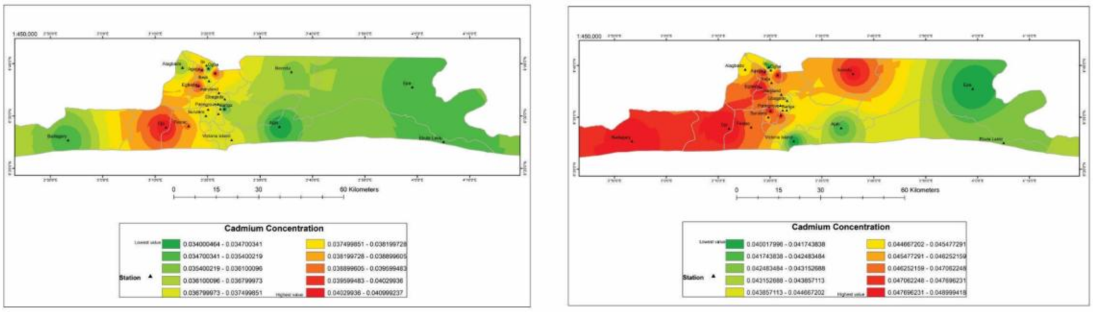
Sample area	pH	Cd (ppm)	Cu (ppm)	Zn (ppm)	Fe (ppm)	Pd(ppm)	Ni (ppm)
Festac	6.86	0.038	0.048	<0.001	0.26	0.11	0.045
Agege	7.68	0.041	0.05	<0.001	0.165	0.12	0.044
Ojo	7.86	0.041	0.04	<0.001	0.065	0.1	0.045
Ojodu	7.75	0.04	0.046	0.0354	0.065	0.12	0.046
Egbeda	7.5	0.039	0.046	<0.001	0.265	0.13	0.035
Yaba	7.85	0.038	0.034	<0.001	0.065	0.12	0.043
Maryland	6.8	0.037	0.048	0.0344	0.068	0.11	0.044
Surulere	6.86	0.036	0.041	<0.001	0.065	0.12	0.033
Gbagada	7.82	0.037	0.032	<0.001	0.065	0.11	0.034
Obalende	7.5	0.037	0.029	<0.001	0.075	0.11	0.035
Palmgrove	6.57	0.036	0.031	<0.001	0.063	0.1	0.033
Ilesamanja	7.63	0.035	0.029	0.2702	0.045	0.12	0.044
Ikeja	6.42	0.035	0.031	<0.001	0.065	0.19	0.034
Bariga	7.33	0.034	0.051	<0.001	0.068	0.12	0.035
Ogba	7.75	0.034	0.035	<0.001	0.065	0.15	0.034
Victoria island	7.8	0.036	0.029	<0.001	0.075	0.12	0.031

Table 5. Heavy Rainy period (Year 2) Mean Value for Heavy Metals

Sample area	pH	Cd (ppm)	Cu (ppm)	Zn (ppm)	Fe (ppm)	Pd(ppm)	Ni (ppm)
Festac	7.02	0.046	0.046	<0.001	0.184	0.12	0.074
Agege	7.62	0.049	0.046	0.166	0.123	0.13	0.073
Ojo	7.56	0.048	0.048	0.001	0.055	0.14	0.073
Ojodu	7.75	0.048	0.043	< 0.001	0.065	0.14	0.07
Egbeda	7.5	0.049	0.044	< 0.001	0.034	0.12	0.073
Yaba	7.9	0.047	0.045	< 0.001	0.094	0.1	0.063
Maryland	7.1	0.045	0.044	< 0.001	0.1	0.1	0.072
Surulere	6.86	0.046	0.048	0.0295	0.077	0.13	0.07
Gbagada	7.82	0.044	0.046	0.0906	0.062	0.12	0.07
Obalende	7.6	0.045	0.046	< 0.001	0.055	0.13	0.063

Sample area	pH	Cd (ppm)	Cu (ppm)	Zn (ppm)	Fe (ppm)	Pd(ppm)	Ni (ppm)
Palmgrove	7.5	0.045	0.046	0.0102	0.109	0.12	0.063
Ilesamanja	7.63	0.047	0.045	0.0626	0.125	0.11	0.07
Ikeja	6.5	0.046	0.046	0.1792	0.104	0.14	0.063
Bariga	7.34	0.046	0.046	0.0215	0.083	0.14	0.063
Ogba	7.78	0.044	0.048	< 0.001	0.015	0.12	0.063
Victoria island	7.9	0.042	0.041	< 0.001	0.044	0.12	0.063

Figure 2. GIS map for Cd concentration in (a) Light rain period (b) Heavy rain period (Year 1)



GIS map for Cd concentration in (a) Light rain period (b) Heavy rain period (Year 2)

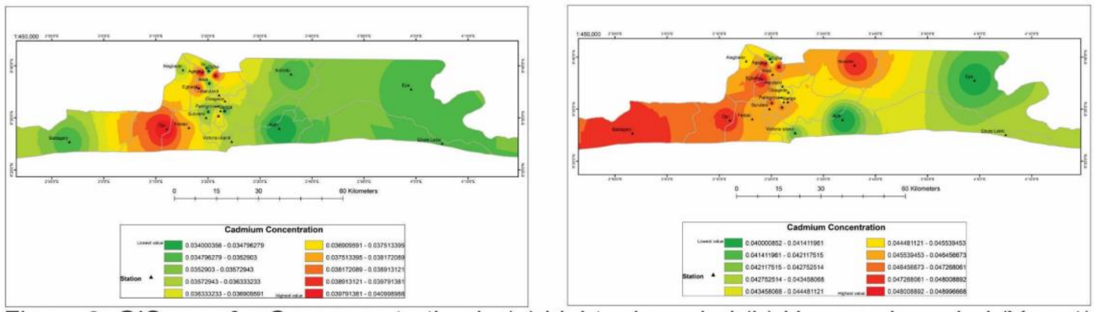
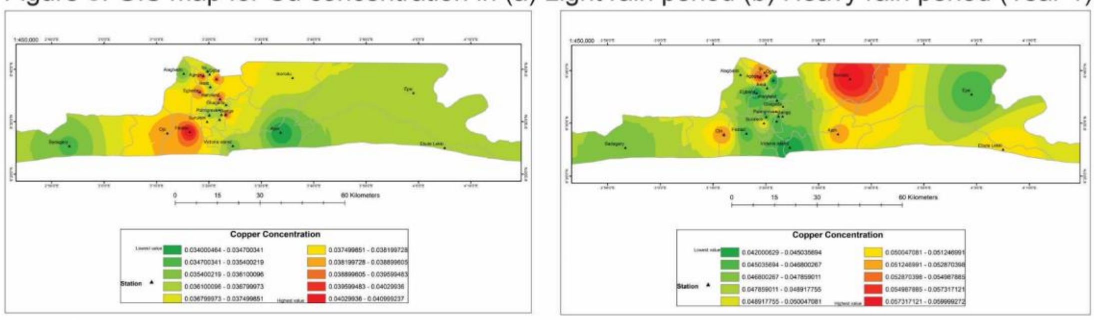


Figure 3. GIS map for Cu concentration in (a) Light rain period (b) Heavy rain period (Year 1)



GIS map for Cu concentration in (a) Light rain period (b) Heavy rain period (Year 2)

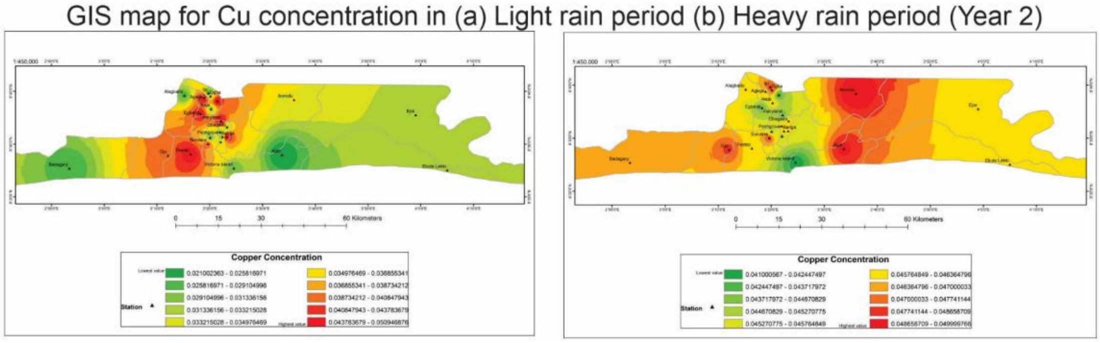
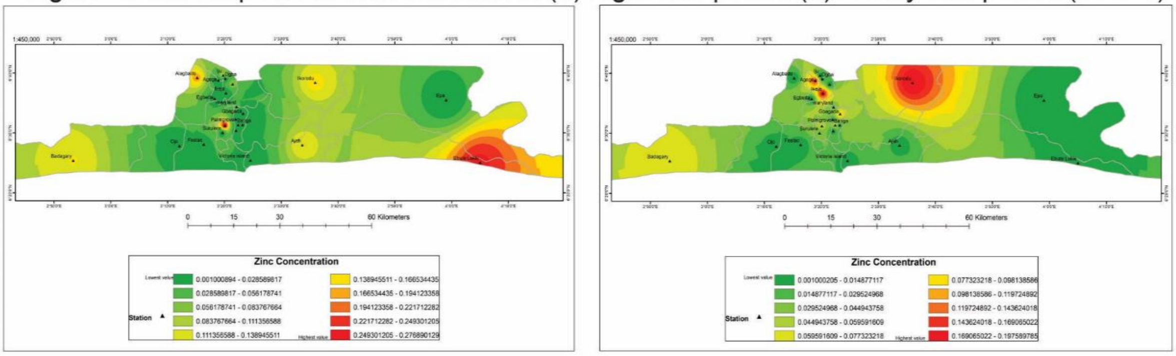


Figure 4. GIS map for Zn concentration in (a) Light rain period (b) Heavy rain period (Year 1)



GIS map for Zn concentration in (a) Light rain period (b) Heavy rain period (Year 2)

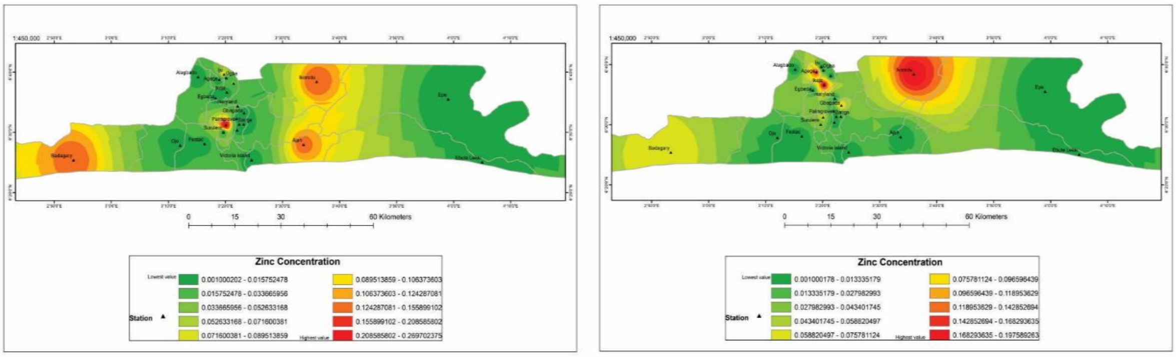
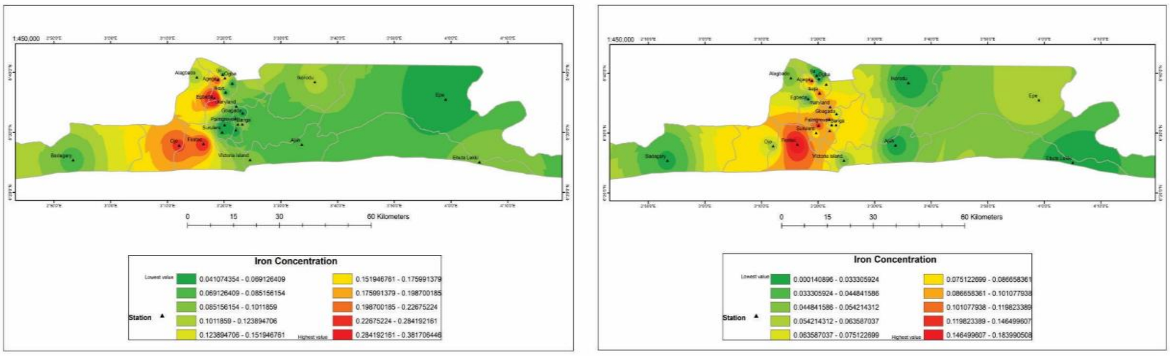


Figure 5. GIS map for Fe concentration in (a) Light rain period (b) Heavy rain period (Year 1)



GIS map for Fe concentration in (a) Light rain period (b) Heavy rain period (Year 2)

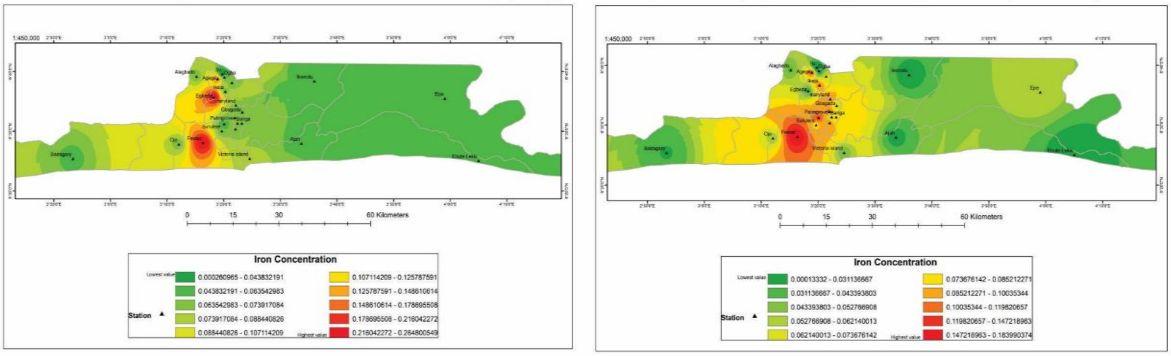
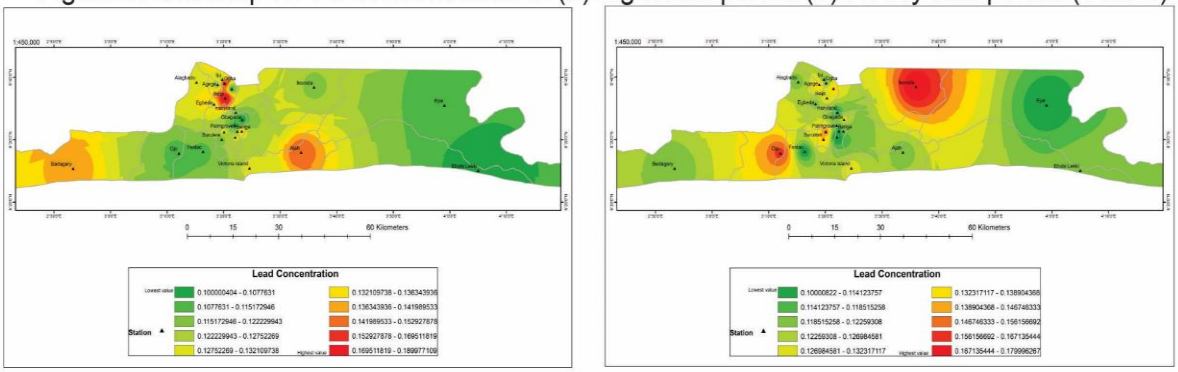


Figure 6. GIS map for Pb concentration in (a) Light rain period (b) Heavy rain period (Year 1)



GIS map for Pb concentration in (a) Light rain period (b) Heavy rain period (Year 2)

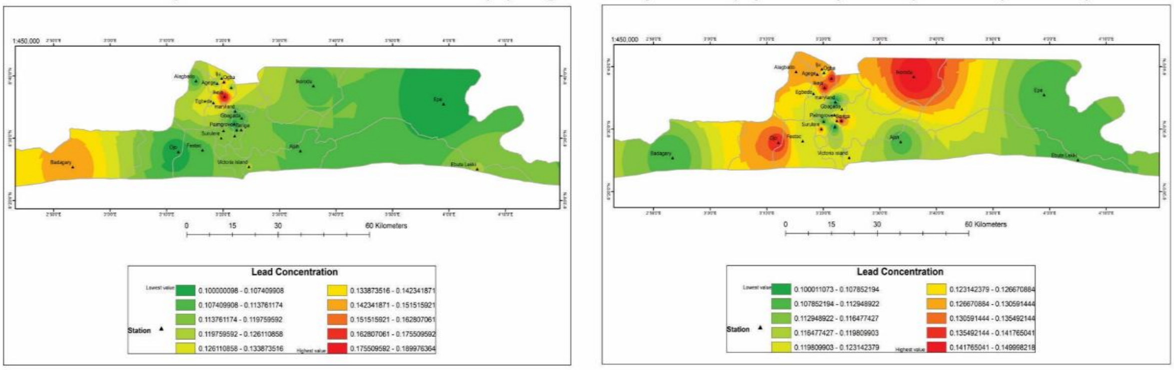
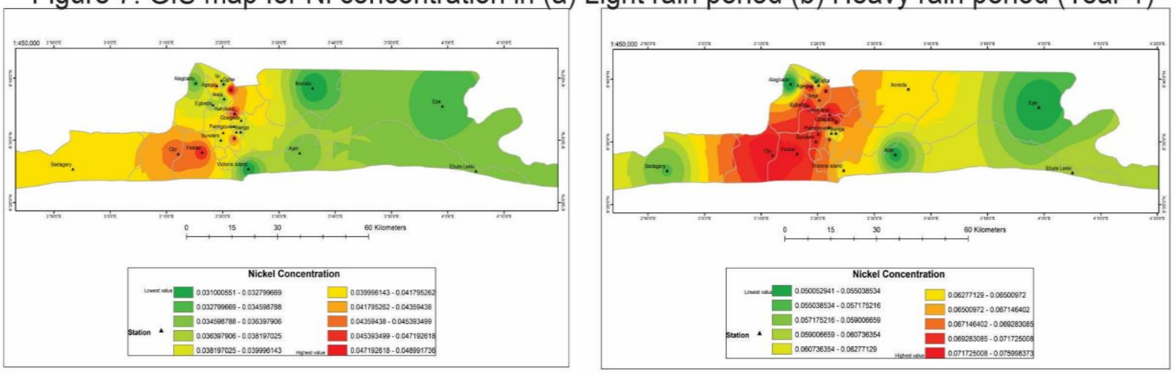


Figure 7. GIS map for Ni concentration in (a) Light rain period (b) Heavy rain period (Year 1)



GIS map for Ni concentration in (a) Light rain period (b) Heavy rain period (Year 2)

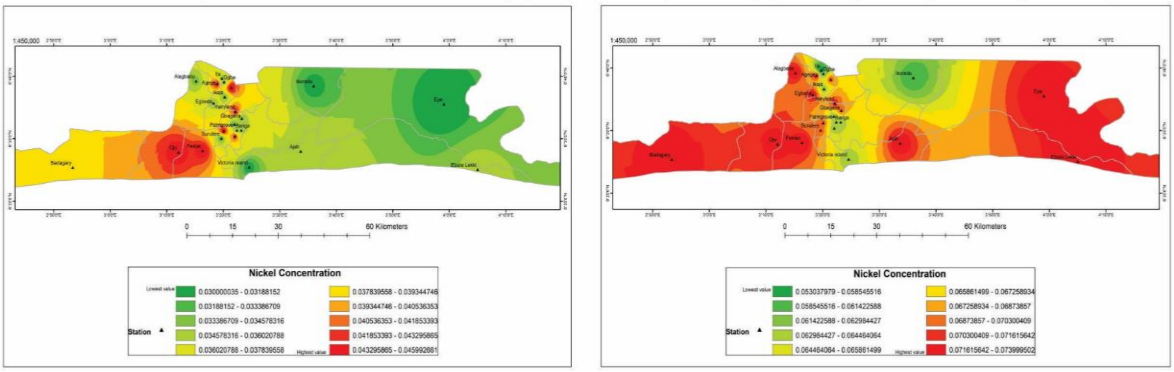


Table 6. Mean values for Cd (ppm) for both years

Sample areas	Yr1 Light rain	Yr2 Light rain	Mean	Yr1 Heavy rainy	Yr2 Heavy rainy	Mean
Festac	0.039	0.038	0.039	0.047	0.046	0.047
Agege	0.04	0.041	0.041	0.049	0.049	0.049
Ojo	0.041	0.041	0.041	0.049	0.048	0.049
Ojodu	0.04	0.04	0.04	0.048	0.048	0.049
Egbeda	0.04	0.039	0.04	0.049	0.049	0.049
Yaba	0.038	0.038	0.038	0.048	0.047	0.048
Maryland	0.038	0.037	0.038	0.046	0.045	0.046
Surulere	0.037	0.036	0.037	0.046	0.046	0.046
Gbagada	0.037	0.037	0.037	0.044	0.044	0.044
Obalende	0.037	0.037	0.037	0.045	0.045	0.045
Palmgrove	0.037	0.036	0.037	0.045	0.045	0.045
Ilesamanja	0.038	0.035	0.037	0.048	0.047	0.048
Ikeja	0.037	0.035	0.036	0.046	0.046	0.046
Bariga	0.034	0.034	0.034	0.045	0.046	0.046
Ogba	0.034	0.034	0.034	0.045	0.044	0.045
Victoria island	0.037	0.036	0.037	0.041	0.042	0.042

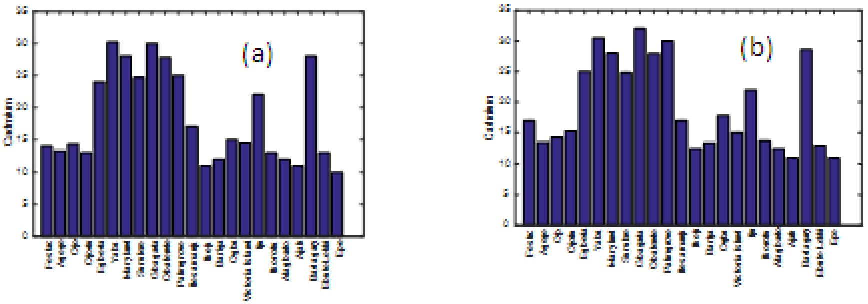
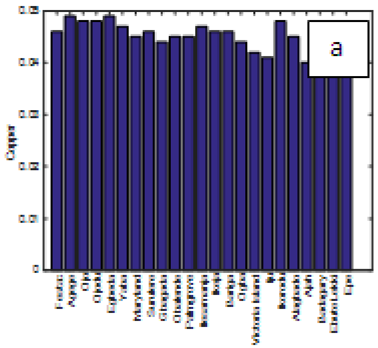


Table 7. Mean value Cu (ppm) for both years

Sample areas	Yr1 Light rain	Yr2 Light rain	Mean	Yr1 Heavy rainy	Yr2 Heavy rainy	Mean
Festac	0.054	0.048	0.051	0.046	0.046	0.046
Agege	0.05	0.05	0.05	0.057	0.046	0.052
Ojo	0.041	0.04	0.041	0.053	0.048	0.051
Ojodu	0.047	0.046	0.047	0.042	0.043	0.043
Egbeda	0.046	0.046	0.046	0.042	0.044	0.043
Yaba	0.034	0.034	0.034	0.045	0.045	0.045
Maryland	0.048	0.048	0.048	0.045	0.044	0.045
Surulere	0.041	0.041	0.041	0.051	0.048	0.050
Gbagada	0.032	0.032	0.032	0.048	0.046	0.047
Obalende	0.029	0.029	0.029	0.046	0.046	0.046
Palmgrove	0.031	0.031	0.031	0.051	0.046	0.049
Ilesamanja	0.029	0.029	0.029	0.046	0.045	0.046
Ikeja	0.031	0.031	0.031	0.047	0.046	0.047
Bariga	0.051	0.051	0.051	0.048	0.046	0.047
Ogba	0.035	0.035	0.035	0.054	0.048	0.051
Victoria island	0.029	0.029	0.029	0.042	0.041	0.042



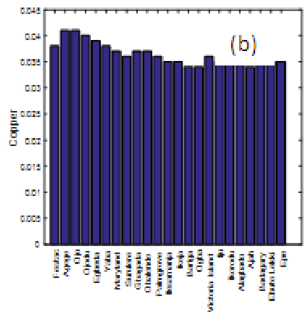
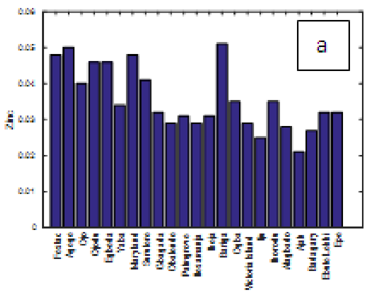


Table 8. Mean value Zn (ppm) for both years

Sample areas	Yr1 Light rain period	Yr2 Light rain period	Mean	Yr1 Heavy rain period	Yr2 Heavy rain period	Mean
Festac	0.0053	<0.001	0.0053	<0.001	<0.001	<0.001
Agege	<0.001	<0.001	<0.001	0.1661	0.166	0.1661
Ojo	<0.001	<0.001	<0.001	0.0016	0.001	0.0014
Ojodu	0.0746	0.0354	0.055	< 0.001	< 0.001	<0.001
Egbeda	<0.001	<0.001	<0.001	< 0.001	< 0.001	<0.001
Yaba	<0.001	<0.001	<0.001	< 0.001	< 0.001	<0.001
Maryland	0.0352	0.0344	0.0348	0.026	< 0.001	0.026
Surulere	<0.001	<0.001	<0.001	0.0295	0.0295	0.0295
Gbagada	<0.001	<0.001	<0.001	0.0906	0.0906	0.0906
Obalende	<0.001	<0.001	<0.001	0.061	< 0.001	0.061
Palmgrove	<0.001	<0.001	<0.001	0.0102	0.0102	0.0102
Ilesamanja	0.2774	0.2702	0.2738	0.0626	0.0626	0.0626
Ikeja	<0.001	<0.001	<0.001	0.1792	0.1792	0.1792
Bariga	<0.001	<0.001	<0.001	0.0215	0.0215	0.0215
Ogba	<0.001	<0.001	<0.001	0.0046	< 0.001	0.0046
Victoria island	<0.001	<0.001	<0.001	< 0.001	< 0.001	<0.001



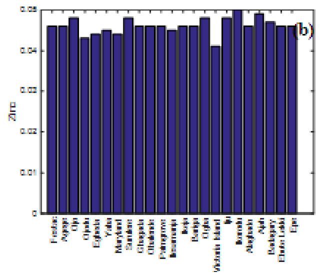


Table 9. Mean value Fe (ppm) for both years

Sample Areas	Yr1 Light rain	Yr2 Light rain	Mean	Yr1 Heavy Rain	Yr2 Heavy Rain	Mean
Festac	0.265	0.26	0.264	0.184	0.184	0.184
Agege	0.249	0.165	0.207	0.124	0.123	0.124
Ojo	0.237	0.065	0.151	0.058	0.055	0.057
Ojodu	0.06	0.065	0.063	0.068	0.065	0.067
Egbeda	0.382	0.265	0.324	0.034	0.034	0.034
Yaba	0.049	0.065	0.057	0.097	0.094	0.096
Maryland	0.082	0.068	0.075	0.102	0.1	0.101
Surulere	0.065	0.065	0.065	0.076	0.077	0.077
Gbagada	0.056	0.065	0.0605	0.063	0.062	0.063
Obalende	0.088	0.075	0.0815	0.053	0.055	0.054
almgrove	0.062	0.063	0.063	0.109	0.109	0.109
lesamanja	0.041	0.045	0.046	0.129	0.125	0.127
Ikeja	0.06	0.065	0.063	0.109	0.104	0.107
Bariga	0.105	0.068	0.0865	0.084	0.083	0.084
Ogba	0.166	0.065	0.1155	0.018	0.015	0.017
Victoria island	0.089	0.075	0.082	0.049	0.044	0.047

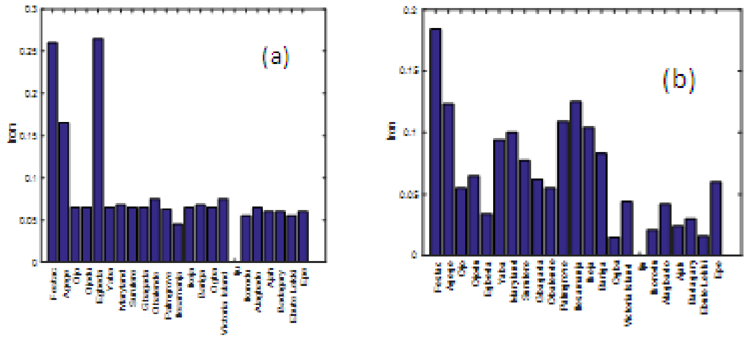
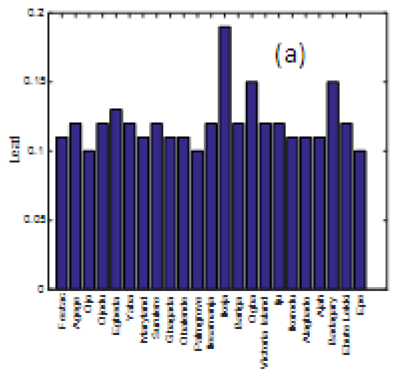


Table 10. Mean value Pb (ppm) for both years

Sample areas	Yr1 Light rain	Yr2 Light rain	Mean	Yr1 Heavy rain	Yr2 Heavy rain	Mean
Festac	0.11	0.11	0.11	0.11	0.12	0.12
Agege	0.12	0.12	0.12	0.14	0.13	0.14
Ojo	0.11	0.1	0.1	0.16	0.14	0.15
Ojodu	0.11	0.12	0.12	0.14	0.14	0.14
Egbeda	0.13	0.13	0.13	0.12	0.12	0.12
Yaba	0.13	0.12	0.13	0.1	0.1	0.1
Maryland	0.12	0.11	0.12	0.11	0.1	0.11
Surulere	0.12	0.12	0.12	0.14	0.13	0.14
Gbagada	0.1	0.11	0.11	0.13	0.12	0.13
Obalende	0.12	0.11	0.12	0.11	0.13	0.12
Palmgrove	0.1	0.1	0.1	0.12	0.12	0.12
Ilesamanja	0.13	0.12	0.13	0.15	0.11	0.13
Ikeja	0.19	0.19	0.19	0.13	0.14	0.14
Bariga	0.14	0.12	0.14	0.12	0.14	0.13
Ogba	0.17	0.15	0.16	0.12	0.12	0.12
Victoria island	0.13	0.12	0.13	0.13	0.12	0.13



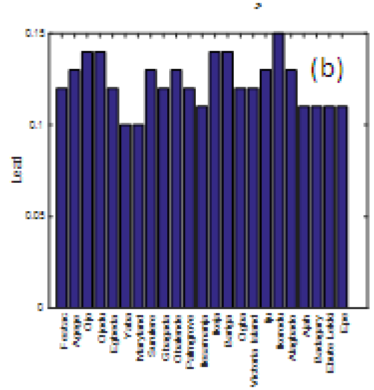
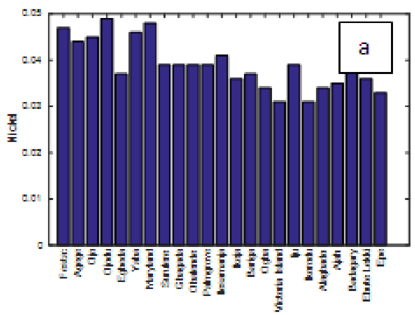
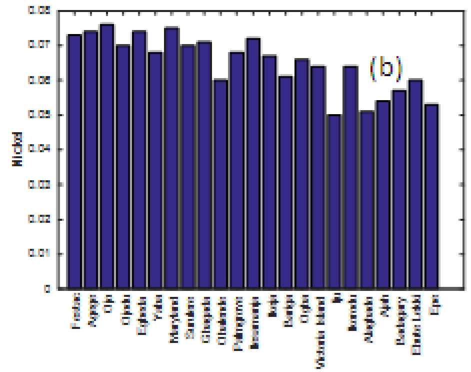
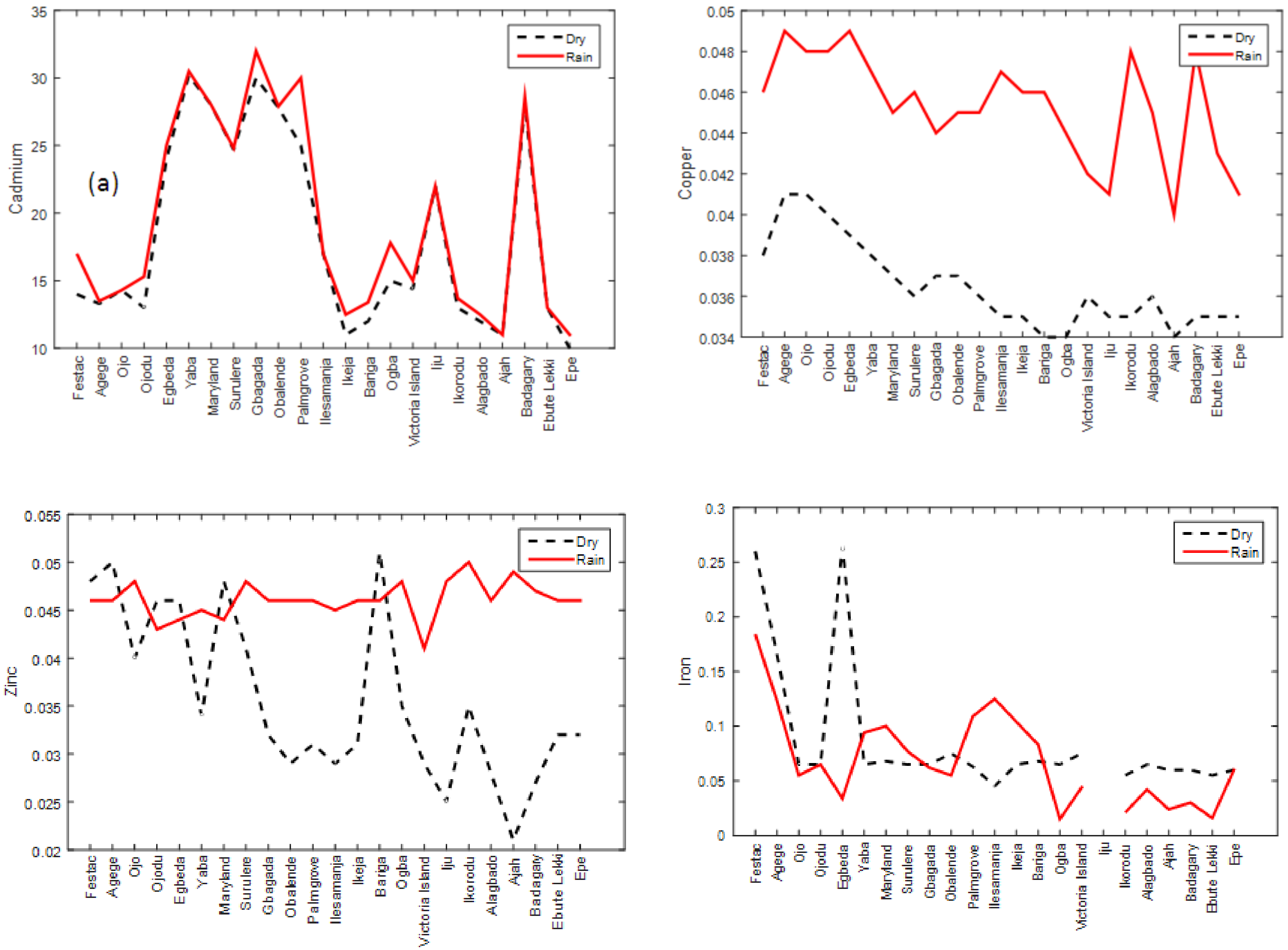


Table 11. Mean value Ni (ppm) for both years

Sample areas	Yr1 Light rain	Yr2 Light rain	Mean	Yr1 Heavy rainy	Yr2 Heavy rainy	Mean
Festac	0.047	0.045	0.046	0.073	0.074	0.074
Agege	0.044	0.044	0.044	0.074	0.073	0.074
Ojo	0.045	0.045	0.045	0.076	0.073	0.075
Ojodu	0.049	0.046	0.045	0.07	0.07	0.07
Egbeda	0.037	0.035	0.036	0.074	0.073	0.074
Yaba	0.046	0.043	0.045	0.068	0.063	0.066
Maryland	0.048	0.044	0.046	0.075	0.072	0.074
Surulere	0.039	0.033	0.036	0.07	0.07	0.07
Gbagada	0.039	0.034	0.037	0.071	0.07	0.071
Obalende	0.039	0.035	0.037	0.06	0.063	0.062
Palmgrove	0.039	0.033	0.037	0.068	0.063	0.066
Ilesamanja	0.041	0.044	0.043	0.072	0.07	0.071
Ikeja	0.036	0.034	0.035	0.067	0.063	0.065
Bariga	0.037	0.035	0.036	0.061	0.063	0.062
Ogba	0.034	0.034	0.034	0.066	0.063	0.065
Victoria island	0.031	0.031	0.031	0.064	0.063	0.064






(a)
Cadmium
35
30
25
20
15
10
Dry
Rain
Festac
Agege
Ojo
Ojodu
Egbeda
Yaba
Maryland
Surulere
Gbagada
Obalende
Palmgrove
Ilesamanja
Ikeja
Bariga
Ogba
Victoria Island
Iju
Ikorodu
Alagbado
Ajah
Badagary
Ebute Lekki
Epe
Copper
0.05
0.048
0.046
0.044
0.042
0.04
0.038
0.036
0.034
Zinc
0.055
0.05
0.045
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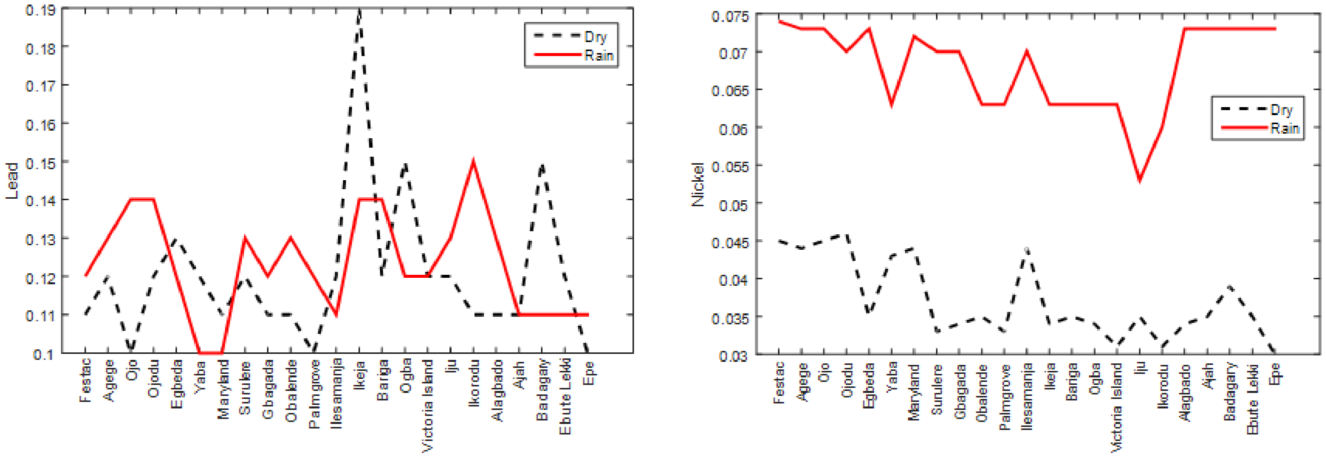
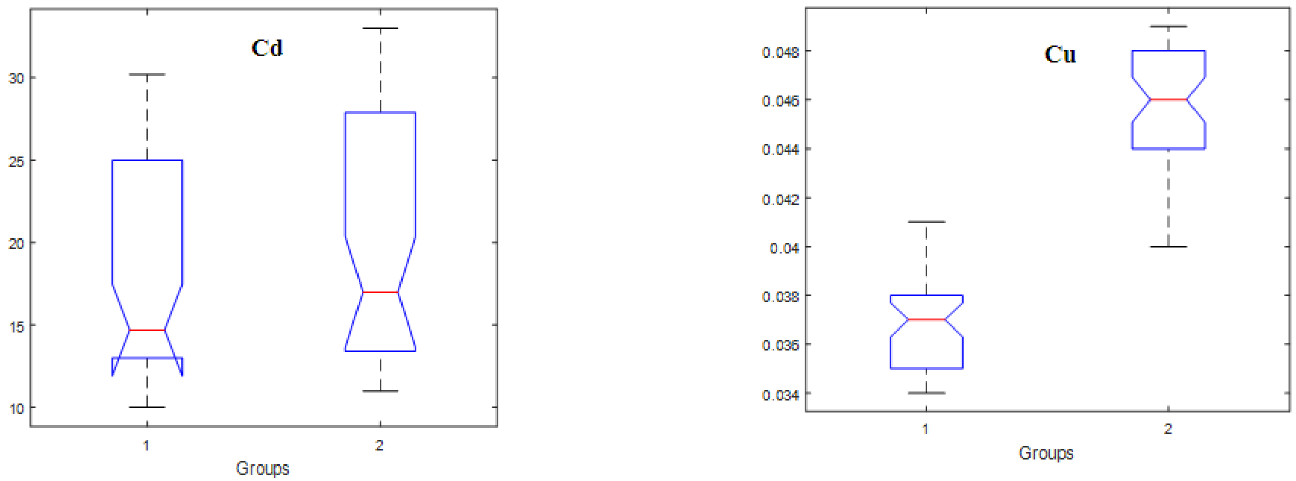


Fig. 8. MATLAB air pollutant comparison graphs for both years (a) Cd (b) Cu (c) Zn (d) Fe (e) Pb (f) Ni



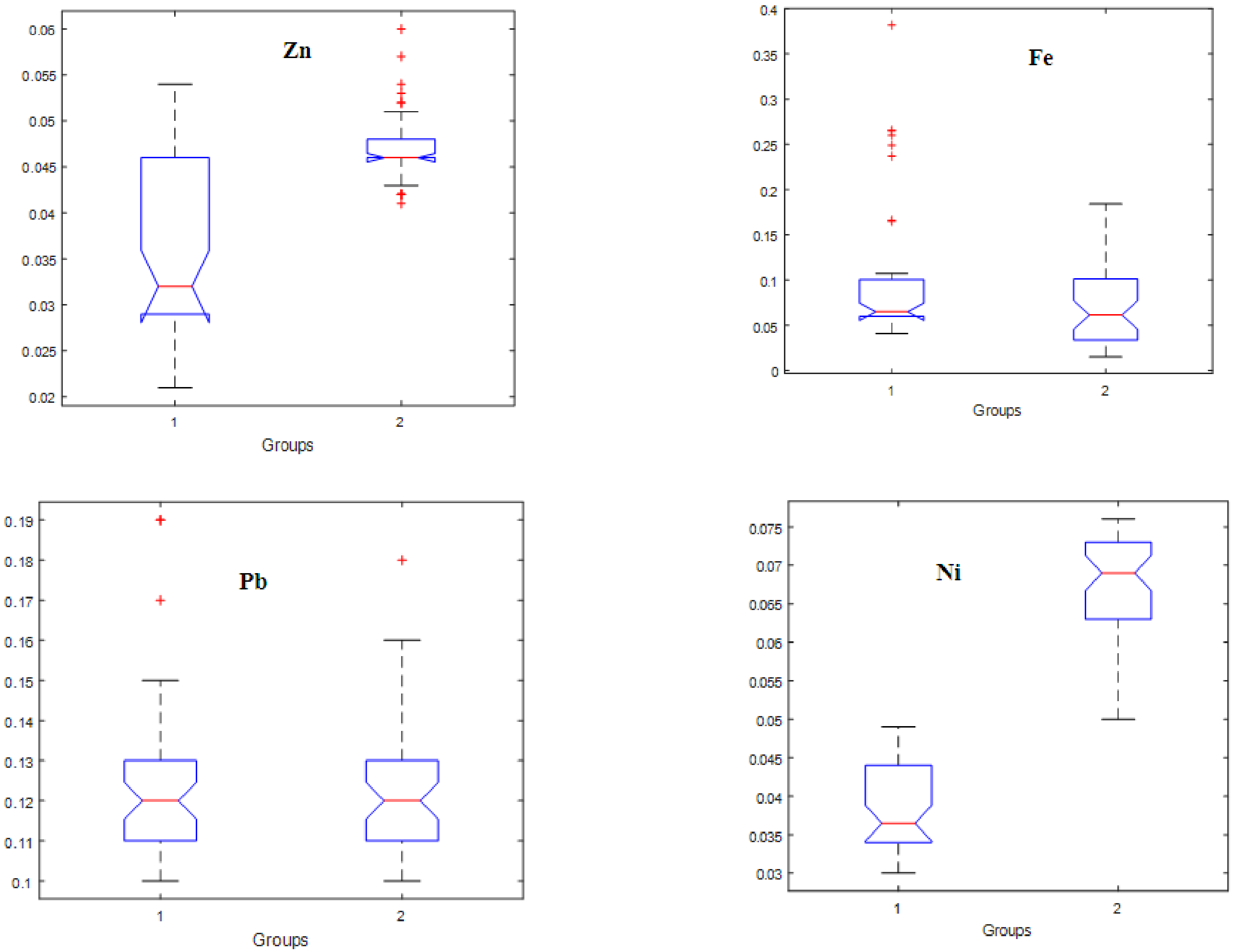


Fig. 9. Box and whiskers plots for pollutants for both years (Group 1- Light rain; Group 2 – Heavy rain)

Table 12. MATLAB mathematical models for both years

Pollutants	Period	Model	R^2	ADJ R^2	RMSE
Cd	Light rain	$y=-1.3e^{-06}x^7+0.00013x^6-0.0058x^5+0.14x^4-1.7x^3+11x^2-28x+35$	0.6099	0.4279	5.491
	Heavy rain	$y=-1.8e^{-06}x^7+0.00017x^6-0.007x^5+0.15x^4-1.9x^3+12x^2-30x+38$	0.6241	0.4486	5.461
Cu	Light rain	$y=1.2e^{-09}x^7-9.9\ e^{-08}x^6+3.4e^{-06}x^5-6.1e^{-05}x^4+0.00062x^3-0.0034x^2+0.0086x+0.033$	0.7795	0.6766	0.0011
	Heavy rain	$y=-9.8e^{-10}x^7+6.2\ e^{-08}x^6-1.3e^{-06}x^5+8e^{-06}x^4+9.1e^{-05}x^3-0.0014x^2+0.0055x+0.043$	0.5611	0.3562	0.0021
Zn	Light rain	$y=5e^{-05}x^7-0.0042x^6-0.14x^5-2.4x^4+21x^3-99x^2+2e^{+02}x-31$	0.6700	0.516	0.0064
	Heavy rain	$y=-9e^{-09}x^7+7.8e^{-07}x^6-2.7e^{-05}x^5+0.00047x^4-0.0044x^3-0.021x^2+0.05x+0.088$	0.3912	0.1071	0.0044
Fe	Light rain	$y=-5.2e^{-08}x^7+4.3e^{-06}x^6-0.00014x^5+0.0023x^4-0.02x^3+0.083x^2-0.18x+0.38$	0.5078	0.278	0.0740
	Heavy rain	$y=-3.7e^{-09}x^7+3.4e^{-07}x^6-1.3e^{-05}x^5+0.00031x^4-0.0045x^3+0.038x^2-0.16x+0.31$	0.7216	0.5824	0.0277
Pb	Light rain	$y=-2.9e^{-08}x^7+2.4e^{-06}x^6-7.7e^{-05}x^5-0.0012x^4-0.011x^3-0.044x^2-0.08x+0.16$	0.3944	0.1118	0.0204
	Heavy rain	$y=-2.9e^{-08}x^7-2.6e^{-06}x^6+9.1e^{-05}x^5-0.0017x^4+0.017x^3-0.088x^2+0.21x-0.032$	0.3825	0.0944	0.0173
Ni	Light rain	$y=-2.8e^{-09}x^7+2.2e^{-07}x^6-7e^{-06}x^5+0.00011x^4-0.001x^3+0.0046x^2-0.01x+0.053$	0.6994	0.5591	0.0035
	Heavy rain	$y=-4.6e^{-09}x^7+3.6e^{-07}x^6-1.1e^{-05}x^5+0.00017x^4-0.0014x^3+0.0054x^2-0.0093x+0.079$	0.7615	0.6502	0.0047

Table 13. MATLAB polynomial regression plots for both years

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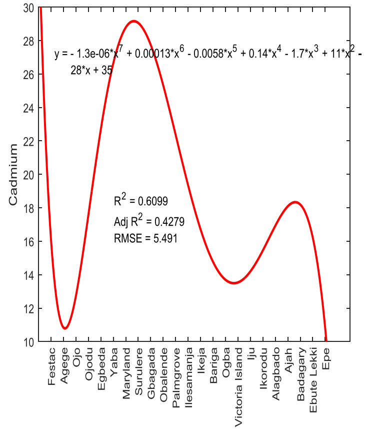
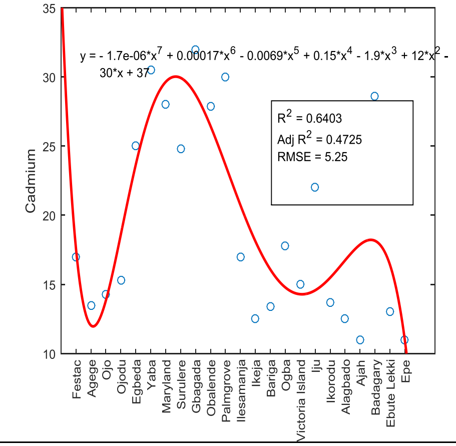
<tr><td>Cd</td><td>
</td><td>
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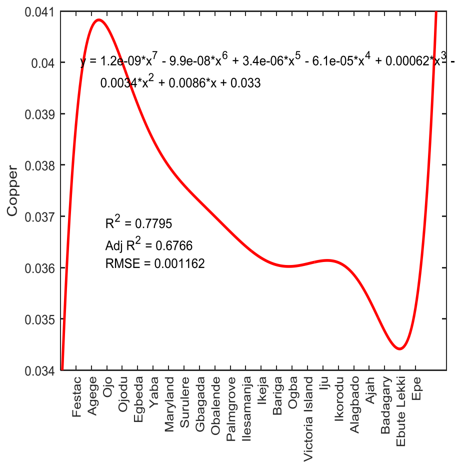
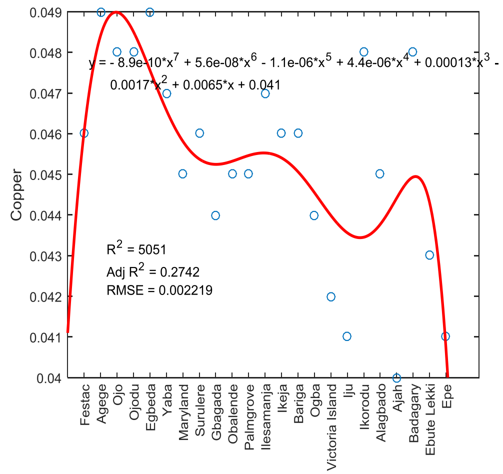
<tr><td>Cu</td><td>
</td><td>
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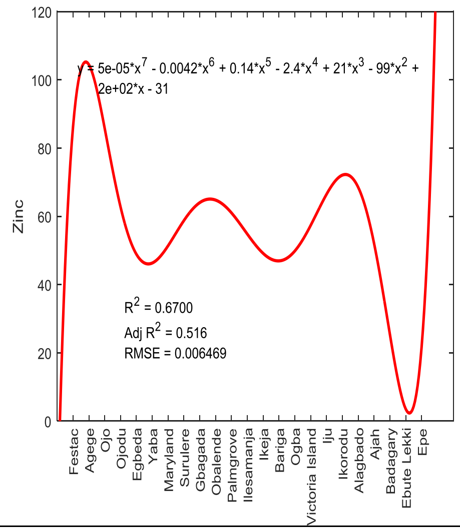
Parameters | **Light rain** | **Heavy rain**

Zn

Light rain:



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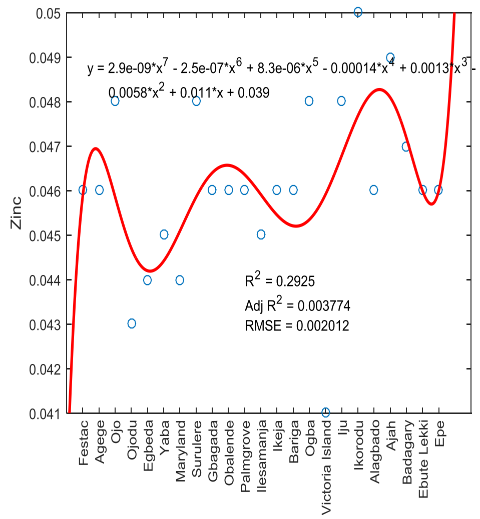
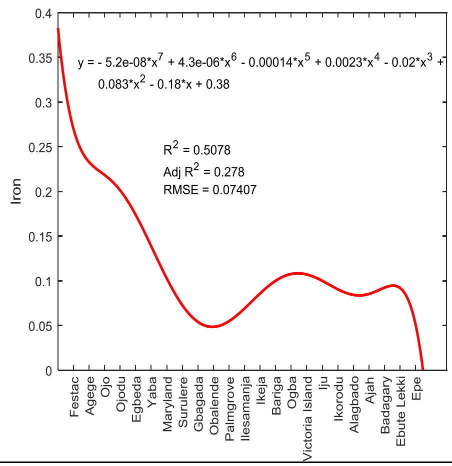
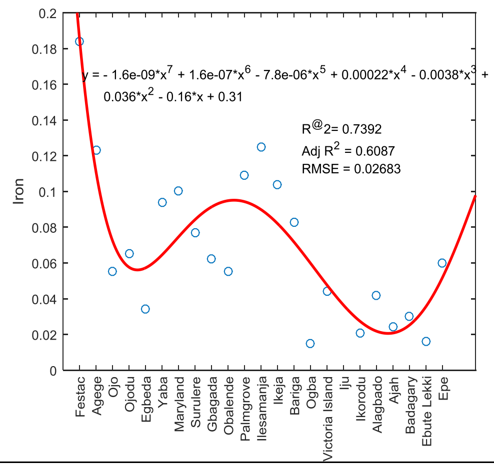


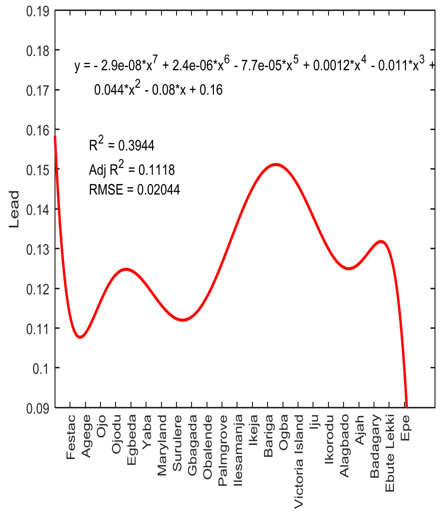
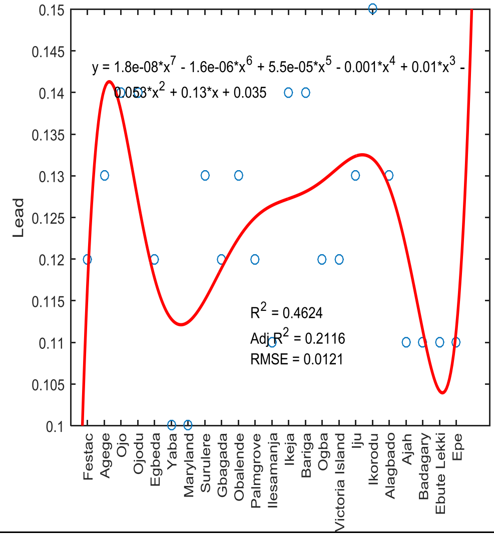
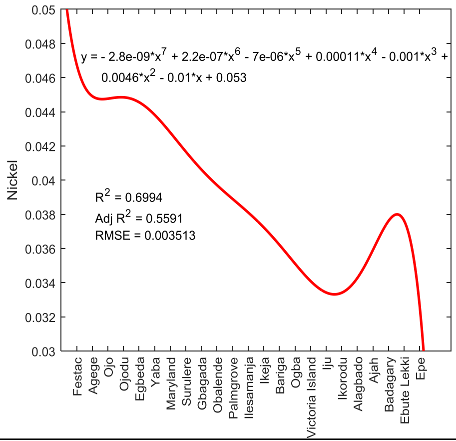
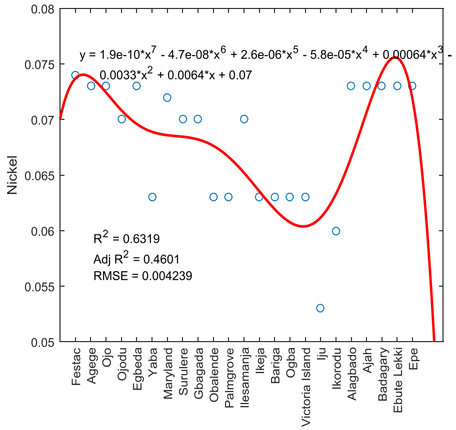
Fe

Light rain:



Heavy rain:



Parameters	Light rain	Heavy rain
Pb		
Ni		

4. DISCUSSION

The concentrations of Cd measured during the dry seasons ranged between 0.035 - 0.041ppm ppm and were lower than that measured during the rainy seasons which fell between 0.042 - 0.049ppm (Table 6). The maximum average Cd concentration of 0.049 ppm was recorded in Ojo, Ojodu and Egbeda during the rainy seasons. Intensive vegetable farming activities in Ojo and industries citied in these areas are seen to be the cause of these high readings. These concentration levels of Cd in the rainwater for both seasons were seen to be above WHO maximum limit [2] (0.003mg/l). The GIS pollution mappings (Fig. 2) revealed the spatial distribution pattern of Cd in the State. It showed that more hot spot locations of Cd appeared during the Rainy seasons. These hot spots appeared in the metropolis areas which were identified as industrialized areas confirming the effect of the presence of the numerous manufacturing companies in the State. Hot spots with high concentration levels appeared during the rainy seasons even in the suburb areas, buttressing the scavenging effect of rains on the pollutant. Furthermore, the mappings disclosed that hot spots where seen in both seasons indicating that Cd was present throughout the year. The histogram in Table 6 and the box and whiskers plot (Fig. 9), confirmed that higher concentration level readings were recorded during the rainy seasons. While, the MATLAB comparison graph (Fig. 8a) showed similar trends occurring in both seasons. The MATLAB models (Table 12) had high R^2 and low p-value in both seasons (the best scenario in modeling), indicating that the models can effectively predict 62% of the Cd variation in the dry season and 70% in the rainy season. The ANOVA analysis showed the $P < 0.05$, therefore indicating that the concentration levels of Cd in the rainwater were significantly affected by change in season.

The concentrations of Cu measured during the dry seasons were from 0.021 - 0.051ppm while that of the rainy seasons were higher at 0.043 - 0.052ppm. The highest concentration readings of 0.052 ppm were recorded in Agege during the rainy season. This area is a densely populated area known for generating so much sewage and fossil fuel combustion. However, these concentration levels of Cu in the rainwater for both seasons were seen to be below WHO (2mg/L).The GIS pollution distribution pattern mappings (Fig. 3) revealed that hot spot locations of Cu appeared in both seasons showing that the pollutant is always present in the state. These hot spots appeared in the metropolis areas which were identified as industrialized areas indicating the effect of the numerous industrial and agricultural activities going on in these areas. During the rainy seasons hot spots did not only appear in the metropolis areas but also in the suburb areas showcasing the scavenging role of the rains in air pollution. The mappings displayed that hot spot locations appeared in both seasons indicating that Cu was present throughout the year. The MATLAB air pollutant graphs (Fig. 8(b)) compared both seasons and showed that the concentration levels of Cu as higher in the rainy season. It showed that the trend of pollution differed in both seasons. Also, the box and whiskers plot (Fig. 9) confirmed that the distribution of the concentration level readings were higher in the rainy season. The MATLAB polynomial regression models (Table 13) had the best scenario in modeling, high R^2 and low p-value, in both seasons indicating that the models can effectively predict 77% of the Cu variation in the dry season and 56% in the rainy season. The ANOVA analysis showed the $P < 0.05$, therefore indicating that the concentration levels of Cu in the rainwater was significantly affected by seasonal variation.

For the years under study, concentrations of Zn measured during the dry season fell between <0.001- 0.2738ppm and that measured during the rainy seasons which fell between <0.001- 0.1792ppm.These concentration levels of Zn in the rain water for both seasons were below the WHO limit (3.0mg/L).The GIS pollution distribution pattern mappings (Fig. 4) revealed that hot spot locations of Zn appeared in both seasons. These hot spots appeared in the metropolis and suburb area. The hot spot locations seen in both seasons indicated that Zn was present throughout the year, albeit in small concentrations. The MATLAB air pollution comparison graphs (Fig. 8(c)) clearly showed that during the rainy seasons the readings were continuously high. The box and whiskers plot (Fig. 9) confirmed this as it portrayed dense high readings in the rainy seasons but more distributed readings in the dry seasons. The MATLAB polynomial regression models (Table 13) had high R^2 and low p-value in both seasons, the models effectively predicted 67% of the Zn variation in the dry season and 39% in the rainy season. The ANOVA analysis showed the $P< 0.05$, therefore indicating that the concentration levels of Zn in the air is significantly affected by change in season.

The concentration levels measured for Fe in the dry seasons was between 0.046 - 0.324ppm, and this was higher than that measured during the rainy seasons from <0.006 - 0.184 ppm. A spike at 0.324ppm was noted in Egbeda during the dry season. This can be attributed to biomass burning and fossil fuel combustion in the area. The concentration levels of Fe in the rain water for both seasons were below WHO maximum limit (0.8mg/L). The GIS air pollution distribution pattern mappings (Fig. 5) revealed that hot spot locations of Fe appeared in both seasons. These hot spots appeared in the metropolis areas which were identified as industrialized areas. Here, hot spots did not appear in the suburb areas in both seasons. However, the hot spot locations where seen in both seasons indicating that Fe was present throughout the year. The MATLAB air pollution comparison graphs (Fig. 8(d)) showed that the concentration levels of Fe peaked at different spots in the dry season but it displayed an overlap. Also the box and whiskers plot showed that the concentration readings taking during the rainy was more evenly spread than during the dry season. The MATLAB polynomial regression models (Table 13) had high R^2 and low p-value in both seasons indicating that the models can effectively predict 50% of the Fe variation in the dry season and 72% in the rainy season. The ANOVA analysis showed the $P< 0.05$, therefore indicating that the concentration levels of Fe in the air is significantly affected by change in season.

The concentration of Pb measured during the dry seasons ranged between 0.1 - 0.19 ppm and were slightly higher than that measured during the rainy seasons, which ranged from 0.1 - 0.17 ppm. The concentration levels of Pb in the rain water for both seasons were above WHO maximum limit (0.01mg/l). This high concentration level of lead is strongly attributed to the vehicular traffic density in the State.The GIS pollution distribution pattern mappings (Fig. 6) disclosed that more hot spot locations of Pb appeared during the rainy seasons. These hot spots appeared in the metropolis areas which were identified as industrialized areas. Hot spots also appeared in the suburb areas in both seasons. The hot spot locations however, where seen in both seasons portraying that Pb was present throughout the year. The MATLAB pollution comparison graphs (Fig. 8(e)) showcased that the concentration levels of Pb for both seasons overlapped but showed some peak levels in the dry season. It also disclosed the spots where this peaks were recorded as Ikeja, Ogba and Badagary. All these areas are known to experience high vehicular traffic. The MATLAB polynomial regression models (Table 13) had low R^2 and high p-value in both seasons indicating that the models can only predicted 39% of the Pb variation in the dry season and 38% in the rainy season. The ANOVA analysis showed the $P > 0.05$, therefore indicating that the concentration levels of Pb in the air is not significantly affected by change in season.

In the years understudy, the concentration of Ni measured during the rainy seasons were between 0.062 - 0.075ppm and were higher than that measured during the dry season were between 0.031 - 0.046ppm. The concentration levels of Ni for both seasons were within WHO maximum limit (0.07mg/L). The GIS air pollution distribution pattern mappings (Fig. 7) disclosed that more hot spot locations of Ni appeared during the rainy seasons. This buttresses the role rains play in air pollution. Hot spots also appeared not only in the metropolis but also in the suburb areas in the rainy seasons. This attributed to the high level of combustion of fossil fuel and incineration of waste and sewage in the areas. These hot spots appeared in the metropolis areas which were identified as industrialized areas and also in the suburb areas in both seasons. The hot spot locations were seen in both seasons indicating that Ni was present throughout the year. The MATLAB air pollution comparison graphs (Fig. 8(f)) revealed that the concentration levels of Ni were higher in the rainy seasons. The box and whiskers plot (Fig. 9) confirmed this. The MATLAB models (Table 12) showed high R^2 and low p-value in both seasons indicating that the models effectively predicted 69% of the Ni variation in the dry season and 76% in the rainy season. The ANOVA analysis showed the $P< 0.05$, therefore indicating that the concentration levels of Ni in the air is significantly affected by change in season.

5. CONCLUSION

The study used GIS and MATLAB software to generate air pollution models, which were applied in the assessment of the effect of seasonal variations on the concentrations of heavy metals air pollutants in Lagos State. The study revealed that all the pollutants were always present in the rainwater throughout the year.

Also, anthropogenic activities were identified as the primary sources of the pollutants. In addition, some of the pollutants were present even in the suburb areas in high concentrations during the rainy seasons. Furthermore, that the metropolis areas which have numerous industrial activities being carried out there, were showcased to be the areas most prone to these pollutants. Cd and Pb exceeded WHO standards, while Cu, Zn, Fe and Ni were within the WHO standards. Fe was the heavy metal with highest concentration in rainwater in the State. This work revealed that the present situation is not alarming but it is recommended that the rainwater be treated before consumption and more monitoring sites should be set up in different locations in the State by relevant stakeholders for constant monitoring.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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