

ASSESSMENT OF HEAVY METALS IN RAINWATER FROM LAGOS METROPOLIS AND SUBURBS TO ASCERTAIN POLLUTION LEVELS.

ASSESSMENT OF HEAVY METALS IN RAINWATER FROM METROPOLIS AND SUBURBS, LAGOS STATE, NIGERIA.

Abstract

Rainwater, the most critical metrological phenomenon on earth and which serves as a major alternative source for water for developing cities like Lagos is under threat because of heavy metal pollution. In this work, concentrations of heavy metal pollutants in rainwater were investigated. Primary data were obtained by conducting relevant analysis on 176 rainwater samples collected directly from the Lagos sky during periods of light rainfall (Oct-Nov) and heavy rainfall (April-July) for two consecutive years (state the years). The results show the pH of all the rainwater samples as > 5.6 in both periods indicating that the pH altered towards alkalinity. Light rainfall period averaged value at 7.33 and heavy rainfall period at 7.4. For easy information dissemination, Geographic Information System (GIS) and Matrix Laboratory (MATLAB) were applied. MATLAB pollution models were generated by integrating measure and spatial databases using polynomial expression. The MATLAB 7th 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 concentration levels. Analysis of Variance (ANOVA) showed $p < 0.05$ for Cadmium (Cd), Copper (Cu), Zinc (Zn), Iron (Fe) and Nickel (Ni), indicating the probability that rainfall affected their concentration levels was high. The GIS Inverse Distance Weighted (IDW) pollution models revealed that the 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 high concentrations which showed as hot spots appeared for Cd, Cu, Zn and Ni in the State. 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: $Fe > Zn > Ni > Cu > Cd > Pb$. Fe was the heavy metal with highest concentration in rainwater in the State. Cd and Pb exceeded WHO standards while Cu, Zn, Fe and Ni were within the standard. While the situation might not be alarming for now, for public health and safety, this work, calls for rainwater treatment by Lagosians before consumption and the constant monitoring of rainwater chemical quality by relevant Government Agencies and parastatals.

Keywords: Rainwater, Heavy Metals, GIS Model, MATLAB Model, Polynomial Regression.

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 CO₂ 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 Cadmium (Cd), Copper (Cu), Lead (Pb), 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 behavioural 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 $\text{pH} < 7$, 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].

Materials and Methods

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 °N and longitude 3.384082 °E making it the smallest state in Nigeria. **On the North and East, it is bounded by Ogun State.** 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 km² are lagoons and creeks. Lagos has two seasons, the tropical wet and dry seasons. The predominant is the rainy seasons as shown in Fig 1 (Lagos state official website, 2022). 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].

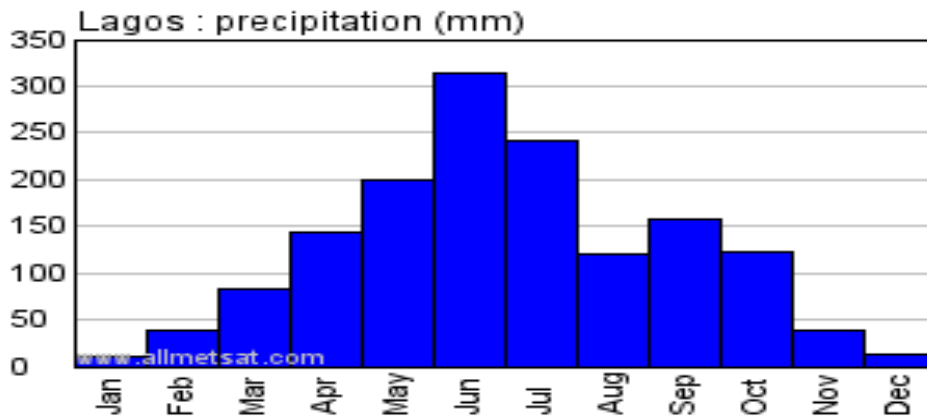


Fig 1: Lagos State annual precipitation graph

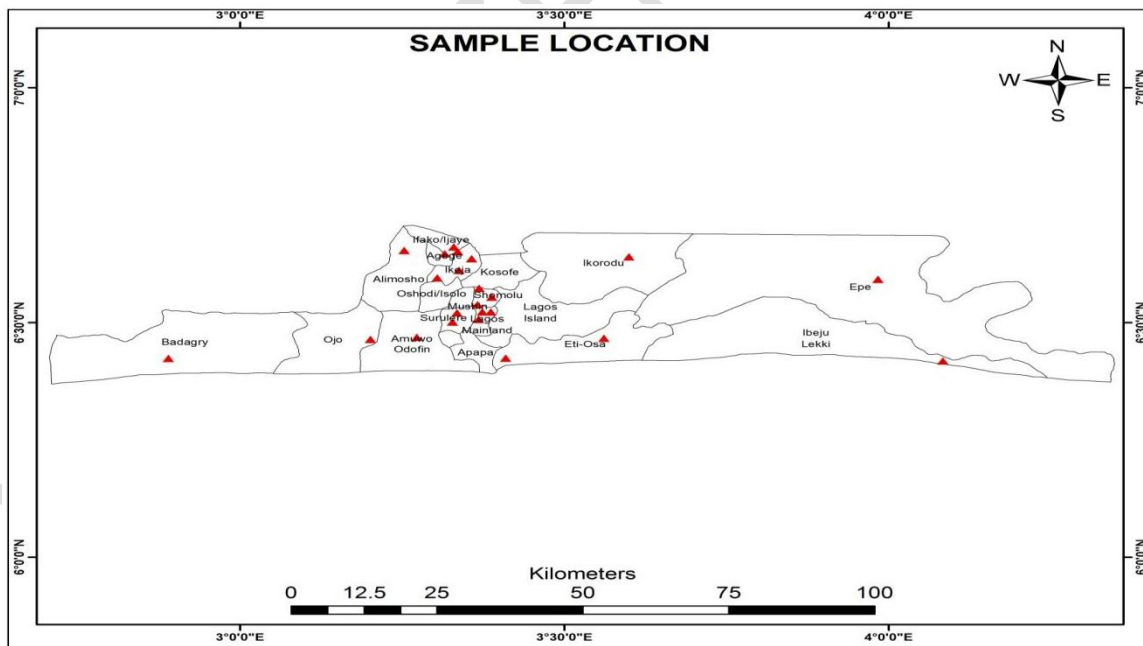


Figure 2: GIS map of the study area showing sampling locations

**The map has no Legend to show the sampled locations.
Refer Figure 2 in your discussion above or where necessary.**

Table 1: The GPS and the description of sample locations

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

Refer Table 1 in your discussion above or where necessary

The table could be placed under the sub topic: Sample collection

Sample Collection

Data acquisitions for heavy metals were performed within the 16 sampling locations (as shown in Figure 2). 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.

Place the Map here

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%.

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.

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

$$y = a_7x^7 + a_6x^6 + a_5x^5 + a_4x^4 + a_3x^3 + a_2x^2 + a_1x^1 + a_0 \quad (1)$$

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

x = input independent variable (locations)

a_0 = factor

a = regression coefficient

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,

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

$$a_0 = \frac{\sum y - a \sum x}{N} \quad (3)$$

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

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.

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

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

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 predictors.

GIS Modeling

The GIS IDW technique applied in this study is a multivariate interpolation technique that obeys the Tobler's 1st 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),

$$\hat{Z}_j = \frac{\sum_i Z_i / d_i^n}{\sum_i 1 / d_i^n} \quad (10)$$

Where; Z = sampled cell value
n = power coefficient

\hat{Z}_j = unsampled cell value at j
 d_i^n = distance from unsampled location

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 9 captured the average mean values of the heavy metal pollutants for both years. MATLAB mathematical models for both years were summarized in Table 10.

Table 2: Light rain period (Year 1) Mean Value data for Heavy Metals

S/N	SAMPLE AREA	pH	Cd (ppm)	Cu (ppm)	Zn (ppm)	Fe (ppm)	Pd(ppm)	Ni (ppm)
1	Festac	6.84	0.039	0.054	0.0053	0.265	0.11	0.047
2	Agege	7.6	0.04	0.05	<0.001	0.249	0.12	0.044
3	Ojo	7.85	0.041	0.041	<0.001	0.237	0.11	0.045
4	Ojodu	7.65	0.04	0.047	0.0746	0.06	0.11	0.049
5	Egbeda	7.56	0.04	0.046	<0.001	0.382	0.13	0.037
6	Yaba	7.85	0.038	0.034	<0.001	0.049	0.13	0.046
7	maryland	6.7	0.038	0.048	0.0352	0.082	0.12	0.048
8	Surulere	6.76	0.037	0.041	<0.001	0.065	0.12	0.039
9	Gbagada	7.85	0.037	0.032	<0.001	0.056	0.1	0.039
10	obalende	7.3	0.037	0.029	<0.001	0.088	0.12	0.039
11	Palmgrove	6.51	0.037	0.031	<0.001	0.062	0.1	0.039
12	Ilesamanja	7.62	0.038	0.029	0.2774	0.041	0.13	0.041
13	Ikeja	6.02	0.037	0.031	<0.001	0.06	0.19	0.036
14	Bariga	7.23	0.034	0.051	<0.001	0.105	0.14	0.037
15	Ogba	7.55	0.034	0.035	<0.001	0.166	0.17	0.034
16	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

S/N	SAMPLE AREA	pH	Cd (ppm)	Cu (ppm)	Zn (ppm)	Fe (ppm)	Pd (ppm)	Ni (ppm)
1	Festac	7.67	0.047	0.046	<0.001	0.184	0.11	0.073
2	Agege	7.6	0.049	0.057	0.1661	0.124	0.14	0.074
3	Ojo	7.86	0.049	0.053	0.0016	0.058	0.16	0.076
4	Ojodu	6.67	0.048	0.042	< 0.001	0.068	0.14	0.07
5	Egbeda	7.6	0.049	0.042	< 0.001	0.034	0.12	0.074
6	Yaba	7.67	0.048	0.045	< 0.001	0.097	0.1	0.068
7	Maryland	6.7	0.046	0.045	0.026	0.102	0.11	0.075
8	Surulere	6.86	0.046	0.051	0.0295	0.076	0.14	0.07
9	Gbagada	7.65	0.044	0.048	0.0906	0.063	0.13	0.071
10	Obalende	7.65	0.045	0.046	0.061	0.053	0.11	0.06
11	Palmgrove	6.8	0.045	0.051	0.0102	0.109	0.12	0.068
12	Ilesamanja	7.63	0.048	0.046	0.0626	0.129	0.15	0.072
13	Ikeja	6.42	0.046	0.047	0.1792	0.109	0.13	0.067
14	Bariga	7.33	0.045	0.048	0.0215	0.084	0.12	0.061
15	Ogba	7.75	0.045	0.054	0.0046	0.018	0.12	0.066
16	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

S/N	SAMPLE AREA	pH	Cd (ppm)	Cu (ppm)	Zn (ppm)	Fe (ppm)	Pd(ppm)	Ni (ppm)
1	Festac	6.86	0.038	0.048	<0.001	0.26	0.11	0.045
2	Agege	7.68	0.041	0.05	<0.001	0.165	0.12	0.044

3	Ojo	7.86	0.041	0.04	<0.001	0.065	0.1	0.045
4	Ojodu	7.75	0.04	0.046	0.0354	0.065	0.12	0.046
5	Egbeda	7.5	0.039	0.046	<0.001	0.265	0.13	0.035
6	Yaba	7.85	0.038	0.034	<0.001	0.065	0.12	0.043
7	Maryland	6.8	0.037	0.048	0.0344	0.068	0.11	0.044
8	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
10	Obalende	7.5	0.037	0.029	<0.001	0.075	0.11	0.035
11	Palmgrove	6.57	0.036	0.031	<0.001	0.063	0.1	0.033
12	Ilesamanja	7.63	0.035	0.029	0.2702	0.045	0.12	0.044
13	Ikeja	6.42	0.035	0.031	<0.001	0.065	0.19	0.034
14	Bariga	7.33	0.034	0.051	<0.001	0.068	0.12	0.035
15	Ogba	7.75	0.034	0.035	<0.001	0.065	0.15	0.034
16	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

S/N	SAMPLE AREA	pH	Cd (ppm)	Cu (ppm)	Zn (ppm)	Fe (ppm)	Pd(ppm)	Ni (ppm)
1	Festac	7.02	0.046	0.046	<0.001	0.184	0.12	0.074
2	Agege	7.62	0.049	0.046	0.166	0.123	0.13	0.073
3	Ojo	7.56	0.048	0.048	0.001	0.055	0.14	0.073
4	Ojodu	7.75	0.048	0.043	< 0.001	0.065	0.14	0.07
5	Egbeda	7.5	0.049	0.044	< 0.001	0.034	0.12	0.073
6	Yaba	7.9	0.047	0.045	< 0.001	0.094	0.1	0.063
7	Maryland	7.1	0.045	0.044	< 0.001	0.1	0.1	0.072
8	Surulere	6.86	0.046	0.048	0.0295	0.077	0.13	0.07
9	Gbagada	7.82	0.044	0.046	0.0906	0.062	0.12	0.07
10	Obalende	7.6	0.045	0.046	< 0.001	0.055	0.13	0.063
11	Palmgrove	7.5	0.045	0.046	0.0102	0.109	0.12	0.063
12	Ilesamanja	7.63	0.047	0.045	0.0626	0.125	0.11	0.07
13	Ikeja	6.5	0.046	0.046	0.1792	0.104	0.14	0.063
14	Bariga	7.34	0.046	0.046	0.0215	0.083	0.14	0.063
15	Ogba	7.78	0.044	0.048	< 0.001	0.015	0.12	0.063
16	Victoria island	7.9	0.042	0.041	< 0.001	0.044	0.12	0.063

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

S/N	Sample areas	Yr1 Light rain	Yr2 Light rain	Mean	Yr1 Heavy rainy	Yr2 Heavy rainy	Mean
1	Festac	0.039	0.038	0.039	0.047	0.046	0.047
2	Agege	0.04	0.041	0.041	0.049	0.049	0.049
3	Ojo	0.041	0.041	0.041	0.049	0.048	0.049
4	Ojodu	0.04	0.04	0.04	0.048	0.048	0.049
5	Egbeda	0.04	0.039	0.04	0.049	0.049	0.049
6	Yaba	0.038	0.038	0.038	0.048	0.047	0.048
7	Maryland	0.038	0.037	0.038	0.046	0.045	0.046
8	Surulere	0.037	0.036	0.037	0.046	0.046	0.046
9	Gbagada	0.037	0.037	0.037	0.044	0.044	0.044
10	Obalende	0.037	0.037	0.037	0.045	0.045	0.045
11	Palmgrove	0.037	0.036	0.037	0.045	0.045	0.045
12	Ilesamanja	0.038	0.035	0.037	0.048	0.047	0.048

13	Ikeja	0.037	0.035	0.036	0.046	0.046	0.046
14	Bariga	0.034	0.034	0.034	0.045	0.046	0.046
15	Ogba	0.034	0.034	0.034	0.045	0.044	0.045
16	Victoria island	0.037	0.036	0.037	0.041	0.042	0.042

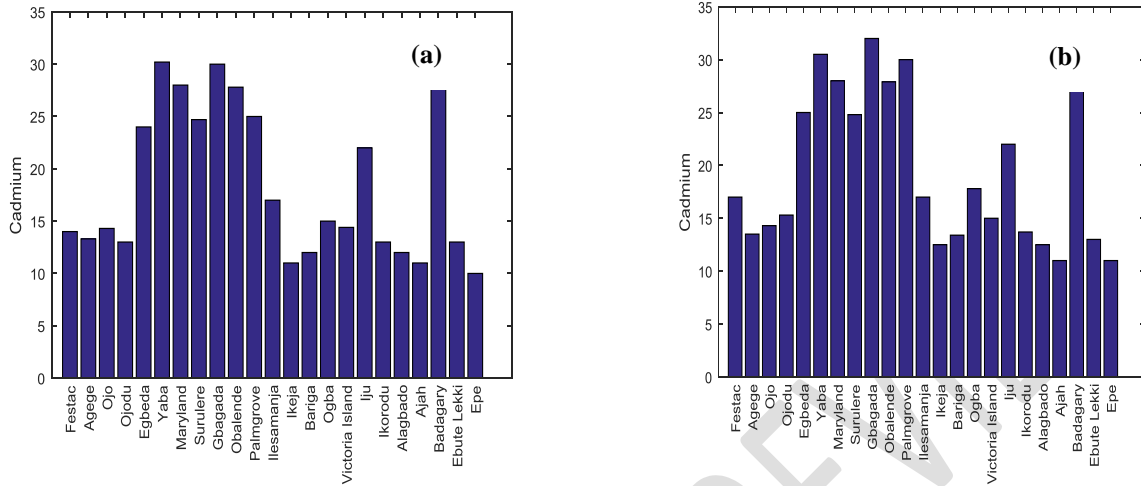
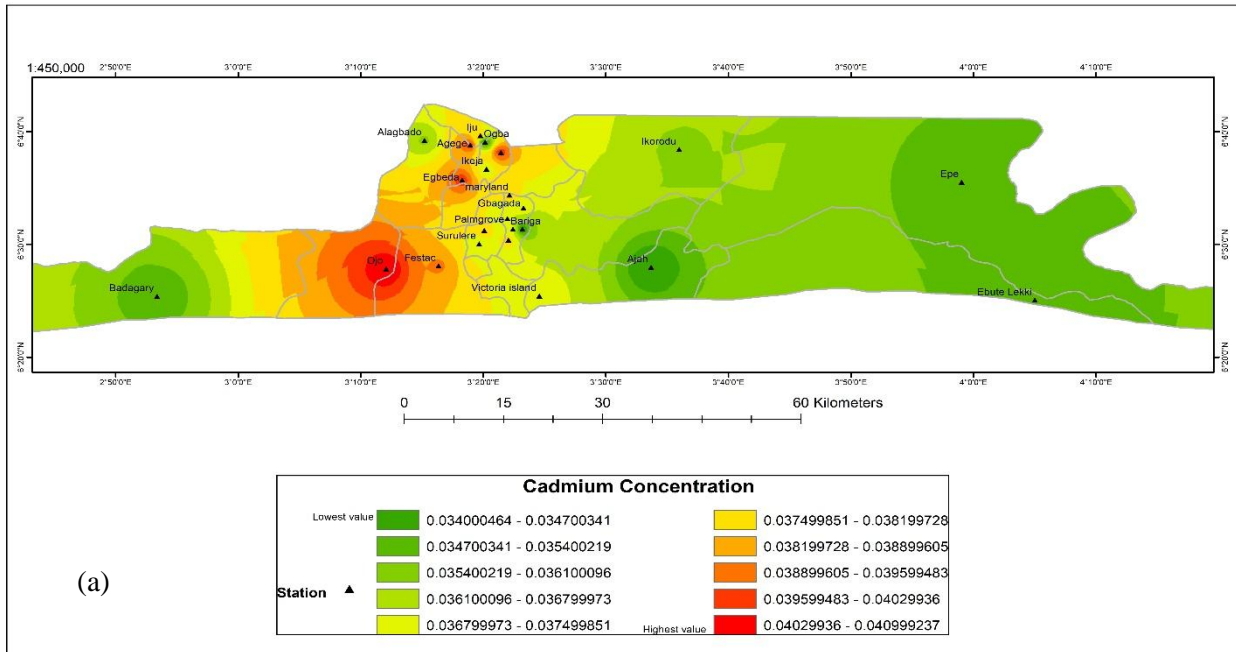


Figure 3: Mean concentration of Cd for both years (a) Light rain period (b) Heavy rain period



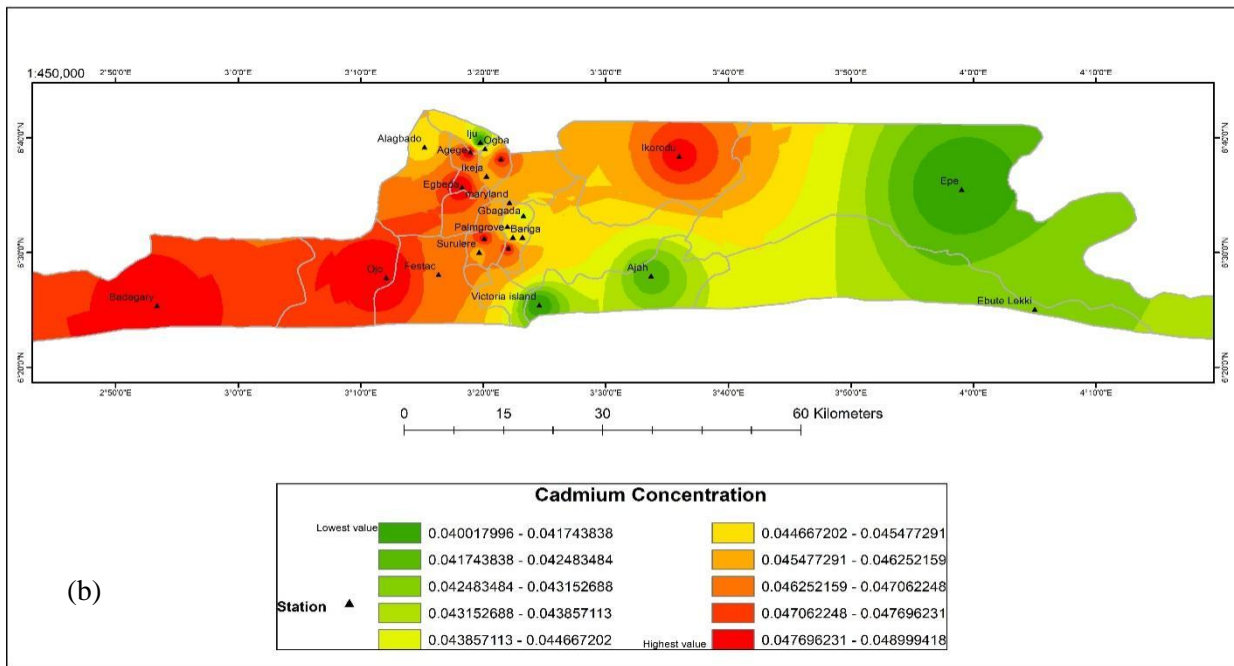
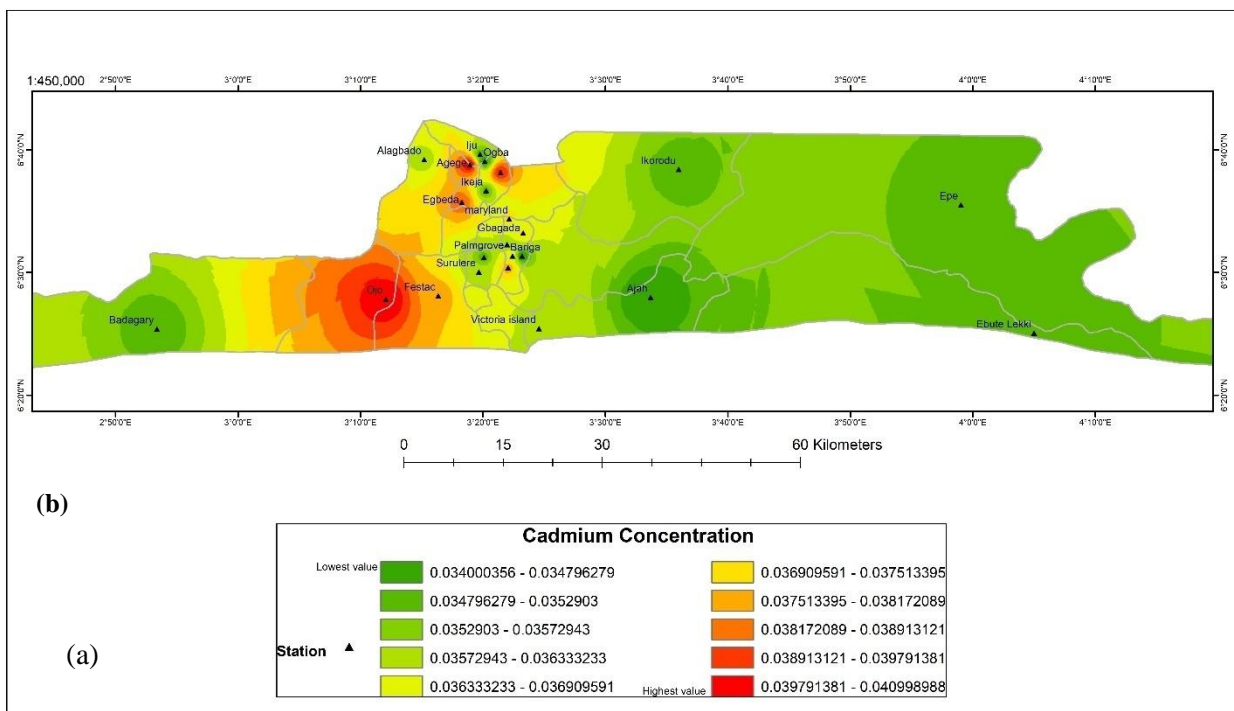


Figure 4: GIS map for Cd concentration in (a) Light rain period (b) Heavy rainy period (Year 1)



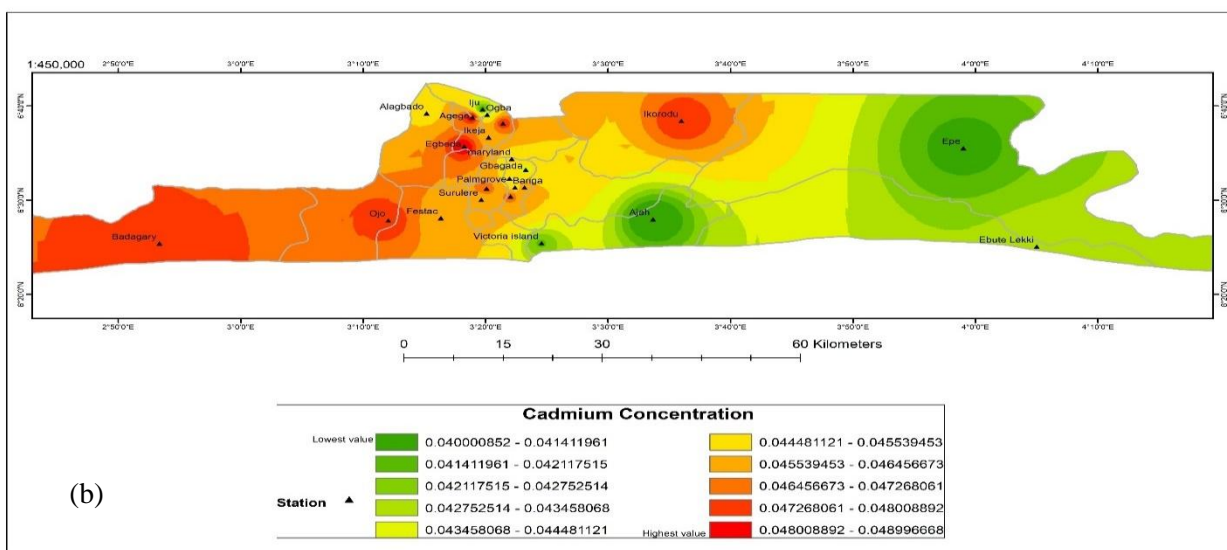


Figure 5: GIS map for Cd concentration in (a)Light rain period (b) Heavy rainy period (Year 2)

Table 7: mean value Cu(ppm) for both years

S/N	Sample areas	Yr1 Light rain	Yr2 Light rain	Mean	Yr1 Heavy rainy	Yr2 Heavy rainy	Mean
1	Festac	0.054	0.048	0.051	0.046	0.046	0.046
2	Agege	0.05	0.05	0.05	0.057	0.046	0.052
3	Ojo	0.041	0.04	0.041	0.053	0.048	0.051
4	Ojodu	0.047	0.046	0.047	0.042	0.043	0.043
5	Egbeda	0.046	0.046	0.046	0.042	0.044	0.043
6	Yaba	0.034	0.034	0.034	0.045	0.045	0.045
7	Maryland	0.048	0.048	0.048	0.045	0.044	0.045
8	Surulere	0.041	0.041	0.041	0.051	0.048	0.050
9	Gbagada	0.032	0.032	0.032	0.048	0.046	0.047
10	Obalende	0.029	0.029	0.029	0.046	0.046	0.046
11	Palmgrove	0.031	0.031	0.031	0.051	0.046	0.049
12	Ilesamanja	0.029	0.029	0.029	0.046	0.045	0.046
13	Ikeja	0.031	0.031	0.031	0.047	0.046	0.047
14 (a)	Bariga	0.051	0.051	0.051	0.048	0.046	0.047
15	Ogba	0.035	0.035	0.035	0.054	0.048	0.051
16	Victoria island	0.029	0.029	0.029	0.042	0.041	0.042

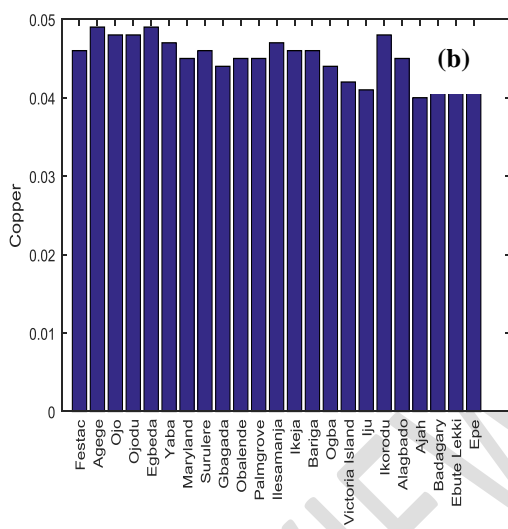
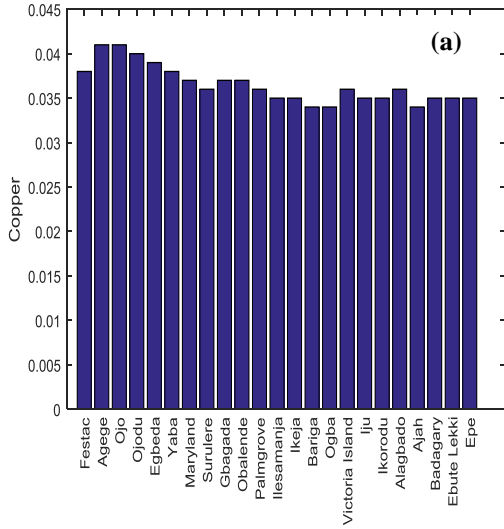
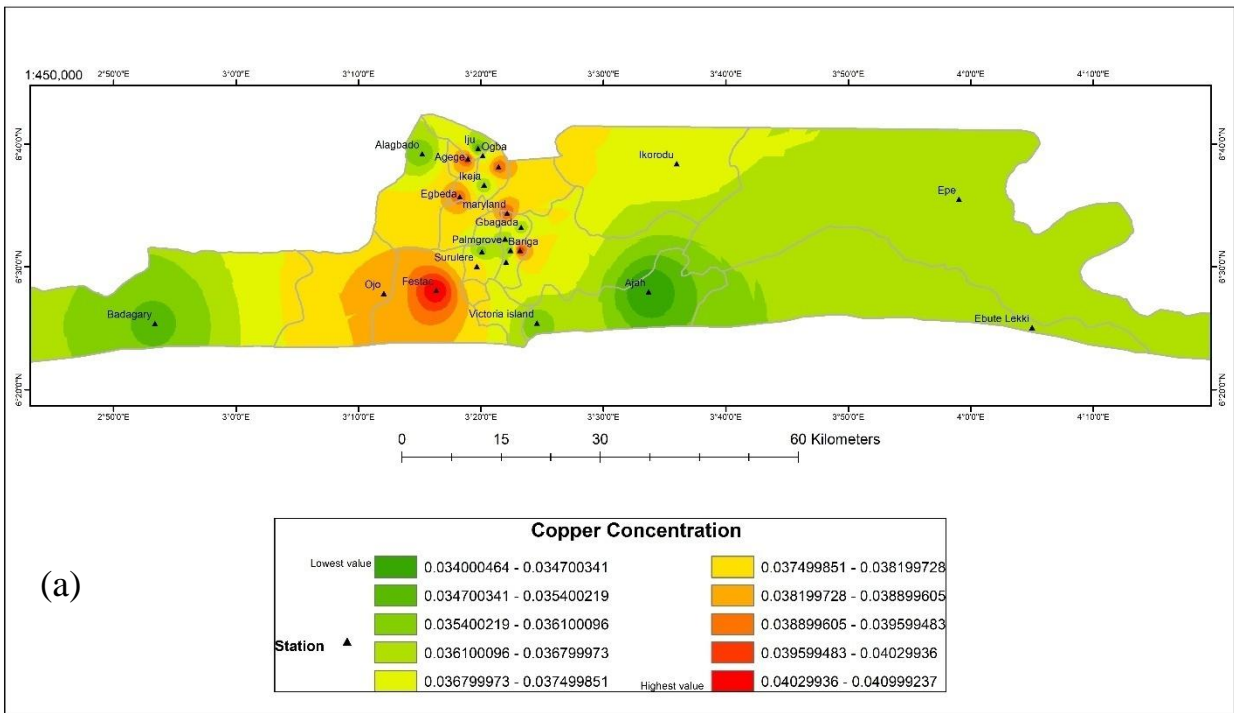


Figure 6: Mean concentration of Cu for both years (a) Light rain (b) Heavy rainy



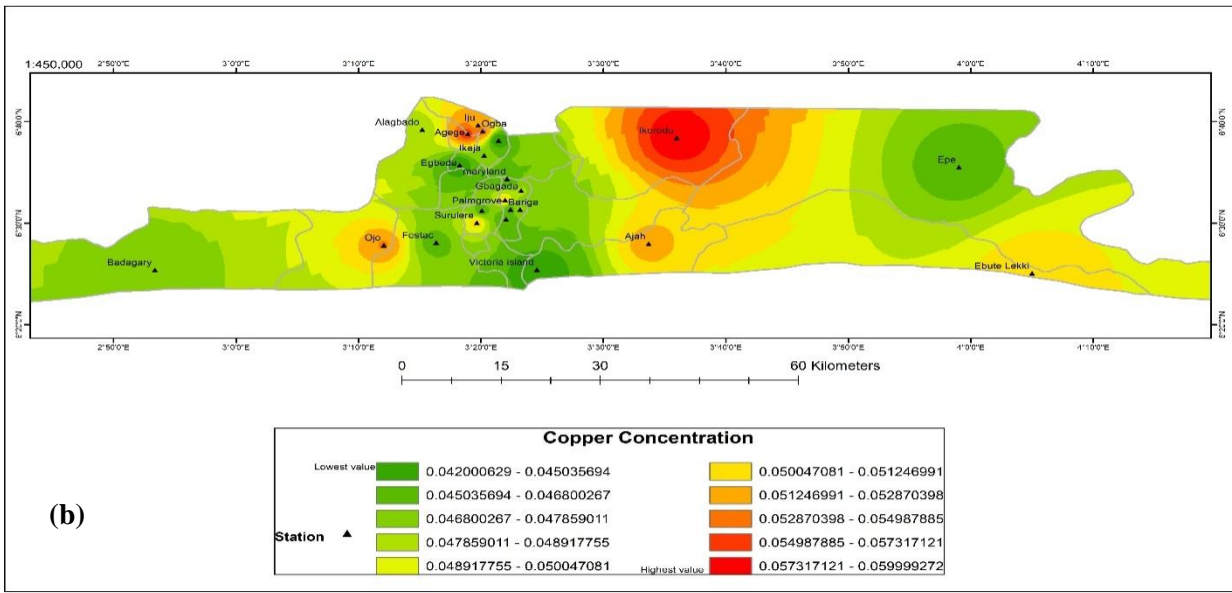
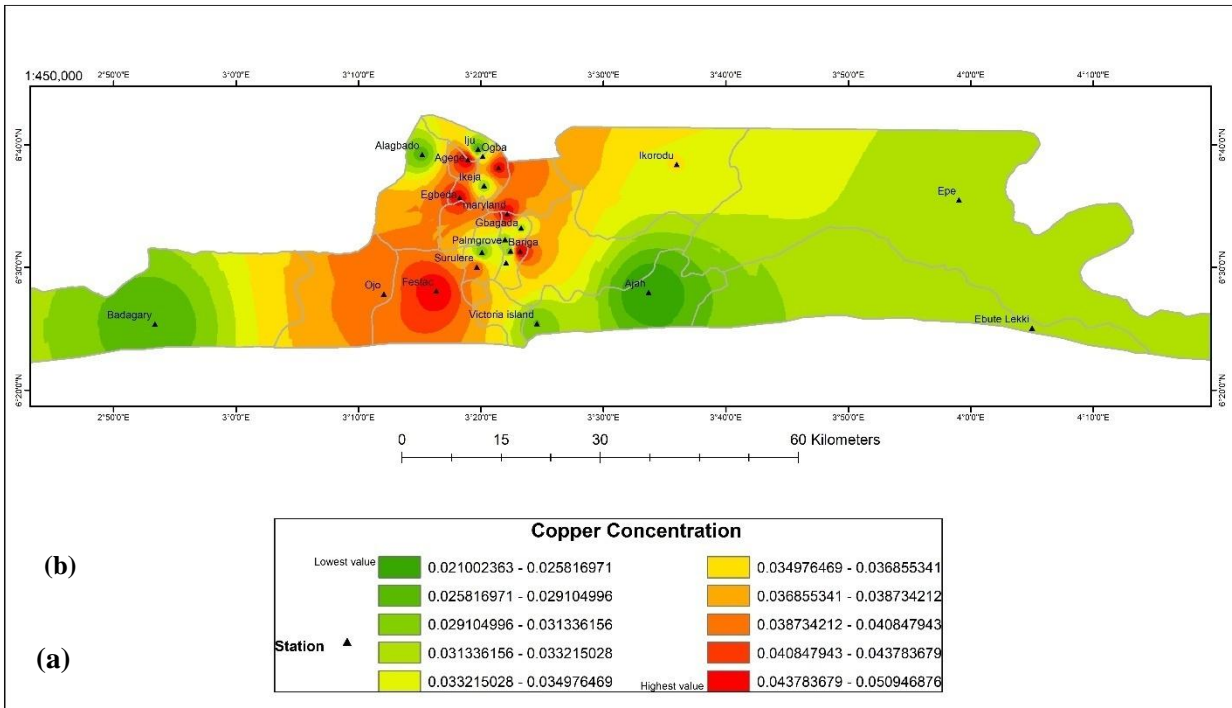


Figure 7: GIS map for Cu concentration in (a) Light rain (b) Heavy rainy (Year 1)



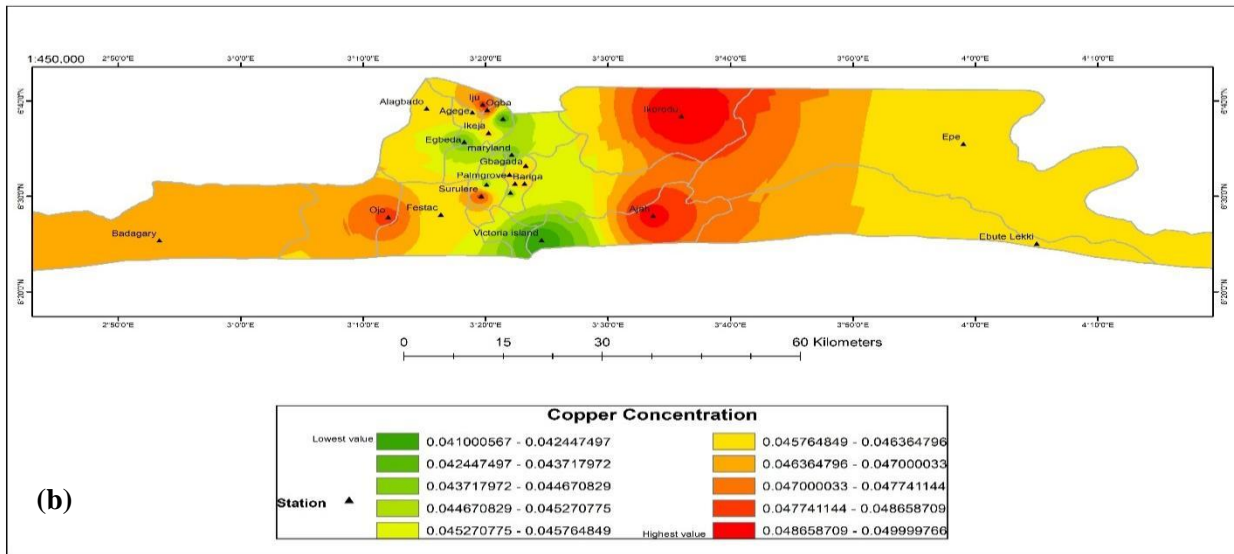


Figure 8: GIS map for Cu concentration in (a) Light rain (b) Heavy rain (Year 2)

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

S/N	Sample areas	Yr1 Light rain period	Yr2 Light rain period	Mean	Yr1 Heavy rain period	Yr2 Heavy rain period	Mean
1	Festac	0.0053	<0.001	0.0053	<0.001	<0.001	<0.001
2	Agege	<0.001	<0.001	<0.001	0.1661	0.166	0.1661
3	Ojo	<0.001	<0.001	<0.001	0.0016	0.001	0.0014
4	Ojodu	0.0746	0.0354	0.055	< 0.001	< 0.001	<0.001
5	Egbeda	<0.001	<0.001	<0.001	< 0.001	< 0.001	<0.001
6	Yaba	<0.001	<0.001	<0.001	< 0.001	< 0.001	<0.001
7	Maryland	0.0352	0.0344	0.0348	0.026	< 0.001	0.026
8	Surulere	<0.001	<0.001	<0.001	0.0295	0.0295	0.0295
9	Gbagada	<0.001	<0.001	<0.001	0.0906	0.0906	0.0906
10	Obalende	<0.001	<0.001	<0.001	0.061	< 0.001	0.061
11	Palmgrove	<0.001	<0.001	<0.001	0.0102	0.0102	0.0102
12	Ilesamanja	0.2774	0.2702	0.2738	0.0626	0.0626	0.0626
13	Ikeja	<0.001	<0.001	<0.001	0.1792	0.1792	0.1792
14	Bariga	<0.001	<0.001	<0.001	0.0215	0.0215	0.0215
15	Ogba	<0.001	<0.001	<0.001	0.0046	< 0.001	0.0046
16	Victoria island	<0.001	<0.001	<0.001	< 0.001	< 0.001	<0.001

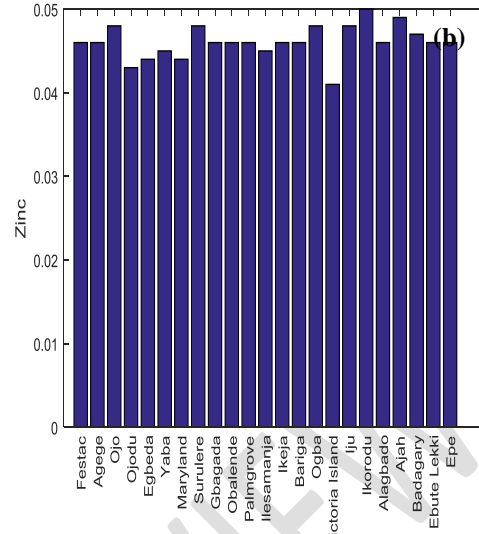
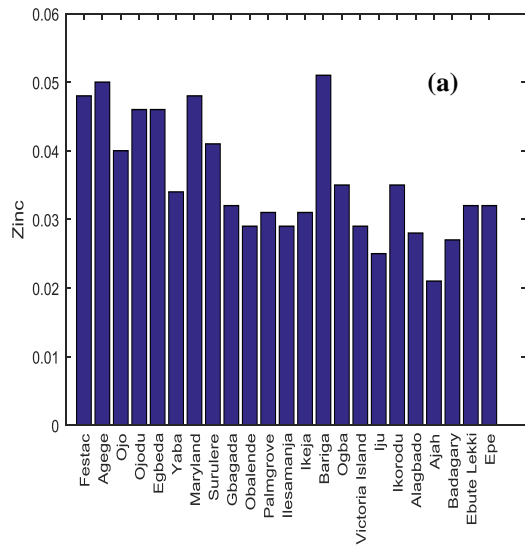
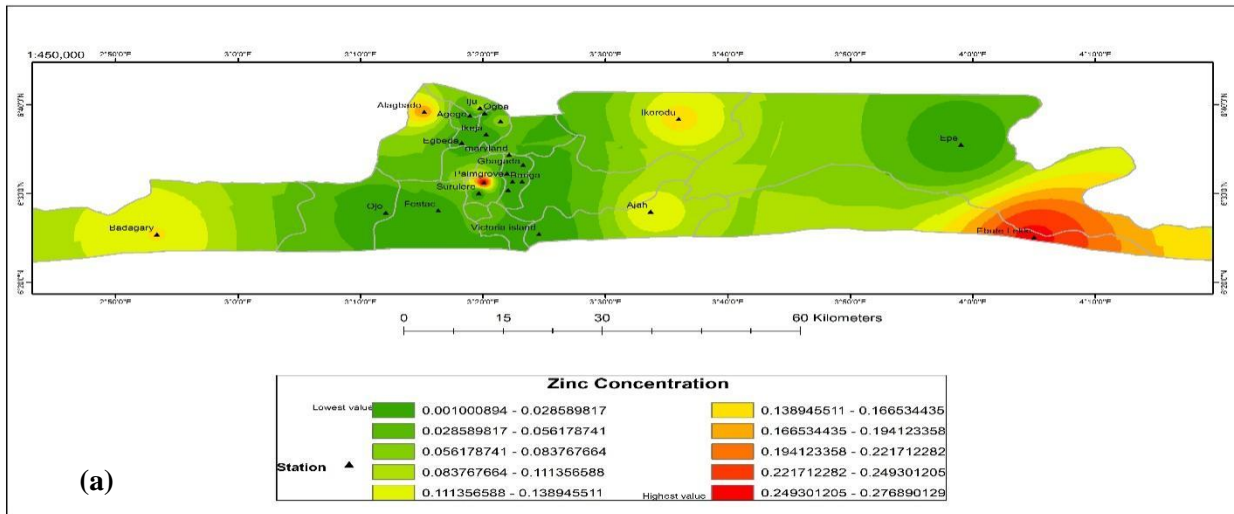


Figure 9: Mean concentration of Zn for both (a) Light rain (b) Heavy rain



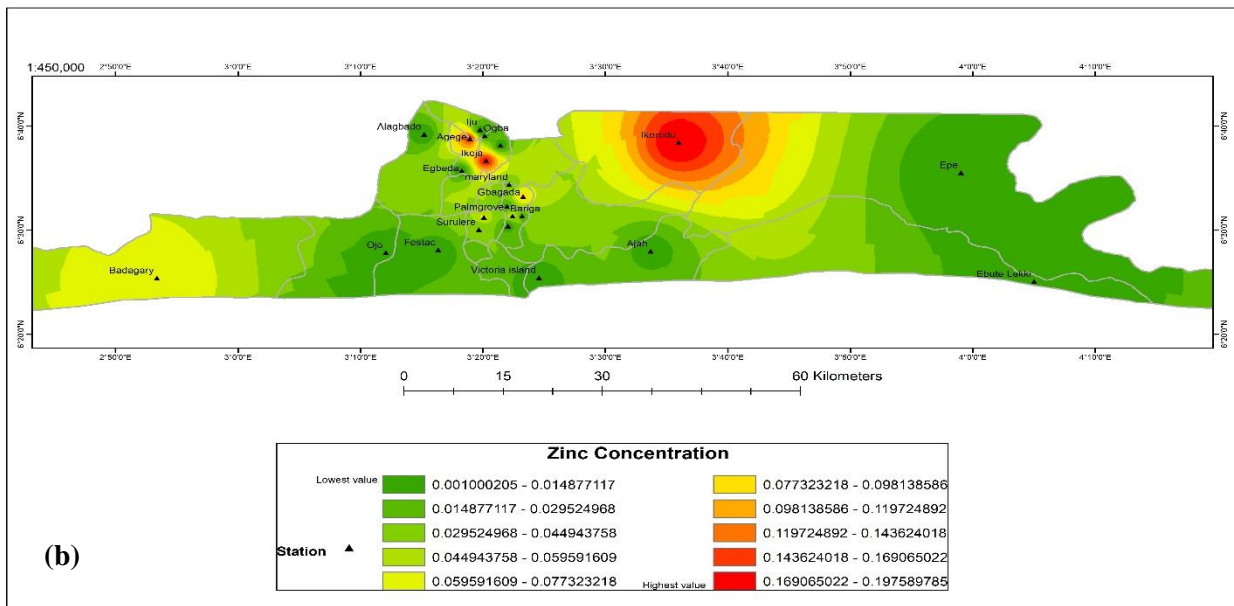
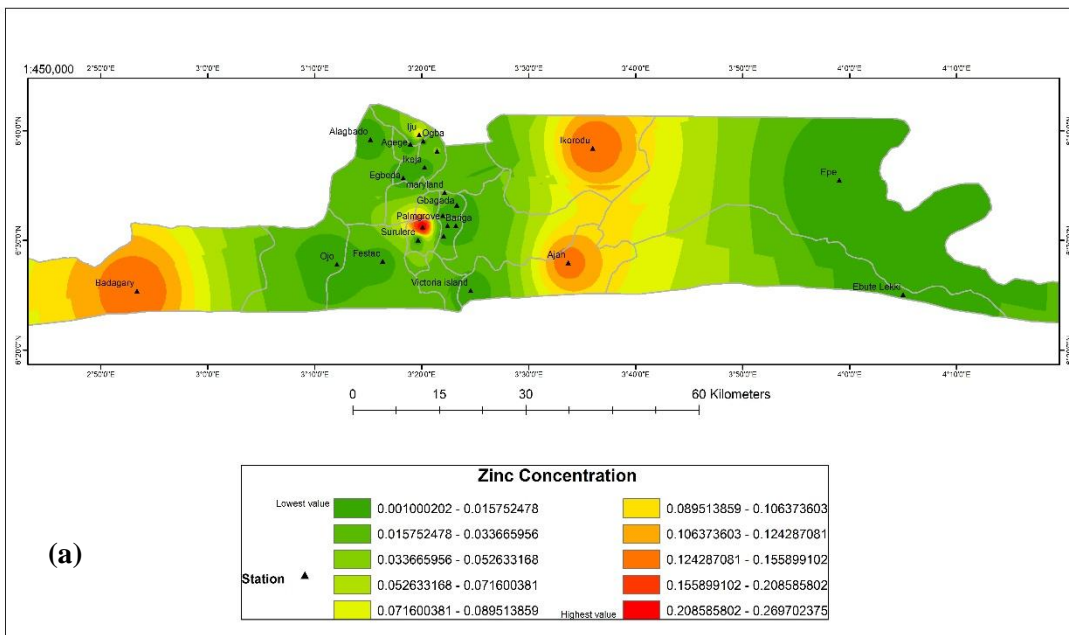


Figure 10: GIS map for Zn concentration in (a)Light rain (b) Heavy rain (Year 1)



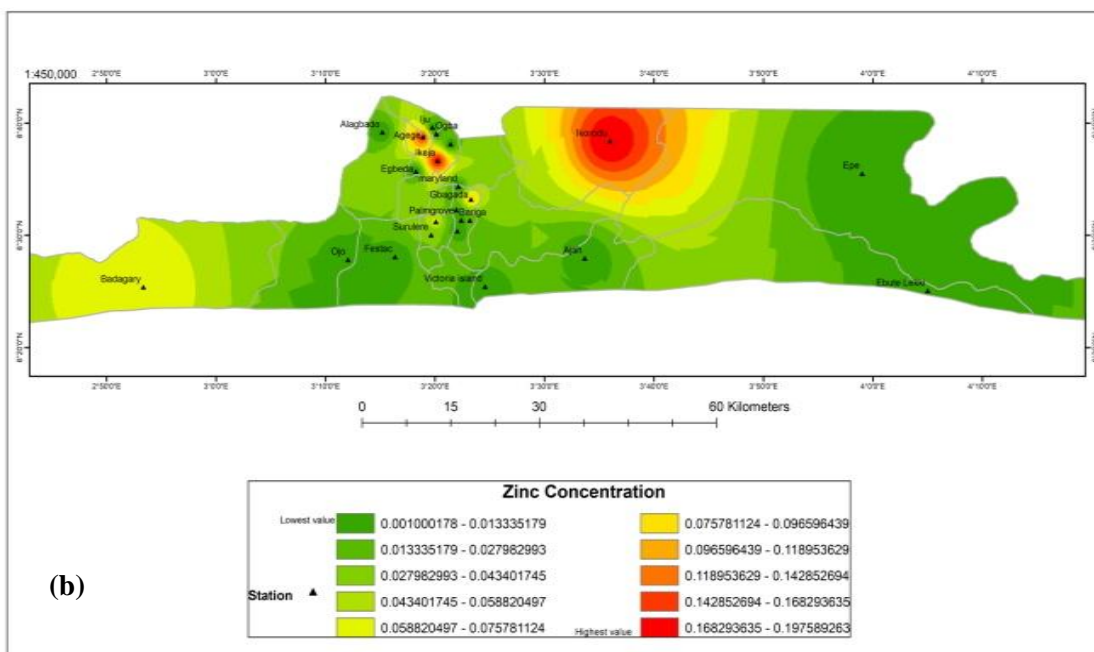


Figure 11: GIS map for Zn concentration in (a) Light rain (b) Heavy rain (Year 2)

Table 9: mean value Fe (ppm) for both years

S/N	Sample Areas	Yr1 Light rain	Yr2 Light rain	Mean	Yr1 Heavy Rain	Yr2 Heavy Rain	Mean
1	Festac	0.265	0.26	0.264	0.184	0.184	0.184
2	Agege	0.249	0.165	0.207	0.124	0.123	0.124
3	Ojo	0.237	0.065	0.151	0.058	0.055	0.057
4	Ojodu	0.06	0.065	0.063	0.068	0.065	0.067
5	Egbeda	0.382	0.265	0.324	0.034	0.034	0.034
6	Yaba	0.049	0.065	0.057	0.097	0.094	0.096
7	Maryland	0.082	0.068	0.075	0.102	0.1	0.101
8	Surulere	0.065	0.065	0.065	0.076	0.077	0.077
9	Gbagada	0.056	0.065	0.0605	0.063	0.062	0.063
10	Obalende	0.088	0.075	0.0815	0.053	0.055	0.054
11	Palmgrove	0.062	0.063	0.063	0.109	0.109	0.109
12	Ilesamanja	0.041	0.045	0.046	0.129	0.125	0.127
13	Ikeja	0.06	0.065	0.063	0.109	0.104	0.107
14	Bariga	0.105	0.068	0.0865	0.084	0.083	0.084
15	Ogba	0.166	0.065	0.1155	0.018	0.015	0.017
16	Victoria island	0.089	0.075	0.082	0.049	0.044	0.047

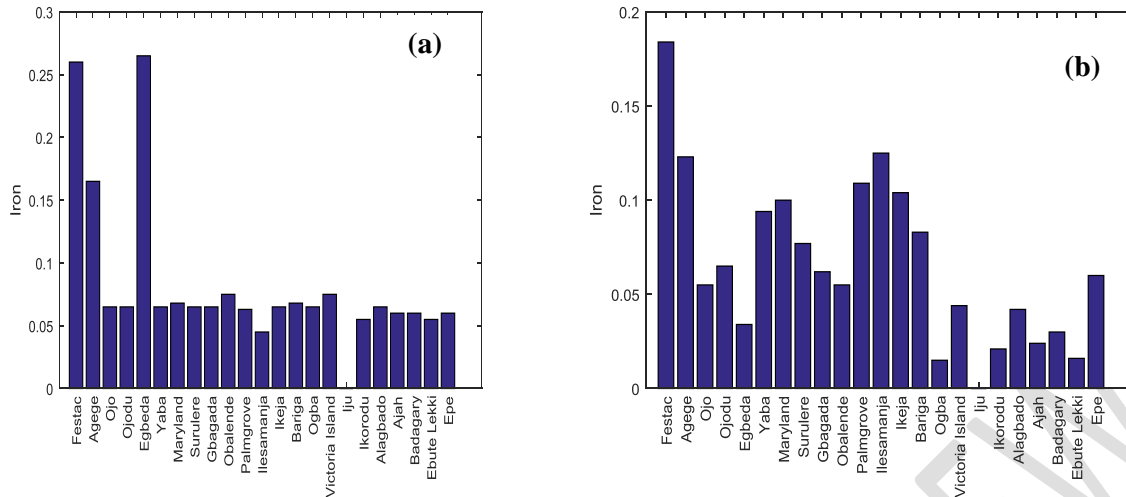
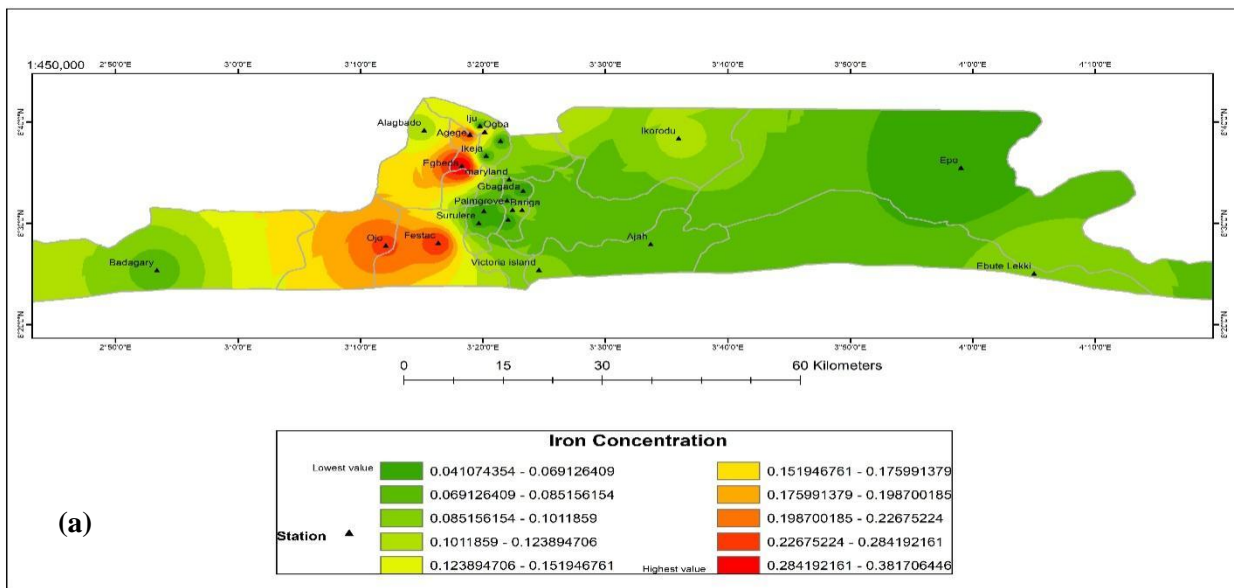


Figure 12: Mean concentration of Fe for both years (a) Light rain (b) Heavy rain



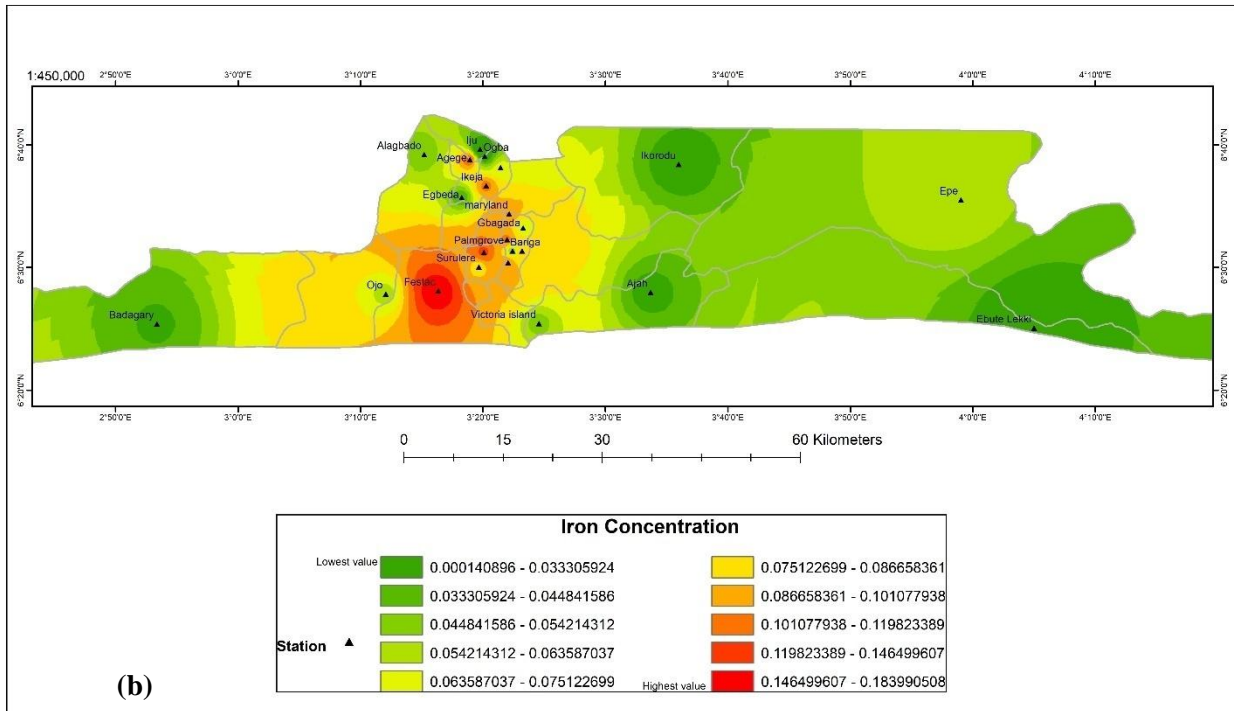
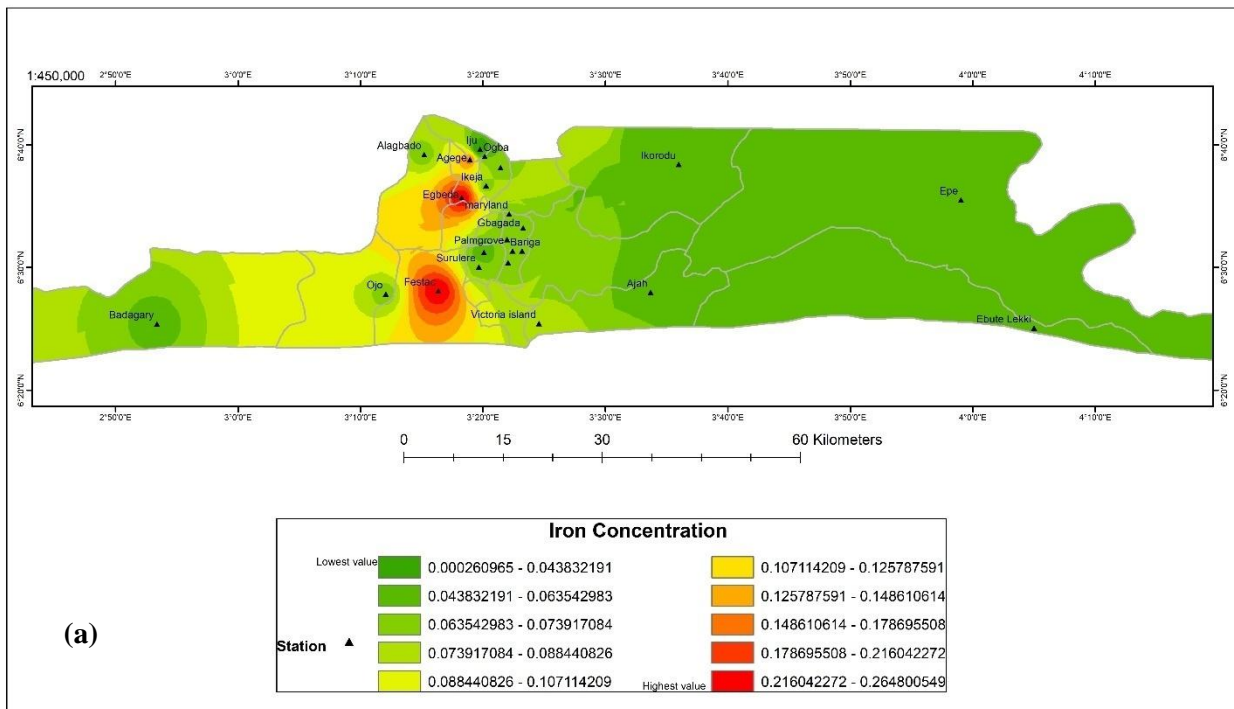


Figure 13: GIS map for Fe concentration in (a) Light rain (b) Heavy rain (Year 1)



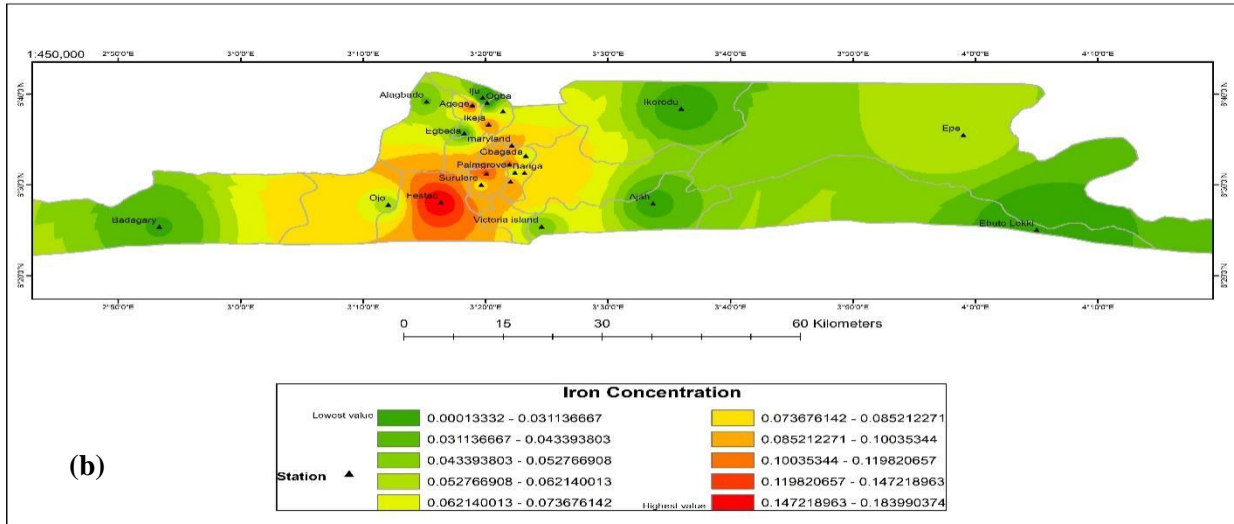


Figure 14: GIS map for Fe concentration in (a) Light rain (b) Heavy rain (Year 2)

Table 10: mean value Pb (ppm) for both years

S/N	Sample areas	Yr1 Light rain	Yr2 Light rain	Mean	Yr1 Heavy rain	Yr2 Heavy rain	Mean
1	Festac	0.11	0.11	0.11	0.11	0.12	0.12
2	Agege	0.12	0.12	0.12	0.14	0.13	0.14
3	Ojo	0.11	0.1	0.1	0.16	0.14	0.15
4	Ojodu	0.11	0.12	0.12	0.14	0.14	0.14
5	Egbeda	0.13	0.13	0.13	0.12	0.12	0.12
6	Yaba	0.13	0.12	0.13	0.1	0.1	0.1
7	Maryland	0.12	0.11	0.12	0.11	0.1	0.11
8	Surulere	0.12	0.12	0.12	0.14	0.13	0.14
9	Gbagada	0.1	0.11	0.11	0.13	0.12	0.13
10	Obalende	0.12	0.11	0.12	0.11	0.13	0.12
11	(a) Iroko	0.1	0.1	0.1	0.12	0.12	0.12
12	-----Ibeju-Lekki	0.13	0.12	0.13	0.15	0.11	0.13
13	Ikeja	0.19	0.19	0.19	0.13	0.14	0.14
14	Bariga	0.14	0.12	0.14	0.12	0.14	0.13
15	Ogba	0.17	0.15	0.16	0.12	0.12	0.12
16	Victoria island	0.13	0.12	0.13	0.13	0.12	0.13

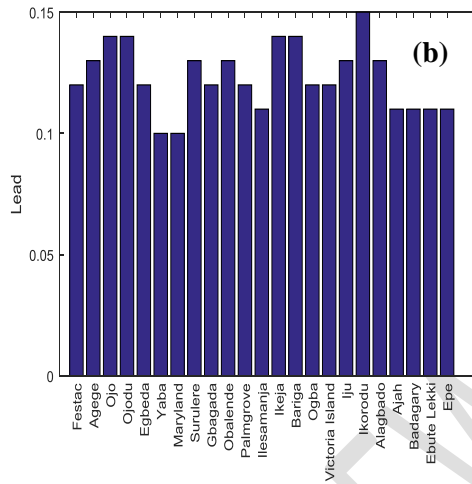
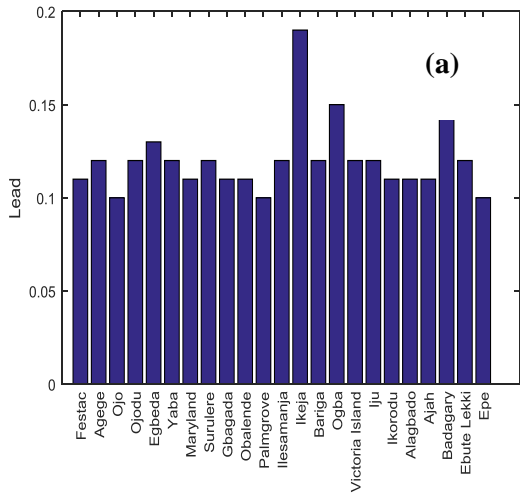
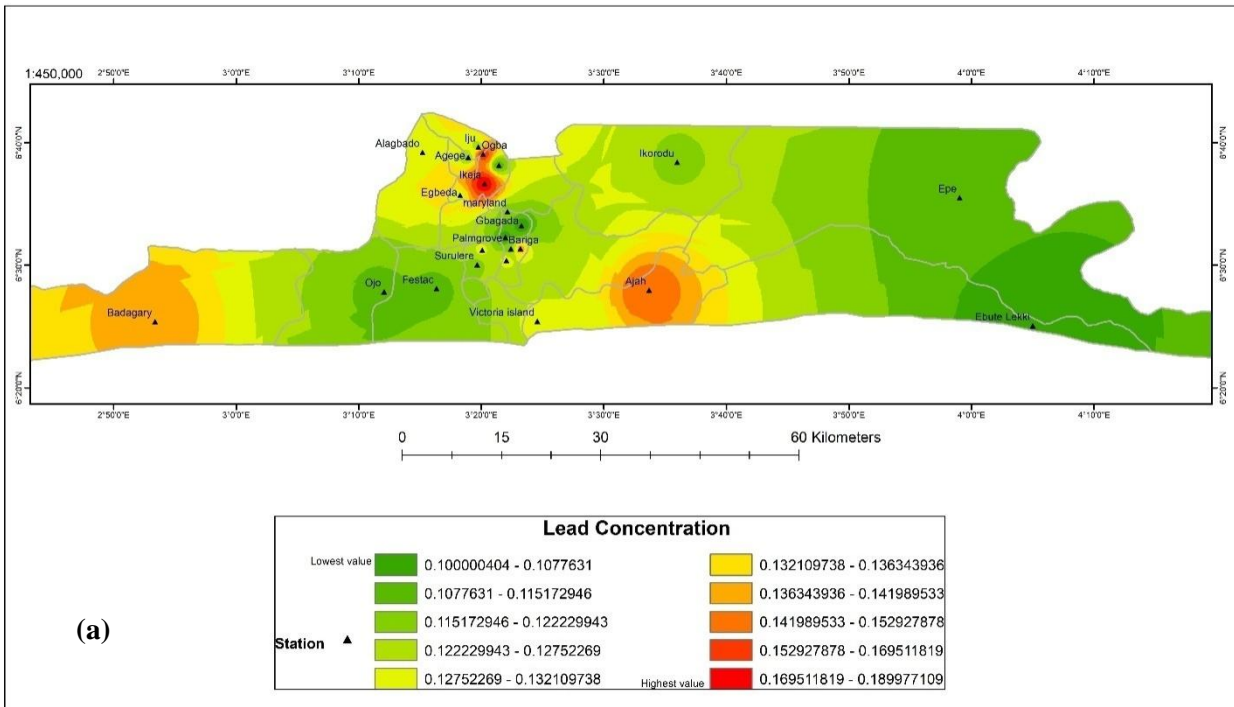


Figure 15: Mean concentration of Pb for both years (a) Light rain (b) Heavy rain



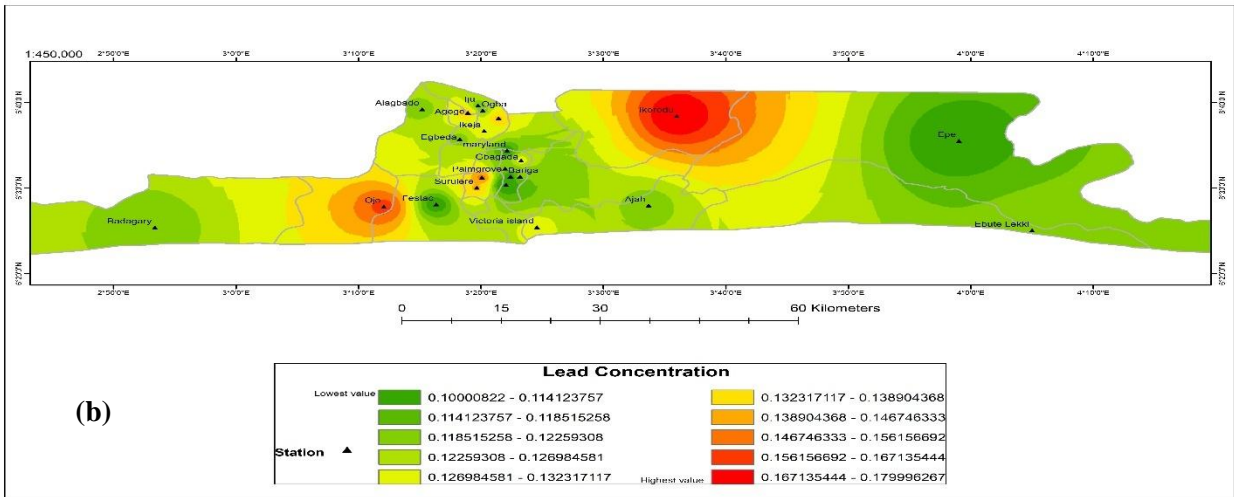
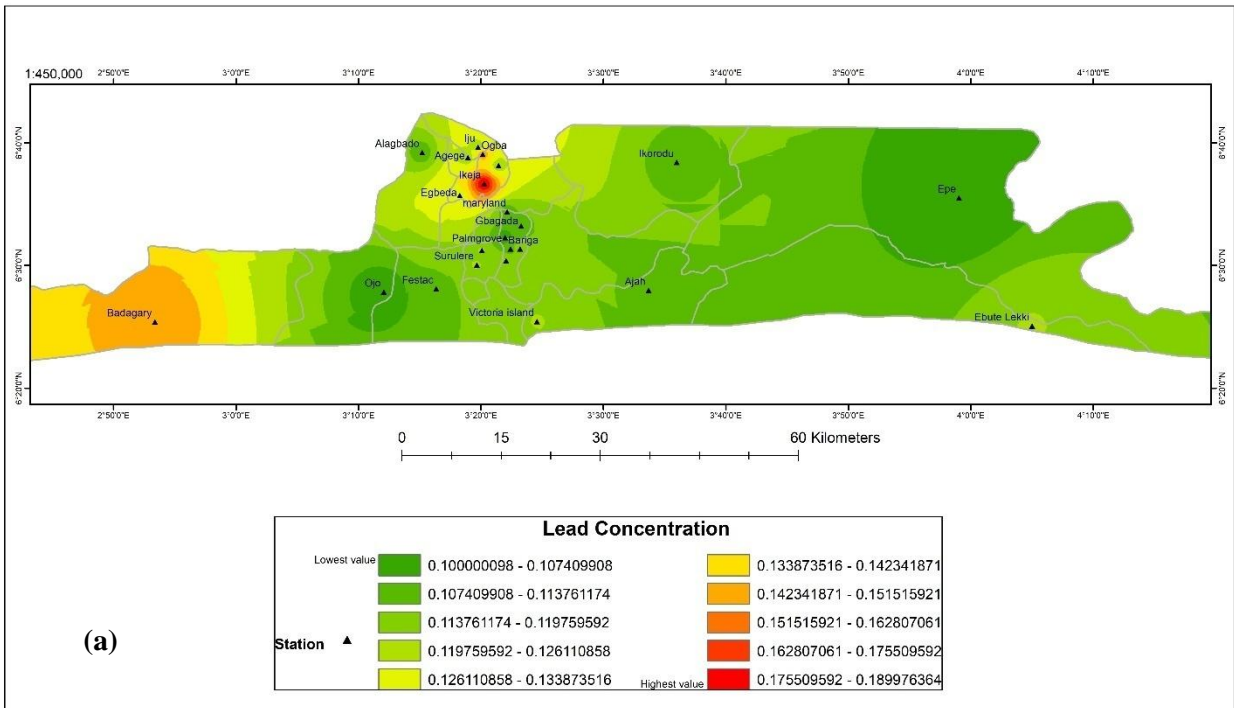


Figure 16: GIS map for Pb concentration in (a) Light rain (b) Heavy rain (Year 1)



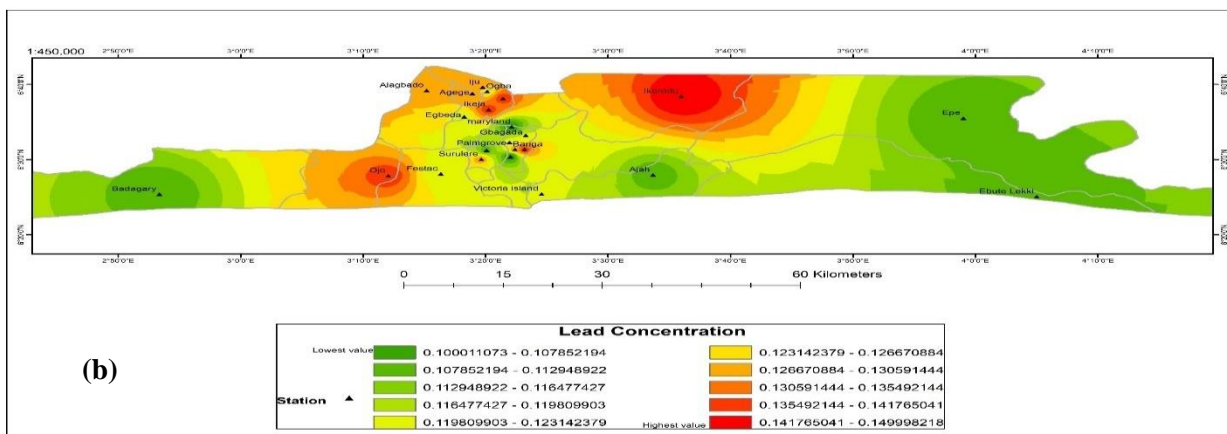


Figure 17: GIS map for Pb concentration in (a) Light rain (b) Heavy rain (Year 2)

(a)

Table 11: mean value Ni (ppm) for both years

S/N	Sample areas	Yr1 Light rain	Yr2 Light rain	Mean	Yr1 Heavy rainy	Yr2 Heavy rainy	Mean
1	Festac	0.047	0.045	0.046	0.073	0.074	0.074
2	Agege	0.044	0.044	0.044	0.074	0.073	0.074
3	Ojo	0.045	0.045	0.045	0.076	0.073	0.075
4	Ojodu	0.049	0.046	0.045	0.07	0.07	0.07
5	Egbeda	0.037	0.035	0.036	0.074	0.073	0.074
6	Yaba	0.046	0.043	0.045	0.068	0.063	0.066
7	Maryland	0.048	0.044	0.046	0.075	0.072	0.074
8	Surulere	0.039	0.033	0.036	0.07	0.07	0.07
9	Gbagada	0.039	0.034	0.037	0.071	0.07	0.071
10	Obalende	0.039	0.035	0.037	0.06	0.063	0.062
11	Palmgrove	0.039	0.033	0.037	0.068	0.063	0.066
12	Ilesamanja	0.041	0.044	0.043	0.072	0.07	0.071
13	Ikeja	0.036	0.034	0.035	0.067	0.063	0.065
14	Bariga	0.037	0.035	0.036	0.061	0.063	0.062
15	Ogba	0.034	0.034	0.034	0.066	0.063	0.065
16	Victoria island	0.031	0.031	0.031	0.064	0.063	0.064

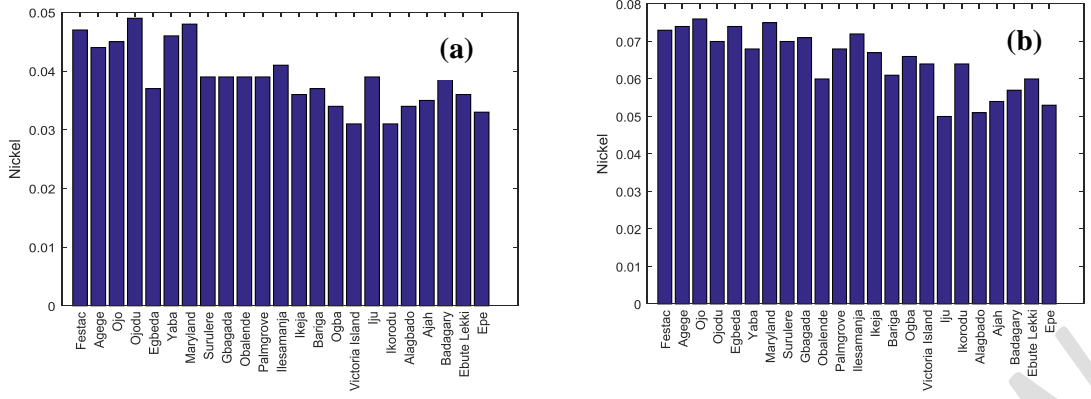
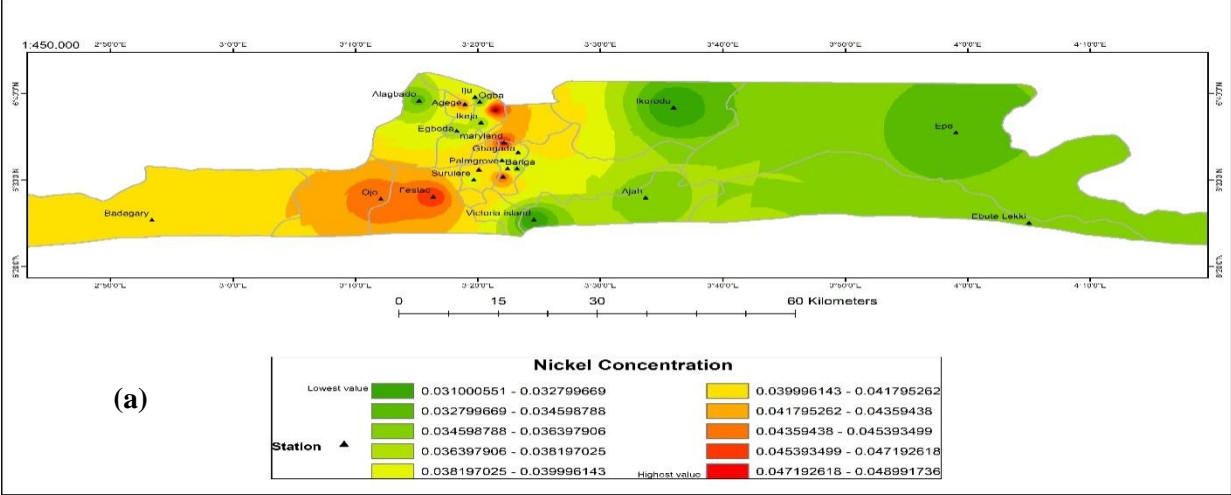


Figure 18: Mean concentration of Ni for both years (a)Light rain (b) Heavy rain



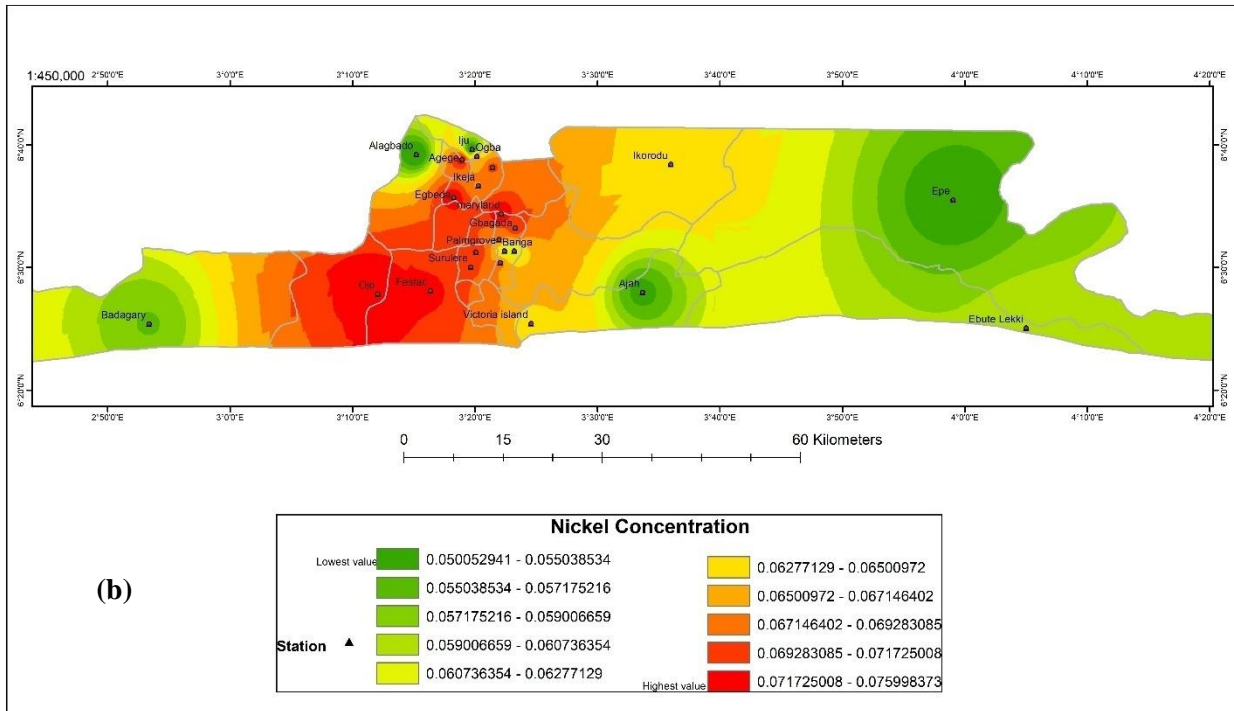


Figure 19: GIS map for Ni concentration in (a) Light rain (b) Heavy rain (Year 1)

UNDER PEER

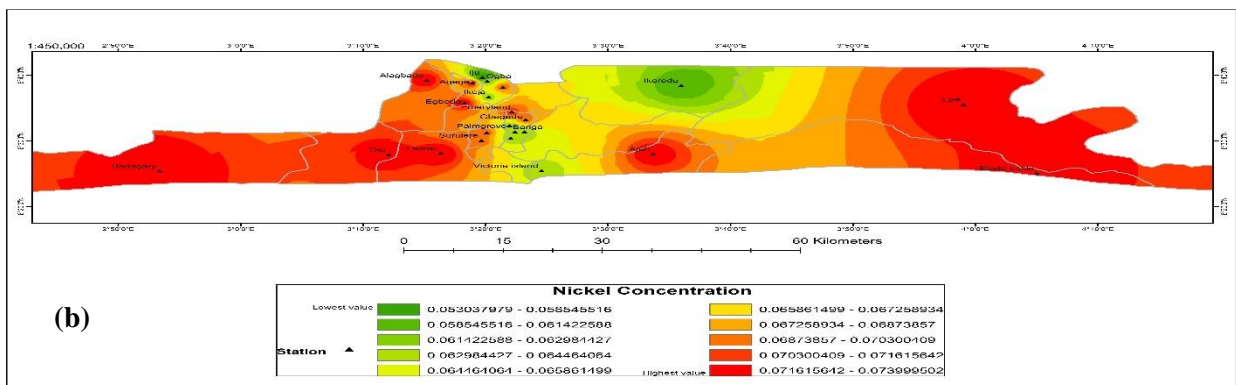
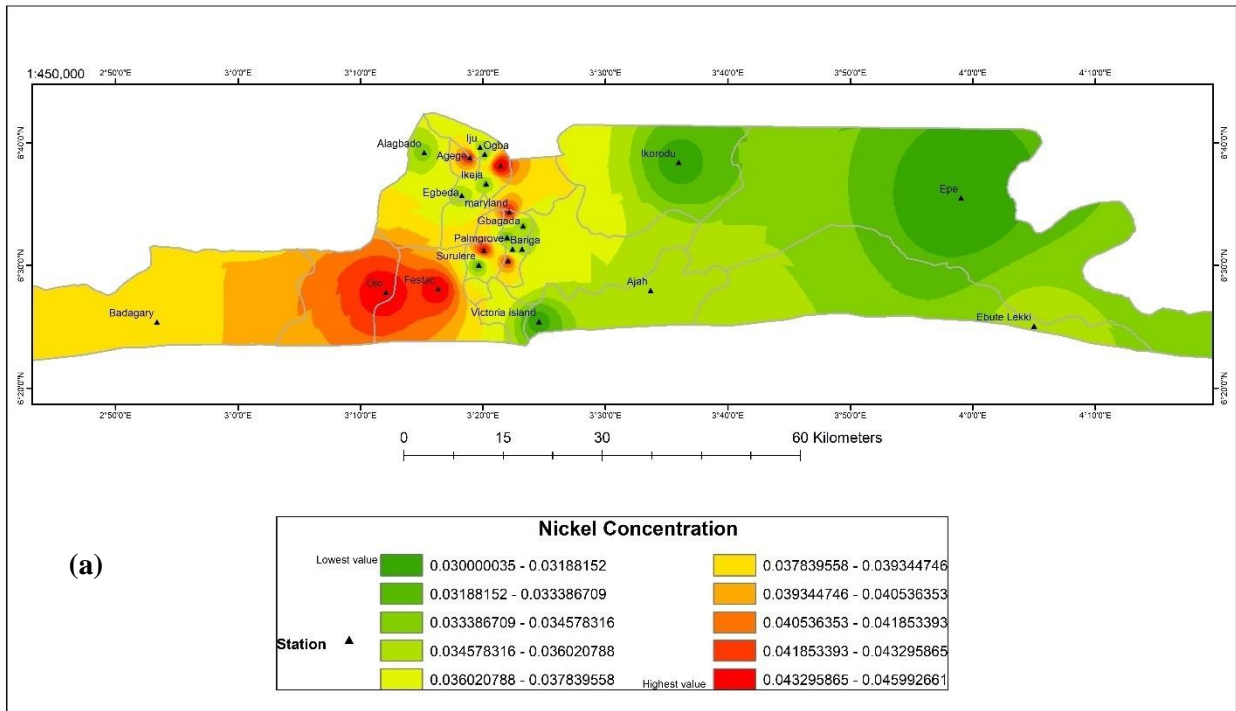


Figure 20: GIS map for Ni concentration in (a) Light rain (b) Heavy rainy (Year 2)

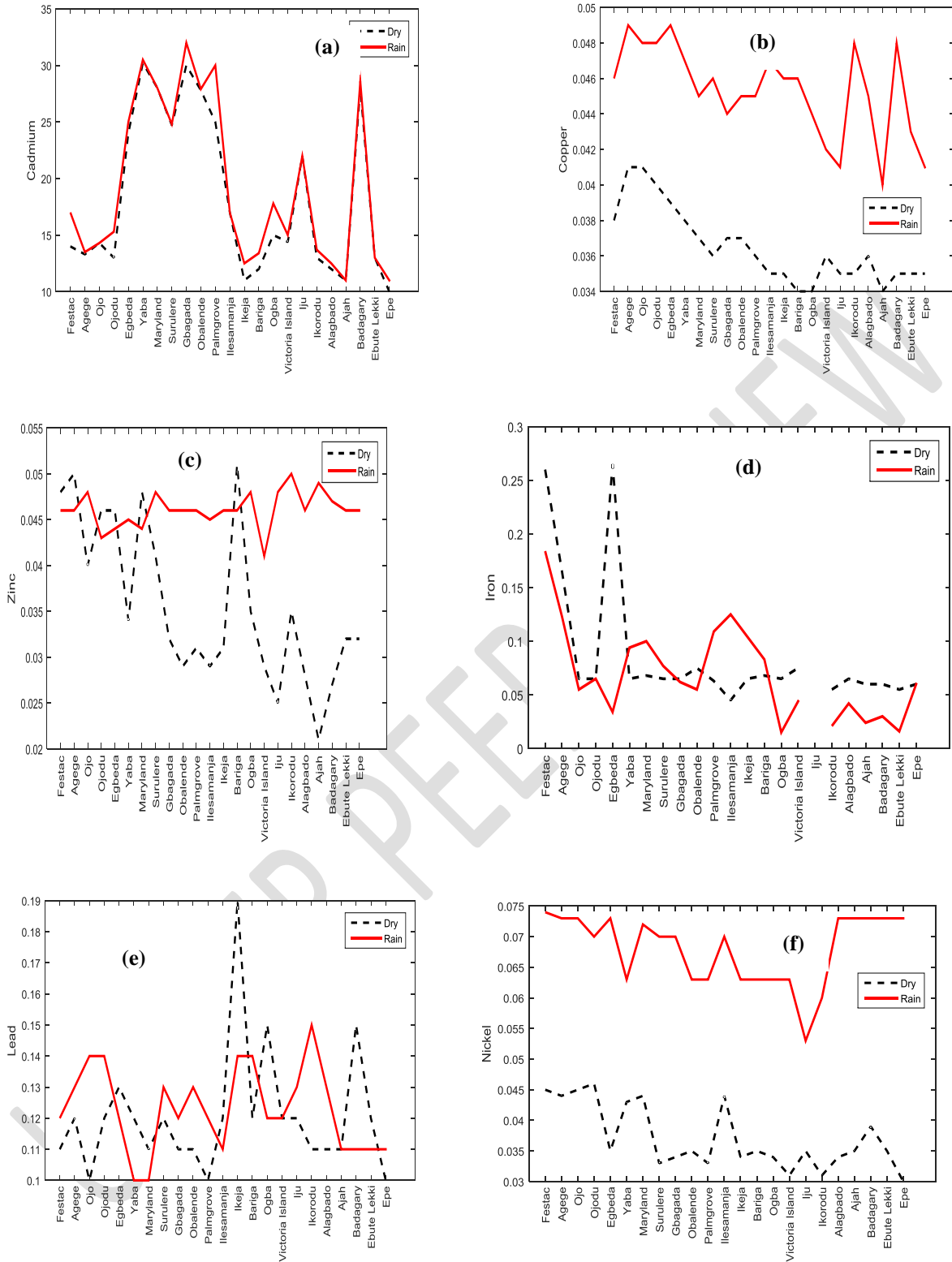


Figure 21: MATLAB air pollutant comparison graphs for both years (a) Cd (b) Cu (c) Zn (d) Fe (e) Pb (f) Ni

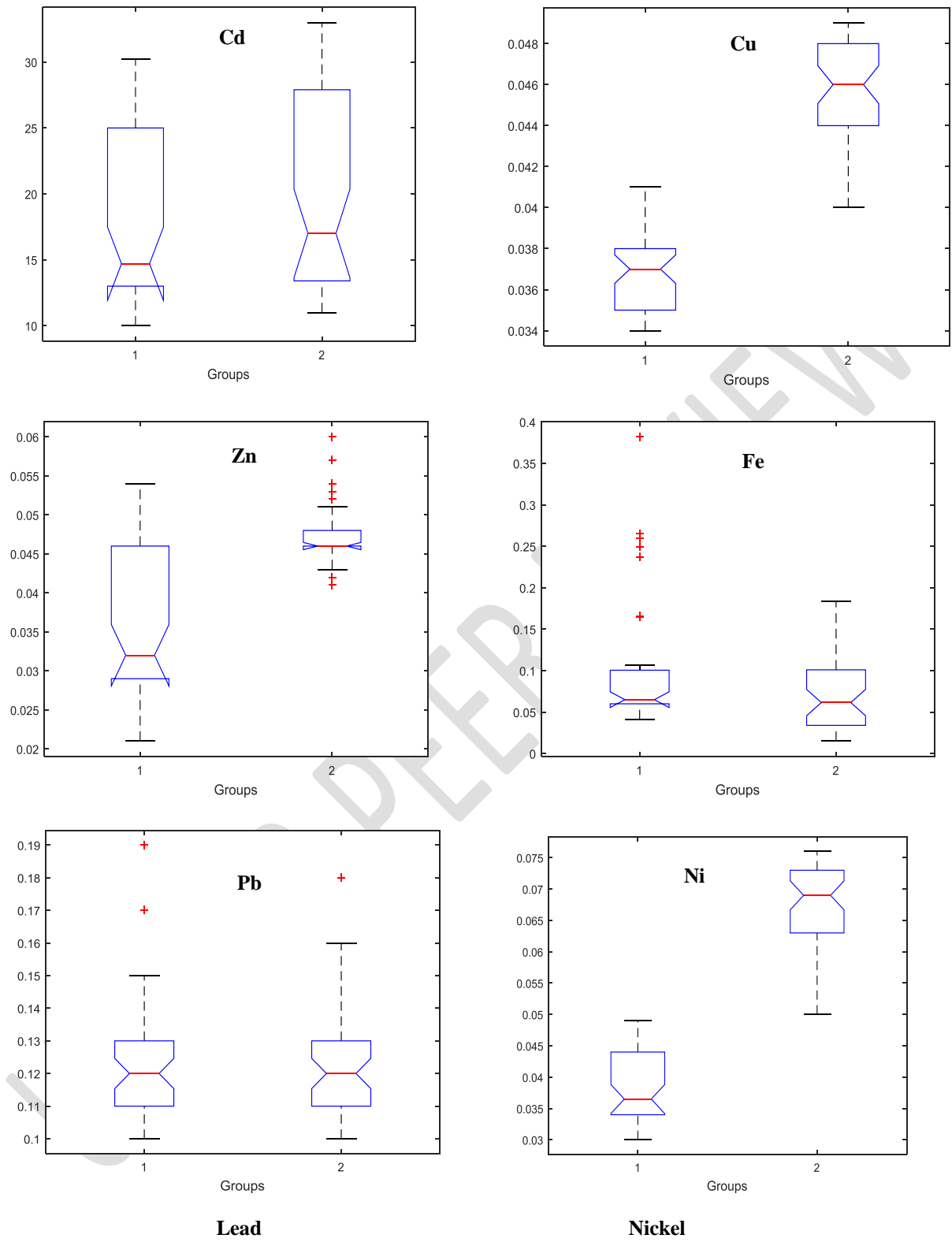
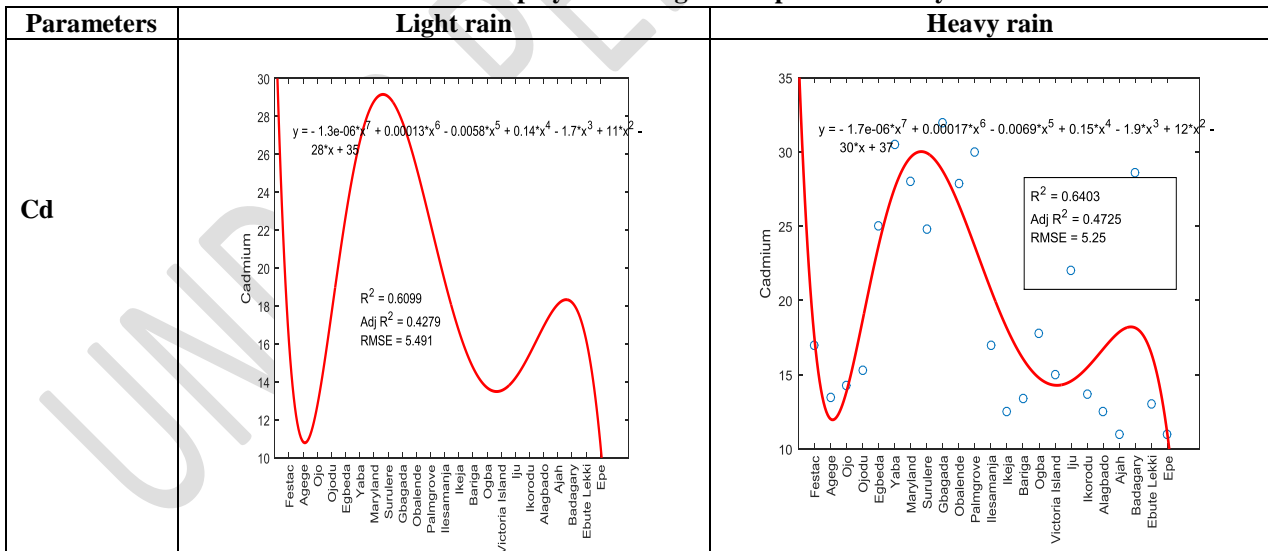


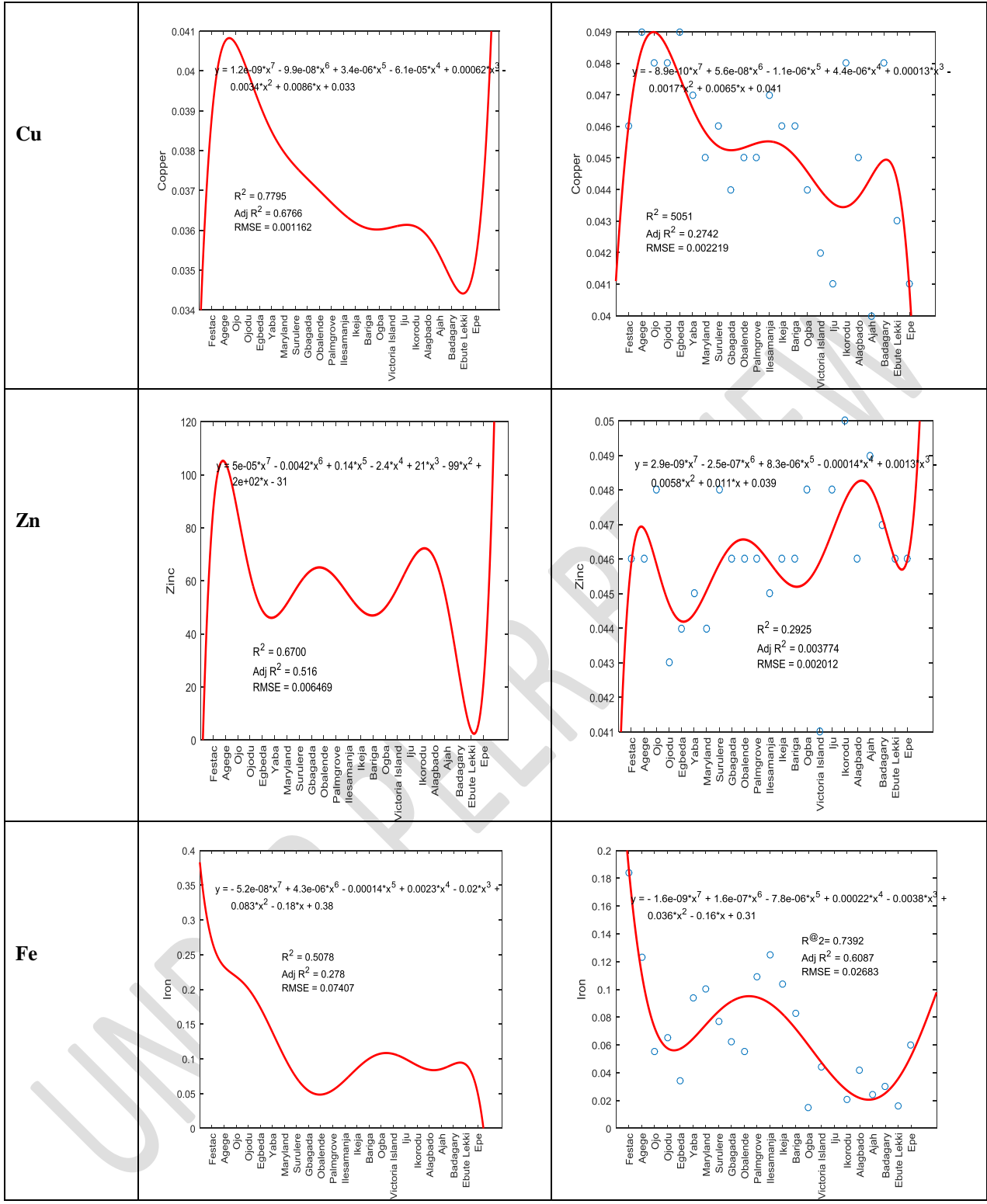
Figure 22: Box and whiskers plots for pollutants for both years (Group 1- Light rain; Group 2 – Heavy rain)

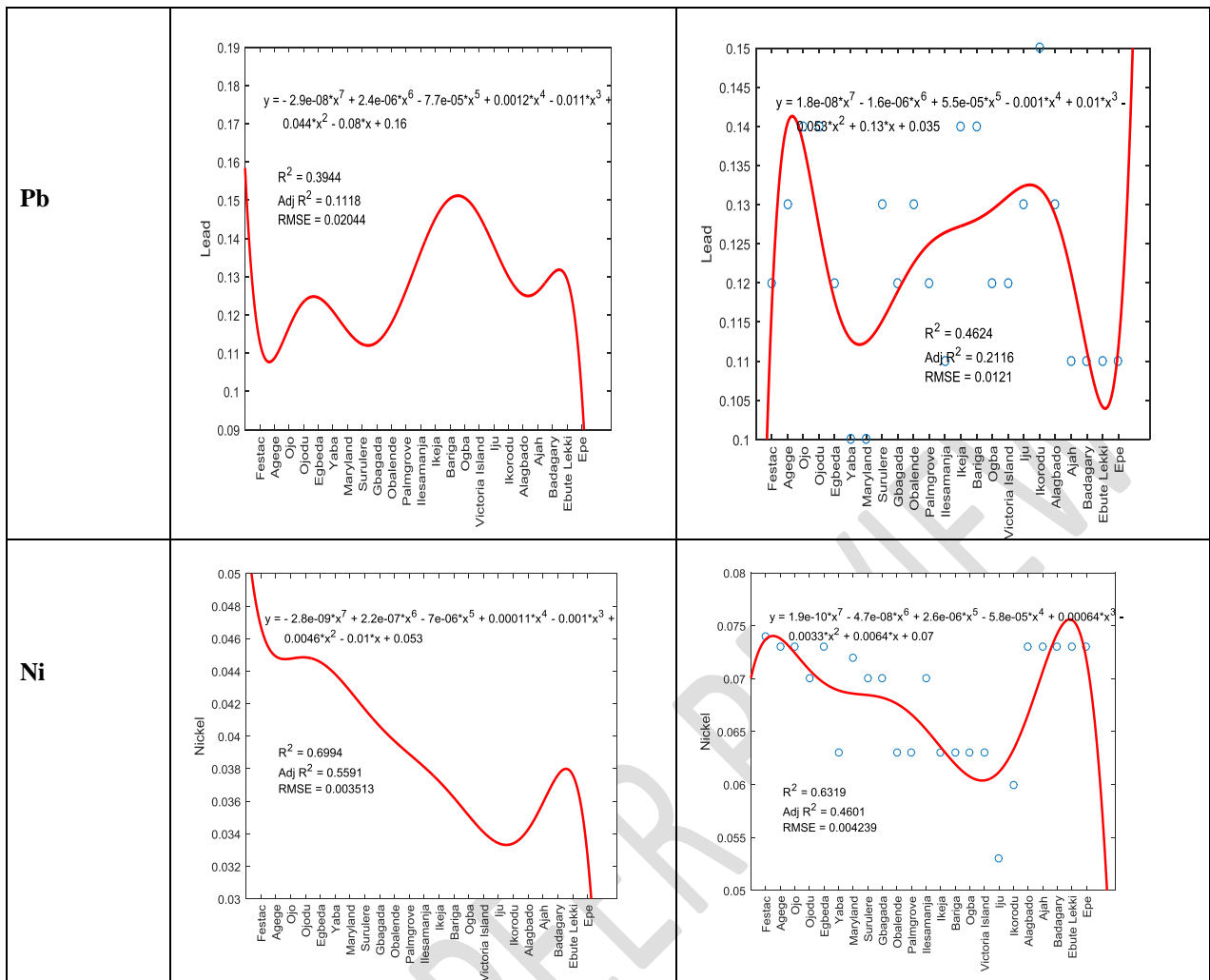
Table 12: MATLAB mathematical models for both years

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	$y = 1.2e^{-09}x^7 - 9.9e^{-08}x^6 + 3.4e^{-06}x^5 - 6.1e^{-05}x^4 + 0.00062x^3 - 0.0034x^2 + 0.0086x + 0.033$	0.7795	0.6766	0.0011
	Heavy rain	$y = -9.8e^{-10}x^7 + 6.2e^{-08}x^6 - 1.3e^{-06}x^5 + 8e^{-06}x^4 + 9.1e^{-05}x^3 - 0.0014x^2 + 0.0055x + 0.043$	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







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 cited 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 (Figures 4 & 5) 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 were seen in both seasons indicating that Cd was present throughout the year. The Bar chart Fig 3 and the box and whiskers plot (Fig22), confirmed that higher concentration level readings were recorded during the rainy seasons. While, the MATLAB comparison graph (Fig 21a) 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 6 &7) 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 21(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 22) 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 8&9) 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 21(c)) clearly showed that during the rainy seasons the readings were continuously high. The box and whiskers plot (Fig 22) 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 11&12) 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 21(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 13&14) 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, were seen in both seasons portraying that Pb was present throughout the year. The MATLAB pollution comparison graphs (Fig 21(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 16 &17) 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 21(f)) revealed that the concentration levels of Ni were higher in the rainy seasons. The box and whiskers plot (Fig22) 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.

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 more monitoring sites should be set up in different locations in the State by relevant stakeholders for constant monitoring.

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OBSERVATIONS

Necessary/Comply

Suggestions

UNDER PEER REVIEW