ISSN: 2350-0328

International Journal of Advanced Research in Science, Engineering and Technology

Vol. 8, Issue 8 , August 2021

Spatiotemporal Distribution of Heavy Metal Concentrations in Groundwater: Case Study of Warri, Delta State, Nigeria

J. E. Agori, H. U. Nwoke, B. C. Okoro , B. U. Dike

Department of Civil Engineering, Faculty of Engineering, Oleh Campus, Delta State University, Abraka, Oleh Campus.
Department of Civil Engineering, School of Engineering and Engineering Technology, Federal University of Technology, Owerri.
Department of Civil Engineering, School of Engineering and Engineering Technology, Federal University of Technology, Owerri.
Department of Civil Engineering, School of Engineering and Engineering Technology, Federal University of Technology, Owerri.

ABSTRACT: The enormous amounts of petroleum refining, exploration, and transportation and marketing of petroleum products within and across Warri is frequent, thus possibilities of oil spills that introduce chemical compounds and heavy metals into groundwater through leaks and cross connections that have caused the groundwater to deteriorate in quality. product marketing in Warri. Effluents from these industries are discharged into surface water and groundwater that eventually contaminate groundwater bodies. These contaminants generally, may contain different heavy metals and hydrocarbon components that may be deleterious to the environment and pose a serious threat human causing various carcinogenic and neurotoxic effects, agricultural products and other living organisms. Groundwater samples were randomly collected from fifty (50) existing boreholes across Warri and its environs and analyzed for four heavy metals (Fe, Cd, Cr, Cu and Pb) using the atomic absorption spectrometer (AAS). The temporal variation of the concentration of these metals in both dry and wet seasons was evaluated. The Kriging interpolation technique of ArcGIS 10.6 software was used to evaluate the spatial distribution of these heavy metals in the study area and prediction maps produced. In the dry season, Cd, Cr and Pb showed strong spatial dependency and Cu showed moderate spatial dependency, but in the wet season, Cu showed moderate spatial dependency and Cd, Cr and Pb showed strong spatial dependency. However, Fe, in both seasons showed weak spatial dependency. The heavy metals concentrations were found to be within WHO recommended permissible standards, apart from Pb which was higher than 0.01mg/l thus presenting serious health problems if consumed without treatment.

KEYWORDS:*Geostatistics, Groundwater, Heavy MetalsWater Quality, Spatiotemporal Distribution, Kriging, Warri.*

I. INTRODUCTION

In the past four decades there had been substantial increase in oil and gas exploration, refining and product marketing in Warri thus possibilities of oil spills that introduce chemical compounds and heavy metals into groundwater through leaks.Contamination of groundwater by heavy metals from petroleum and hydrocarbon components is becoming a matter of global concern [1]. Though effects of heavy metals contamination of drinking water are not felt on short-term bases, their accumulation over a long period in the body has significant health effects [2]. The situation is worsened by the proliferations of individual boreholes as a result of government not been able to meet the water needs of her citizens. Water from these boreholes are not adequately treated before consumption. The presence of heavy metals in drinking water higher than acertain concentration can cause detrimental impacts on human health and major environmental concern due to their pervasiveness, persistence and not been biodegradable.

ISSN: 2350-0328

International Journal of Advanced Research in Science, Engineering and Technology

Vol. 8, Issue 8 , August 2021

II. STUDY AREA

Warri is located in the western end and coastal region of the Nigerian Niger Delta about some 40 kilometres away from the shores of the Atlantic Ocean in Delta State, in Southern Nigeria. It is situated at latitude 5°54′00’’N and 5°35′00’’N of the Equator and longitude 5°42′00’’E and 5°54′00’’E of the Greenwich Meridian, Figure 1.

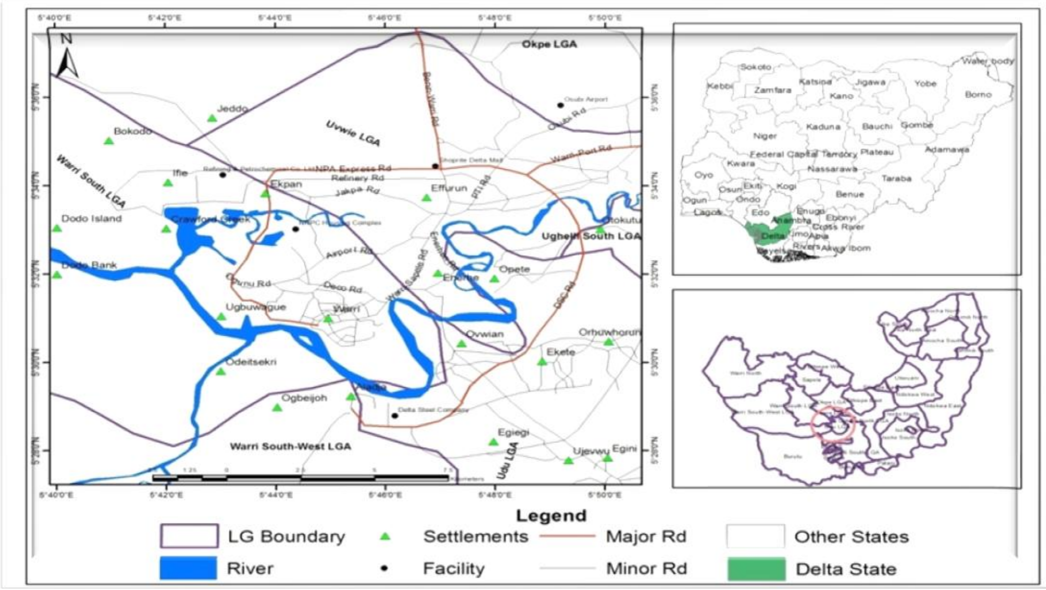


Fig. 1. Map of Warri and its environs [Source: 3,4]

The study area is situated on a low-lying plain generally below six metres above sea level, consisting mainly of unconsolidated sediments [5]. Warri and its environs are made up ofa geological formation which consists of more than 90% sands and about 10% shale/clays. The sands range in size from fine-to-medium and coarse-grained unconsolidated sands, with occasional intercalations of gravelly beds that are also poorly-sorted, sub-angular to well-rounded, and bear lignite streaks and wood fragments peat or lenses of plastic clay [6, 7, 8]. This formation contains the most productive and hence most tapped aquifer in the Niger delta region due to the fact that it is shallow [9]. The average annual of about 3000mm and occurs mostly due to the south-west monsoon wind[10].Groundwater and surface water in the study area is under threat of contamination from crude oil exploration and exploitation activities. The near absence of government water schemes has compelled individuals to drill and own their personal boreholes to meet their water needs.

III. MATERIALS AND METHODS

A. Establishment of sampling Locations

Fifty (50) sampling locations were randomly selected though reasonably spread across the study area based on the population density, areas of industrial or anthropogenic activities such as crude oil refining activities, open solid waste dump sites, high- and low-density areas and the river catchment areas. The UTM coordinates of all selected borehole locations were read with a hand-held GPS (GARMIN GPSMAP 76CSx model), recorded in Table 1 and allocated sampling codes as depicted in Figure 2for the purpose of geo-referencing.

ISSN: 2350-0328
International Journal of Advanced Research in Science, Engineering and Technology
Vol. 8, Issue 8 , August 2021

Table 1: Sampling locations and their GPS in UTM coordinates

S/N	Sample Locations	Sample Location Code	UTM Coordinates	
			Longitudes (E)	Latitudes (N)
1	Okuokoko	OKU	873764.26	617561.74
2	Effurun GRA	EFG	809311.71	616265.61
3	Army Barracks	ARB	806343.49	617014.43
4	Niger CAT	NCAT	803585.72	617216.33
5	Airport Road	APR	807682.28	613754.57
6	Jakpa Road	JKR	808039.86	614880.60
7	Shagholoh	SHA	802034.58	616405.78
8	Ekpan	EKP	803288.04	615763.82
9	Urhobo College Effurun	UCE	807932.75	612162,37
10	Effurun Market	EFM	808734.27	614759.96
11	Ogborode	OGD	796661.77	619874.80
12	Ughoton	UGT	795589.43	620671.69
13	Jeddo	JED	799838.04	618888.51
14	Ubeji 1	UBJ 1	799644.98	616528.51
15	Ubeji 2	UBJ 2	798928.54	616368.90
16	Osubi Market	OSM	810399.60	617088.74
17	Osubi Airport	OSA	812355.65	619128.23
18	Ogbuwangue	OGB	801383.19	611606.79
19	Warri Port	WAP	801978.92	611118.32
20	Ogunu	OGU	800441.59	612708.26
21	Edjebah	EDJ	803381.05	612880.96
22	Edjeba Housing Estate	EDHE	803354.16	614121.37
23	Federal Government College	FGC	801725.36	612241.99
24	Ajamimogha	AJA	803523.10	611447.95
25	Warri GRA	WAG	803089.34	610613.97
26	Okumagba Layout	OKL	805132.67	611876.84
27	Okere Road	OKR	804414.63	610867.87
28	Marine Quarters	MRQ	806349.18	611574.71
29	Essi Layout	ESL	806328.36	610275.72
30	Igbudu Market	IGM	805866.77	611039.40
31	Agbassa	AGS	805043.38	610226.30
32	Bowen Avenue	BOA	804792.89	609943.85
33	Iyara	IYA	805907.77	609616.93
34	Pessu Market	PEM	805373.32	609158.42
35	Orhunworun	ORH	814412.45	609039.09
36	Enerhen	ENE	809072.91	611100.90
37	Udu Road	UDR	812370.15	604744.47
38	Otokutu	OTO	814056.74	613752.53
39	Bendel Estate	BDE	806477.20	613425.55
40	Upper Erejuwah	UPE	804644.73	611059.84
41	Mammy Market	MAM	808310.16	617280.79
42	DSC Township	DST	812824.27	609360.84
43	Okumagba Estate	OKE	803923.81	612262.10
44	Mofor	MOF	811465.26	609295.86
45	FUPRE	FUP	810120.84	615008.04

ISSN: 2350-0328
International Journal of Advanced Research in Science, Engineering and Technology
Vol. 8, Issue 8 , August 2021

46	Shoprite	SHP	808339.43	616442.94
47	Robbinson Plaza	ROP	805827.10	611528.83
48	Esisi Road	ESR	803801.62	610690.62
49	Robert Road	ROR	804203.17	610182.10
50	PTI Road	PTR	810142.35	616473.42

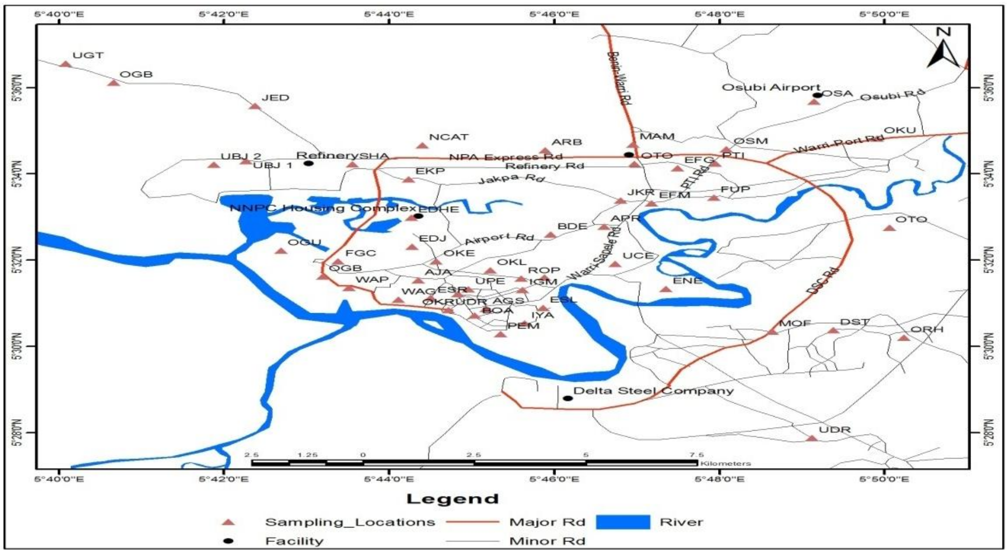


Fig. 2: Digitized map of Warri and its environs (Study Area) showing sampling locations

B. **Collection of Water Samples**

New high-density PET screw-capped containers of 1.5litres capacity were used to collect water samples from the selected 50 existing boreholes tapping the Somebreiro-Warri Deltaic Plain Sands aquifer of Warri and its immediate environs during the dry season (December, 2019 – January, 2020) and the wet season (June, 2020 – August, 2020). The PET containers and stoppers were thoroughly washed with distilled water three times and once with the water to be sampled before collecting the actual sample. The bottles were filled, allowed to overflow and immediately corked, properly labelled to avoid mix up, placed in an ice block chest and transported to the already chosen laboratory within a prescribed period of not more than three hours after collection. Collection, preservation and transportation of the water samples to the laboratory followed the [11]standard methods for examination of water and waste water.The water samples were preserved in refrigerators at 4^{o}C in the laboratory to keep the samples intact until analysis was carried out.

C. **Laboratory Analysis of Water Quality Parameters**

The collected samples used for water quality analysis were transported to Jacio Environmental Limited located at No. 2 Refinery Road, Effurun, Delta State, Nigeriaon a daily basis. The water samples were analyzed for five heavy metals (iron (Fe), cadmium (Cd), chromium (Cr), copper (Cu) and lead (Pb)), using SP2900 Pye-UnicamAtomic Spectrometer (AAS)and the concentration of each parameter was read directly at their specific wavelength, Fe (248.3nm), Cd (228.8nm), Cr (357.9nm), Cu (324.8nm) and Pb (217nm).

D. **Geostatistical Modelling of Groundwater Quality Parameters**

The Geostatistical Analyst Extension Tool of the ArcGIS 10.6 software was used in the geostatistical modelling of groundwater at unsampled locations based on kriging interpolation method in standard technique as stipulated by [12]. The results of laboratory analysis of water samples collected from sampling locations both for the dry and wet seasons were used as input data. The steps in the Geostatistical modelling using the ArcGIS 6.0 software is shown in Figure 3 below.

ISSN: 2350-0328
International Journal of Advanced Research in Science, Engineering and Technology
Vol. 8, Issue 8 , August 2021

i. Evaluation of Normality Test and Data transformation
ii. Identifying the Global Trend
iii. Semivariogram/Variogram Models Fittings and Testing
iv. Spatial Dependency Determination
v. Cross Validation
vi. Creation of Groundwater Quality Parameters Spatial Variation Distribution Maps

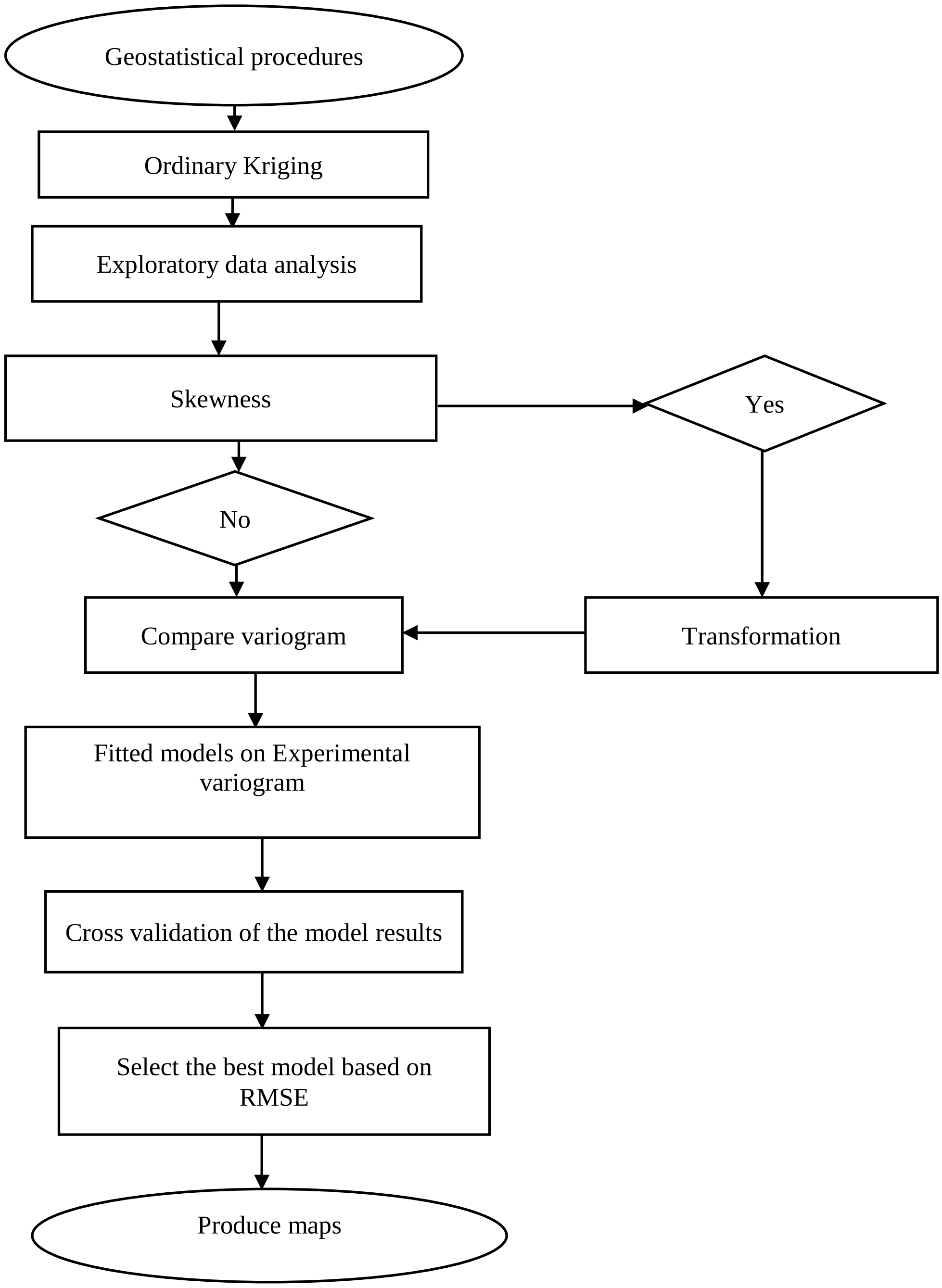


Fig.3: Flow chart of the steps followed for the geostatistical analysis
[Source: 13]

ISSN: 2350-0328
International Journal of Advanced Research in Science, Engineering and Technology
Vol. 8, Issue 8 , August 2021

IV. RESULTS AND DISCUSSIONS

A. RESULTS

Statistical Analysis

Theconcentration of the analysed five heavy metals for both seasons are presented in Table 2. The descriptive statistics was analysed using the Microsoft office excel to obtain the minimum, maximum, mean and standard deviation and the results are presented in Table 3. The result showed variation among the measured values of these parameters at different locations is not too high and variation range is narrow.

Table 4presents the descriptive statistics of each water quality parameter from each location compared to the WHO standard for both seasons in groundwater of the study area.

Table 2: Results of groundwater quality parameters analysis

Sampling Location (SL)	SL Code	Fe (mg/L)		Cd (mg/L)		Cr (mg/L)		Cu (mg/L)		Pb (mg/L)	
		D	W	D	W	D	W	D	W	D	W
Okuokoko	OKU	0.20	0.22	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001
Effurun GRA	EFG	0.21	0.23	0.001	0.001	0.001	0.001	0.002	0.002	0.001	0.001
Army Barracks	ARB	0.20	0.22	0.002	0.002	0.001	0.001	0.010	0.010	0.001	0.001
Niger CAT	NCAT	0.20	0.22	0.005	0.005	0.004	0.004	0.310	0.310	0.040	0.040
Airport Road	APR	0.24	0.26	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001
Jakpa Road	JKR	0.21	0.23	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001
Shagholoh	SHA	0.20	0.19	0.004	0.004	0.004	0.004	0.310	0.310	0.040	0.040
Ekpan	EKP	0.20	0.22	0.002	0.002	0.003	0.003	0.100	0.100	0.050	0.050
Urhobo College	UCE	0.20	0.22	0.001	0.001	0.001	0.001	0.002	0.002	0.001	0.001
Effurun Market	EFM	0.21	0.23	0.001	0.001	0.001	0.001	0.200	0.200	0.001	0.001
Ogborode	OGD	0.21	0.23	0.003	0.003	0.002	0.002	0.120	0.120	0.010	0.010
Ughoton	UGT	0.22	0.24	0.005	0.005	0.005	0.005	0.900	0.900	0.050	0.050
Jeddo	JED	0.22	0.24	0.005	0.005	0.003	0.003	0.420	0.420	0.060	0.060
Ubeji 1	UBJ 1	0.21	0.23	0.006	0.006	0.004	0.004	0.700	0.700	0.060	0.060
Ubeji 2	UBJ 2	0.20	0.22	0.003	0.003	0.003	0.003	0.090	0.090	0.030	0.030
Osubi Market	OSM	0.20	0.22	0.006	0.006	0.004	0.004	0.700	0.700	0.060	0.060
Osubi Airport	OSA	0.22	0.24	0.006	0.006	0.004	0.004	0.600	0.600	0.050	0.050
Ogbuwangue	OGB	0.22	0.24	0.001	0.001	0.001	0.001	0.010	0.010	0.001	0.001
Warri Port	WAP	0.20	0.22	0.003	0.003	0.002	0.002	0.100	0.100	0.010	0.010
Ogunu	OGU	0.21	0.20	0.001	0.001	0.001	0.001	0.001	0.001	0.010	0.010
Edjebah	EDJ	0.23	0.25	0.001	0.001	0.002	0.002	0.019	0.019	0.001	0.001

ISSN: 2350-0328
International Journal of Advanced Research in Science, Engineering and Technology
Vol. 8, Issue 8 , August 2021

Edjeba H. Estate	EDHE	0.20	0.22	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001
Fed. Govt. College	FGC	0.20	0.22	0.002	0.002	0.001	0.001	0.060	0.060	0.020	0.020
Ajamimogha	AJA	0.20	0.22	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001
Warri GRA	WAG	0.20	0.22	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001
Okumagba Layout	OKL	0.20	0.22	0.002	0.002	0.002	0.002	0.100	0.100	0.001	0.001
Okere Road	OKR	0.21	0.23	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001
DECO Road	MRQ	0.20	0.22	0.003	0.003	0.003	0.003	0.300	0.300	0.030	0.030
Essi Layout	ESL	0.21	0.23	0.001	0.001	0.002	0.002	0.100	0.100	0.001	0.001
Igbudu Market	IGM	0.20	0.22	0.006	0.006	0.003	0.003	0.500	0.500	0.060	0.060
Agbassa	AGS	0.20	0.22	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001
Bowen Avenue	BOA	0.20	0.22	0.002	0.002	0.002	0.002	0.250	0.250	0.001	0.001
Iyara	IYA	0.20	0.22	0.004	0.004	0.002	0.002	0.400	0.400	0.030	0.030
Pessu Market	PEM	0.20	0.20	0.003	0.003	0.002	0.002	0.200	0.200	0.001	0.001
Orhunworun	ORH	0.20	0.22	0.004	0.004	0.004	0.004	0.500	0.500	0.020	0.020
Enerhen	ENE	0.20	0.22	0.002	0.002	0.002	0.002	0.300	0.300	0.020	0.020
Udu Road	UDR	0.20	0.22	0.001	0.001	0.001	0.001	0.020	0.020	0.001	0.001
Otokutu	OTO	0.20	0.22	0.003	0.003	0.002	0.002	0.030	0.030	0.001	0.001
Bendel Estate	BDE	0.20	0.22	0.008	0.008	0.005	0.005	0.700	0.700	0.060	0.060
Upper Erejuwah	UPE	0.20	0.22	0.006	0.006	0.003	0.003	0.500	0.500	0.050	0.050
Mammy Market	MAM	0.20	0.22	0.001	0.001	0.001	0.001	0.100	0.100	0.001	0.001
DSC Township	DST	0.22	0.24	0.001	0.001	0.001	0.001	0.080	0.080	0.001	0.001
Okumagba Estate	OKE	0.21	0.23	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001
Mofor	MOF	0.20	0.22	0.005	0.005	0.002	0.002	0.400	0.400	0.030	0.030
FUPRE	FUP	0.21	0.19	0.005	0.005	0.003	0.003	0.100	0.100	0.020	0.020
Otokutu	SHP	0.20	0.22	0.001	0.001	0.001	0.001	0.010	0.010	0.006	0.006
Robbinson Plaza	ROP	0.20	0.22	0.001	0.001	0.001	0.001	0.100	0.100	0.001	0.001
Esisi Road	ESR	0.20	0.22	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001
Udu Road	ROR	0.21	0.23	0.007	0.007	0.005	0.005	0.700	0.700	0.070	0.070
Pet. Training Inst.	PTR	0.20	0.22	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001

ISSN: 2350-0328

International Journal of Advanced Research in Science, Engineering and Technology

Vol. 8, Issue 8 , August 2021

Table 3: Groundwater quality statistics of domestic boreholes samples analyses during dry season and wet season. (where, n = number of samples collected = 50)

Parameter (mg/l)	Dry season (n = 50)				Wet season (n = 50)			
	Range		Mean	SD	Range		Mean	SD
	min	max			min	Max		
Fe	0.20	0.24	0.21	0.01	0.19	0.26	0.22	0.01
Cd	0.00	0.01	0.00	0.002	0.00	0.01	0.00	0.002
Cr	0.000	0.002	0.00	0.001	0.000	0.002	0.00	0.001
Cu	0.01	0.19	0.20	0.246	0.01	0.19	0.20	0.246
Pb	0.01	0.36	0.02	0.023	0.01	0.36	0.02	0.023

Table 4:Comparison of Water Quality Parameters with WHO Standards

Parameter (mg/l)	Dry Season		Wet Season		WHO Perm. Standards (WHO, 2011)	Remark
	Mean Values	Std. error	Mean Values	Std. error		
Fe	0.21±0.001	0.01	0.22±0.002	0.01	0.3	WL
Cd	0.00±0.000	0.002	0.00±0.003	0.002	0.003	WL
Cr	0.00±0.000	0.001	0.00±0.000	0.001	0.05	WL
Cu	0.20±0.047	0.246	0.20±0.035	0.246	2	WL
Pb	0.02±0.077	0.023	0.02±0.088	0.023	0.01	AL

KEY: AL – Above Limit, WL – Within Limit, NL – No Limit, Perm. – permissible

Geostatistical Analysis

The results obtained from the geostatistical analyst tool in ArcGIS 10.6 that was used to explore the dataset in order to build good interpolation models are presented hereafter. This was achieved through examination of the data distribution (normality check and transformation), trends in the dataset, variogram fitting and testing, cross validation of models, understanding the spatial autocorrelation and directional influence and generation of prediction maps using the ordinary kriging model.

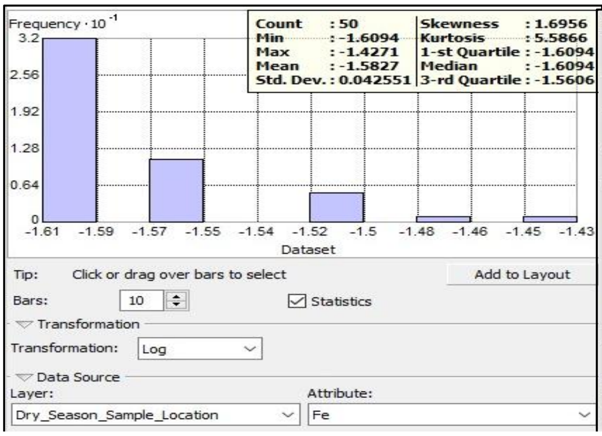
Evaluation of Normality Test using Histogram

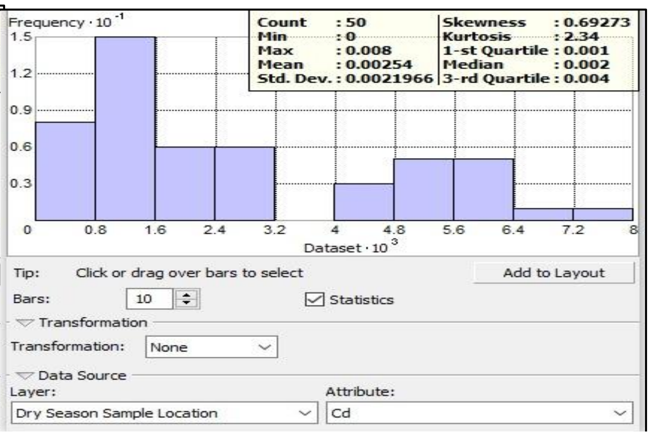
Results of the best histograms for the heavy metals are shown in Figures 4(a-e) for the dry season and 5(a-e) in the wet season. The criteria for adopting the best transformation was based on the transformation that produced a skewness of or close to zero (0) and a kurtosis of nearly three (3) with a mean and media values almost the same.

ISSN: 2350-0328

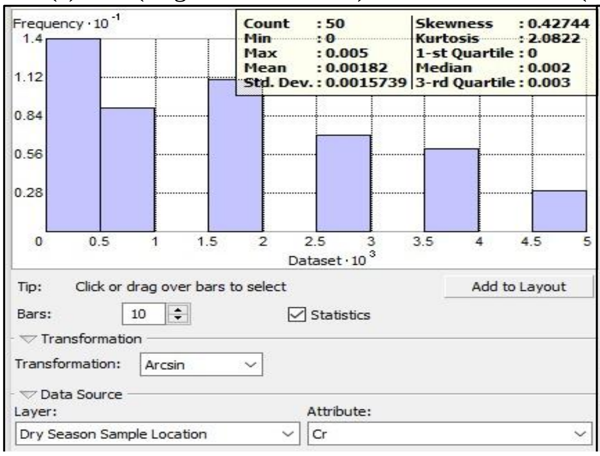
International Journal of Advanced Research in Science, Engineering and Technology

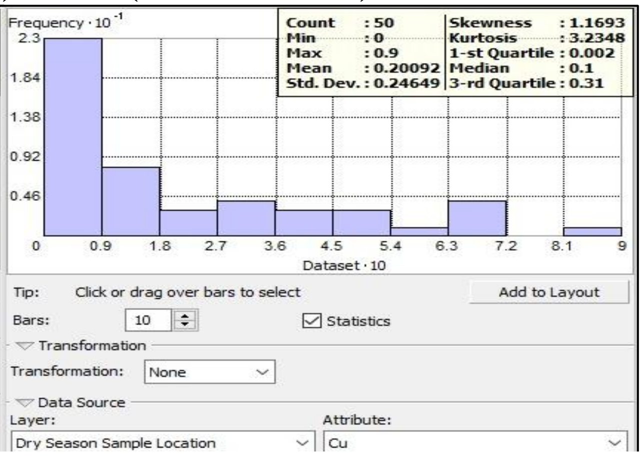
Vol. 8, Issue 8 , August 2021



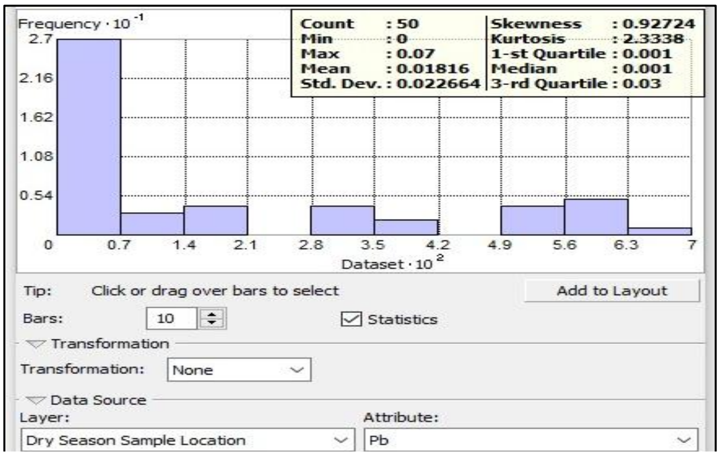


(a) Iron (Log. transformation) (b) Cadmium (None transformation)





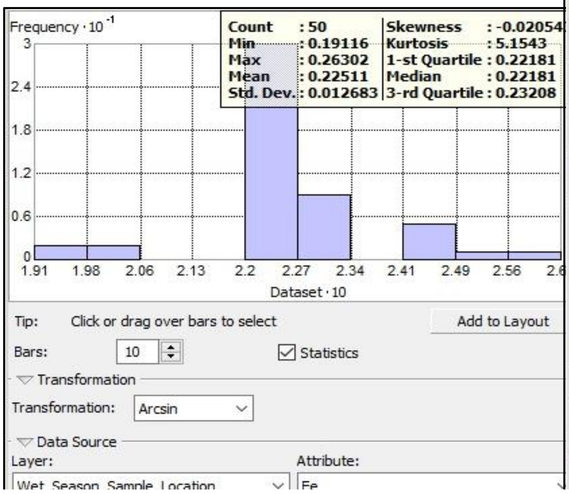
(c) Chromium (Arcsine transformation) (d) Copper (None transformation)



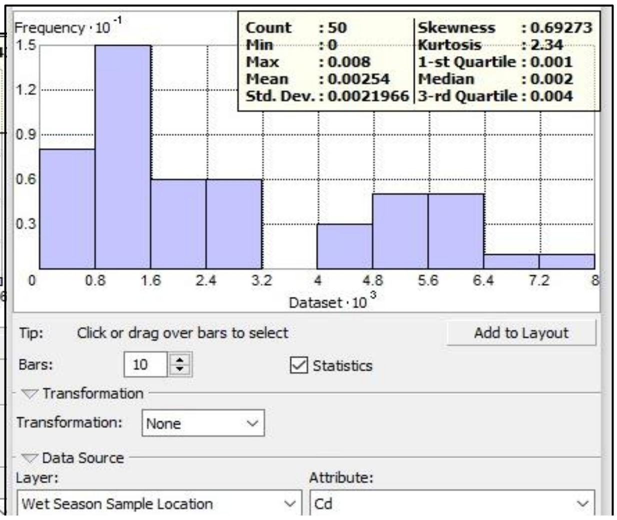
(e) Lead (None transformation)

Fig.4 (a-e): Dry Season Histogram

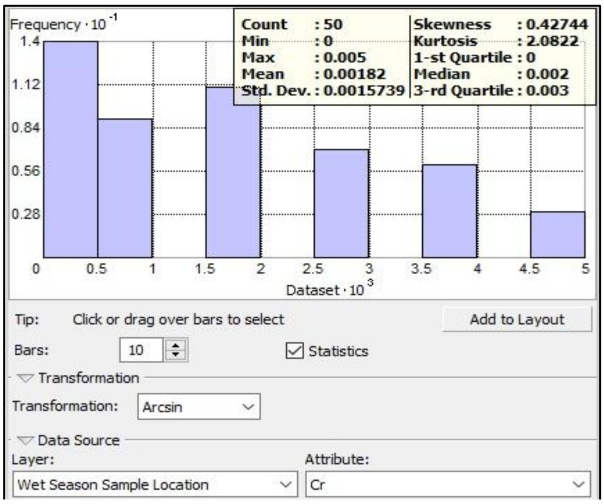
ISSN: 2350-0328
International Journal of Advanced Research in Science, Engineering and Technology
Vol. 8, Issue 8 , August 2021



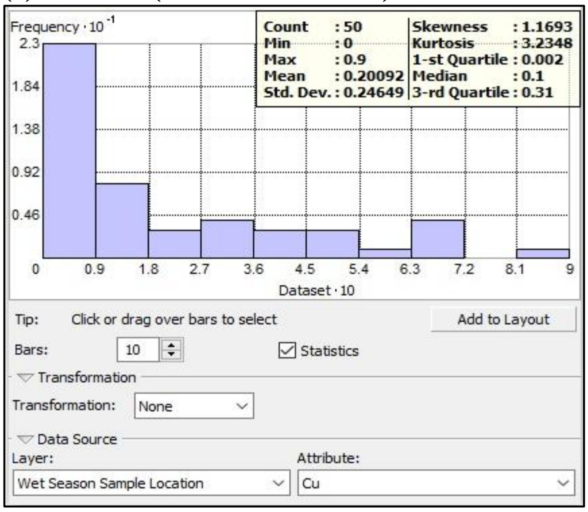
(a) Iron (Arcsine Transformation)



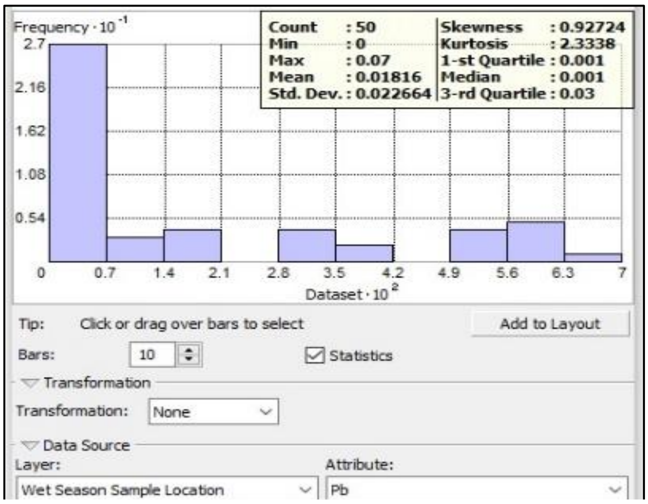
(b) Cadmium (None transformation)



(c) Chromium (Arcsine transformation)



(d) Copper (None transformation)



(e) Lead (None transformation

Fig.5 (a-e): Wet Season Histogram

ISSN: 2350-0328

International Journal of Advanced Research in Science, Engineering and Technology

Vol. 8, Issue 8 , August 2021

The best transformations for water quality heavy metals for both seasons are presented in Table 5. Also, presented are the mean, median, skewness, kurtosis and the type of transformation applied for each water quality parameter for both dry and wet season. The groundwater quality analysis of the heavy metal composition of the water samples are presented in Table 5.

Table 5: Transformation of water quality parameters for dry and wet seasons

Para-meters	Dry Season (DS)					Wet Season (WS)				
	Mean	Median	Skew-ness	Kurto-sis	Type of Transfor-mation	Mean	Med-ian	Skew-ness	Kurt-osis	Type of Transfor-mation
Fe	-1.583	-1.609	1.696	5.587	Log.	0.225	0.221	-0.021	5.154	ArcSine
Cd	0.0025	0.002	0.6927	2.34	None	0.008	0.0025	0.6927	2.34	None
Cr	0.002	0.002	0.427	2.082	Arcsine	0.002	0.002	0.427	2.082	Arcsine
Cu	0.201	0.1	1.169	3.235	None	0.201	0.1	1.169	3.235	None
Pb	0.018	0.001	0.9272	2.334	None	0.018	0.001	0.9272	2.334	None

Trend Analysis

The plot of the trend analysis during the dry season is presented in Figure 6(a-g) while the trend analysis plot for the wet season are presented in Figure 7(a-e).

Trend Analysis for Dry Season

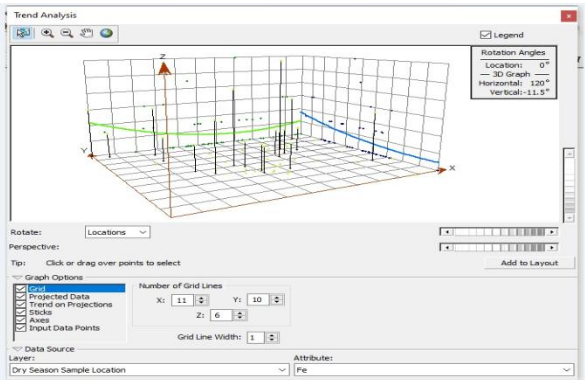


Fig.6a: Trend Analysis for Fe

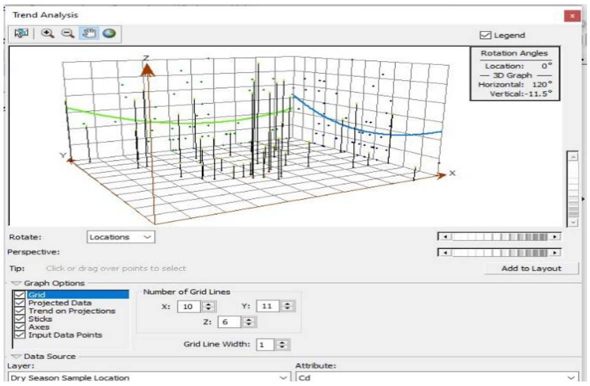


Fig.6b: Trend Analysis for Cd

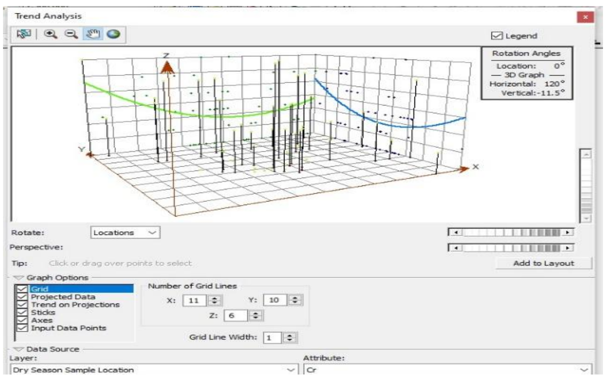


Fig.6c: Trend Analysis for Cr

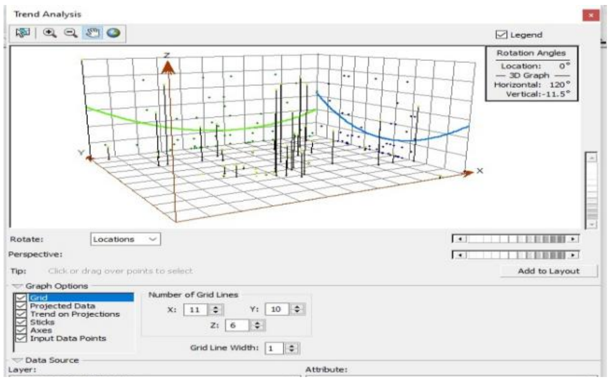


Fig.6d: Trend Analysis for Cu

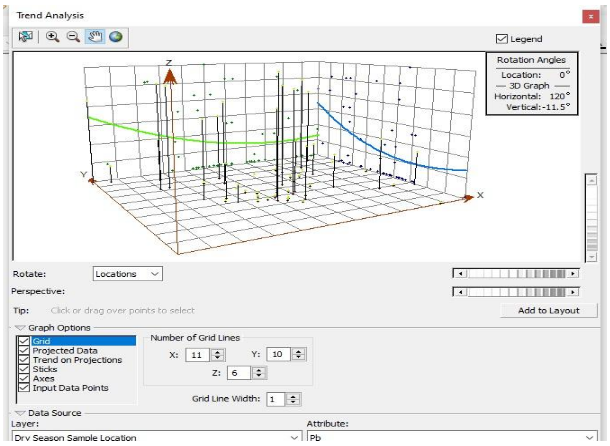


Fig.6e: Trend Analysis for Pb

Fig. 6(a-e): Analysis for Trend (Dry Season)

Trend Analysis for Wet Season

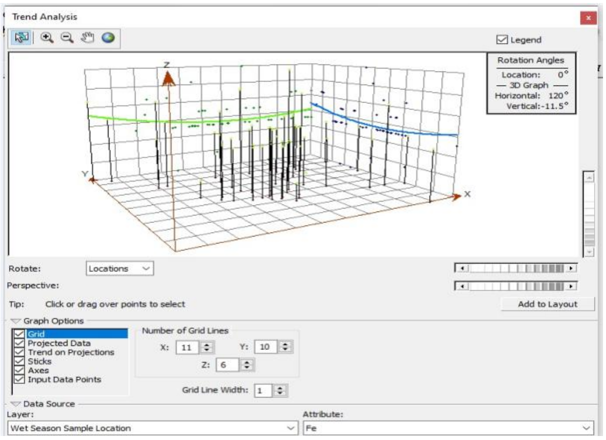


Fig.7a: Trend Analysis for Fe

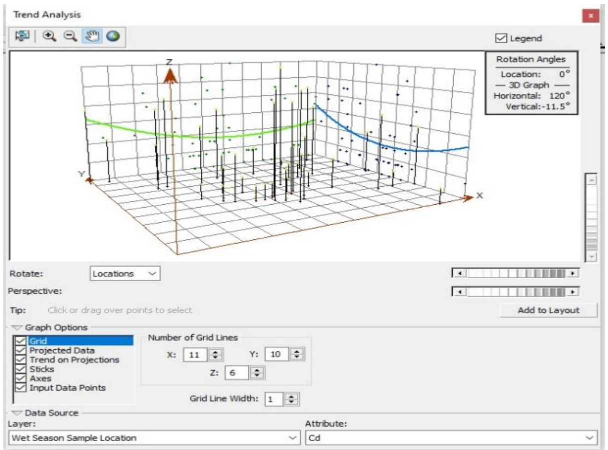


Fig.7b: Trend Analysis for Cd

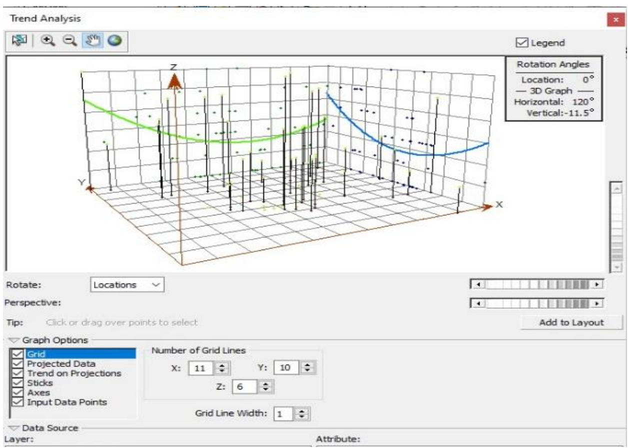


Fig.7c: Trend Analysis for Cr

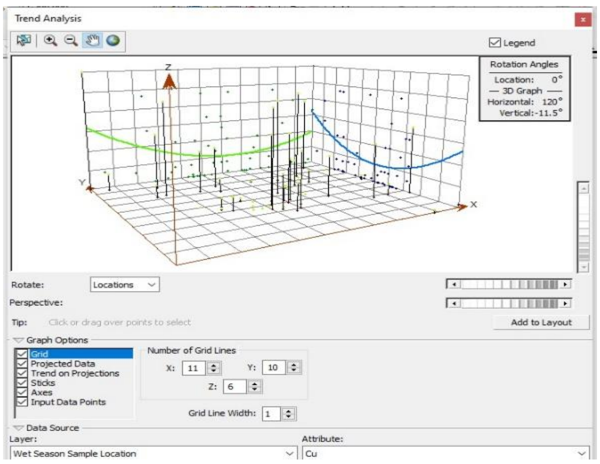


Fig.7d: Trend Analysis for Cu

ISSN: 2350-0328
International Journal of Advanced Research in Science, Engineering and Technology
Vol. 8, Issue 8 , August 2021

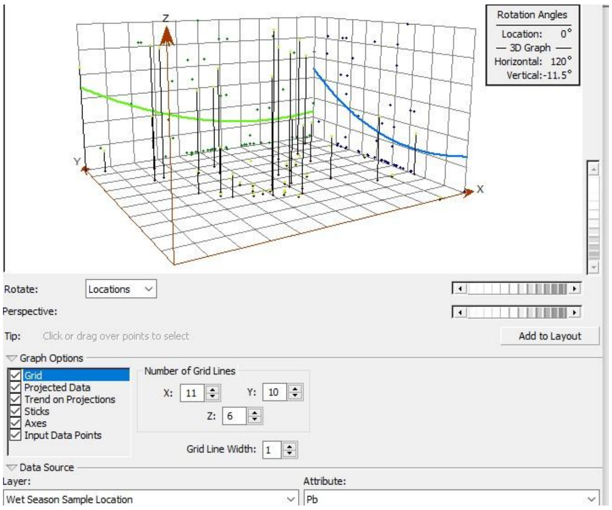


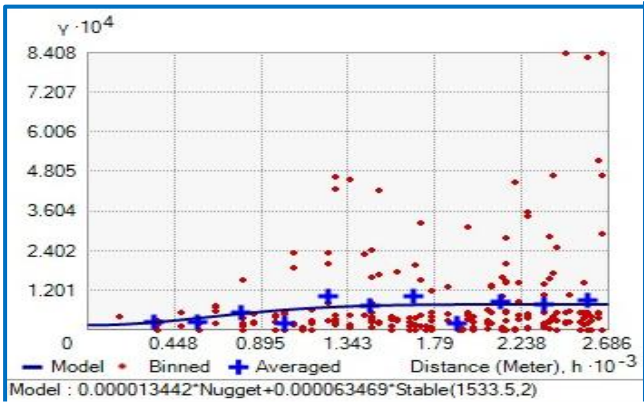
Fig.7e: Trend Analysis for Pb

Fig. 7(a-e): Analysis for Trend (Wet Season)

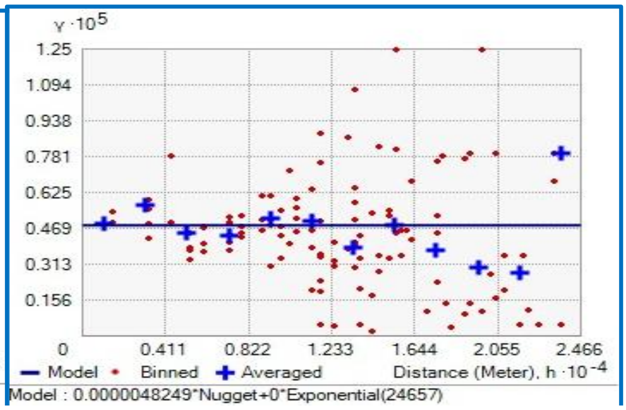
The results obtained from the trend analysis of the geostatistical analyst tool showed that the groundwater quality parameters showed that large scale trends were absent. This kept the Kriging model as simple as possible.

Semivariogram Fitting and Test

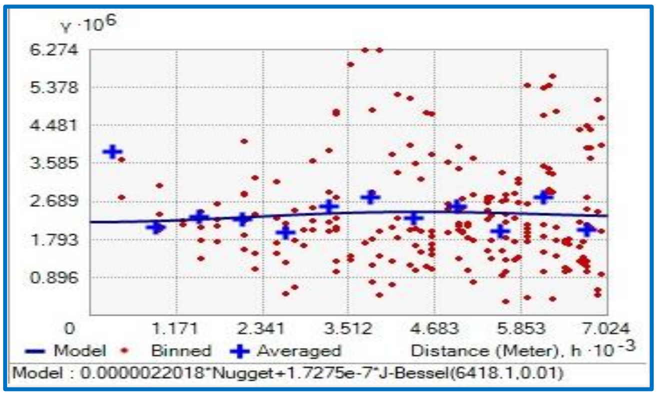
From the results of the eleven (11) Experimental semivariogram models (circular, spherical, tetraspherical, pentaspherical, exponential, Gaussian, rational quadratic, hole effect, K – Bessel, J – Bessel and stable) fitted for each of the heavy metals in both seasons the best fitted for each heavy metal is presented in Figures 8 and Figure 9 for dry and wet seasons.



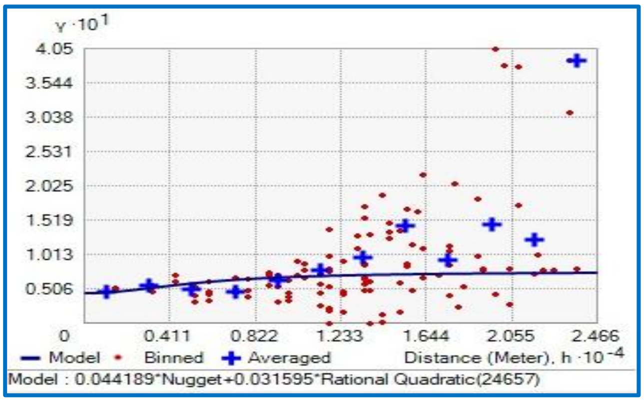
(a) Fe: Stable Semivariogram Model



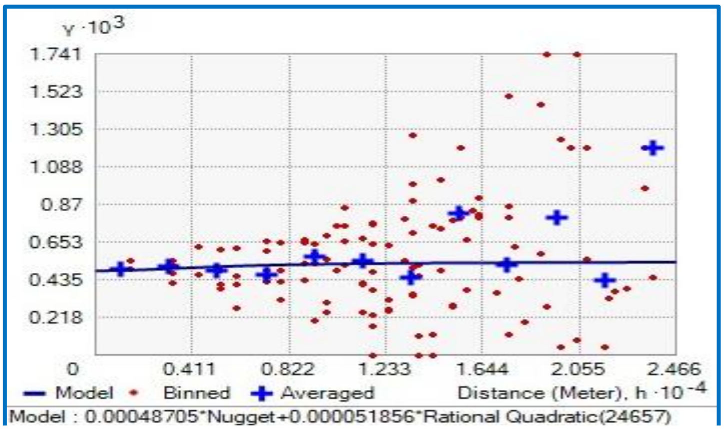
(b) Cd: Exponential Semivariogram Model



(c) Cr: J-bessel Semivariogram Model

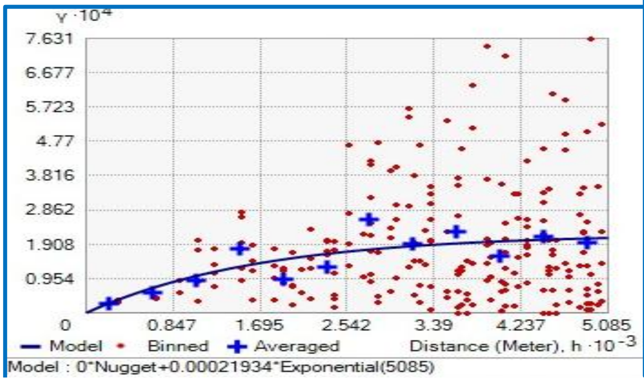


(d) Cu: Rational Quadratic Semivariogram Model

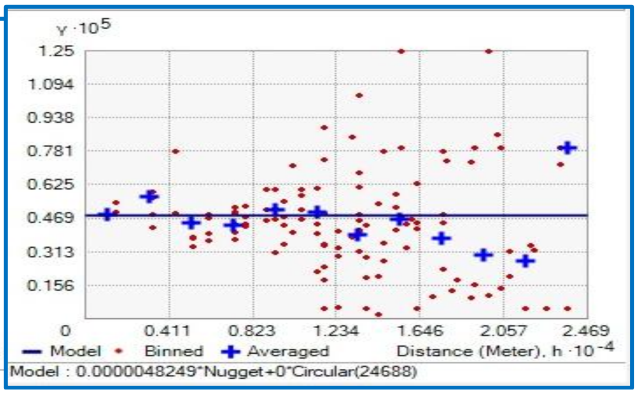


(e) Pb: Rational Quadratic Semivariogram Model

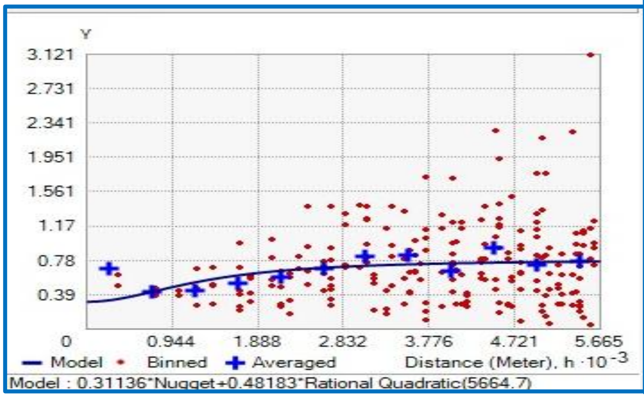
Fig.8: Best fitted variogram model in the dry season



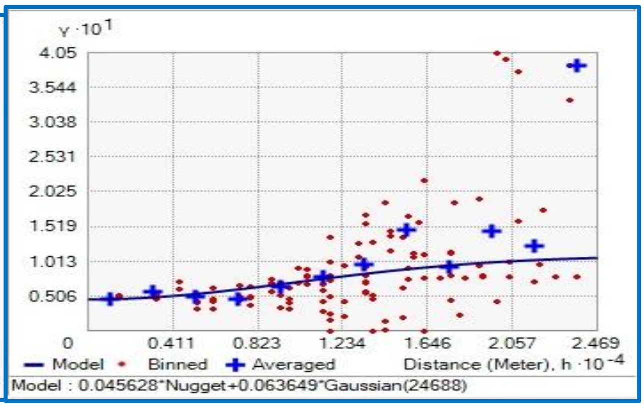
(a) Fe: Exponential Semivariogram Model



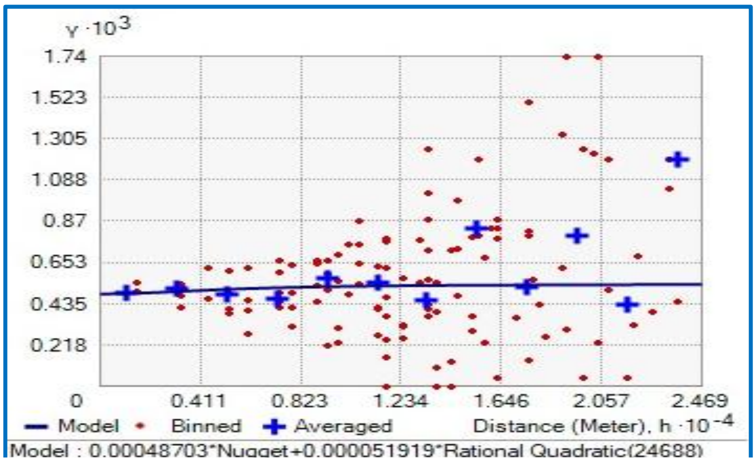
(b) Cd: Circular semivariogram Model



(c) Cr: Exponential Semivariogram Model



(d) Cu: Gaussian Semivariogram Model



(e) Pb: Rational Quadratic Semivariogram Model

Figure 9: Best fitted variogram model in the wet season

The properties of the variograms adopted (partial sill, nugget and range values) for each of the best fitted variogram models are presented in Table 6.

Table 6: Fitted semivariogram models for EC in the dry season

S/N	Parameter	Fitted model	Range	Nugget (c_n)	Partial sill(σ)
Dry season					
1.	Fe	Stable	1533.5	0.00006	0.000013
2.	Cd	Exponential	24657	0.00	0.000005
3.	Cr	J-bessel	6418.1	1.7275e-7	0.000002
4.	Cu	Rational Quad.	24657	0.0316	0.0442
5.	Pb	Rational Quad.	24657	0.00005	0.0005
Wet season					
1.	Fe	Exponential	5085	0.0002	0.00
2.	Cd	Circular	24688	0.00	0.000005
3.	Cr	Exponential	24688	0.00005	0.00049
4.	Cu	Gaussian	24688	0.06365	0.045628

ISSN: 2350-0328
International Journal of Advanced Research in Science, Engineering and Technology
Vol. 8, Issue 8 , August 2021

5.	Pb	Rational Quad.	24688	0.00005	0.00049

This is necessary inorder to assess prediction performances of the models by cross validation. In dry season, exponential model was best fitted for three (3) water quality parameters namely Fe and Cd. Cr was best fitted with Rational Quadratic model. Also, Hole Effect model was used for Cu, Pb was best fitted with Pentaspherical model. The results showed that the best semivariogram model based on RMSE varies for each water quality parameter. The best fitted semivariograms for each water quality parameter are presented in Tables 6 and 7.

In wet season, Exponential and J-bessel model was best fitted models for two (2) water quality parameters each, namely Fe and Pb respectively. Rational Quadratic model was best fitted for Cu. Cd and Cr were best fitted with Hole Effect semivariogram model. Fitted semivariogram models for each of the water quality parameter provided information about the range, nugget and partial sill (model parameters) which are used to measure the degree of spatial dependency of sampled borehole points as a result of distance between them [14]. It also provides the input parameters that are utilized for the kriging interpolation.

Cross Validation

The prediction errors (mean error (ME), root mean square error (RMSE), mean standardized error (MSE), root mean squared standardized error (RMSSE) and average standard error (ASE))of each of the best fitted variogram models using the lowest RMSE criterion for choice of the best fitted semivariogram model. The best fitted model for each water quality parameter was selected as the best theoretical variogram with their prediction errors for the purpose of the model prediction [15] and presented in Table 7 for dry season and Table 8 for wet season.

Table 7: Best fitted models for water quality parameters and prediction errors for dryseason

Water Parameter (mg/l)	Fitted Semivariogram Model	PREDICTION ERRORS				
		ME	RMSE	MSE	RMSSE	ASE
Fe	Stable	-0.00011	0.0099	-0.2242	1.2377	0.0079
Cd	Exponential	-0.00014	0.0023	-0.0615	0.9985	0.0023
Cr	J-bessel	-0.00006	0.0016	-0.0330	0.9945	0.0016
Cu	Rational Quad.	-0.0082	0.2600	-0.0314	1.1142	0.2289
Pb	Rational Quad.	-0.0007	0.0225	-0.0297	0.9787	0.0231

Table 8: Best fitted models for water quality parameters and prediction errors for wet season

Water Parameter (mg/l)	Fitted Semivariogram Model	Prediction Errors				
		ME	RMSE	MSE	RMSSE	ASE
Fe	Exponential	0.0003	0.0136	0.0122	1.2054	0.0111
Cd	Circular	-0.0001	0.0023	-0.0621	0.9934	0.0023
Cr	Exponential	-0.0001	0.0016	-0.0312	0.9871	0.0016
Cu	Gaussian	-0.0063	0.2551	-0.0238	1.1105	0.2256
Pb	Rational Quad.	-0.0007	0.0224	-0.0308	0.9743	0.0231

The objective of cross-validation is to help make informed decision about which model provides the most accurate predictions. It gives the researcher an idea of how well the model predicts the unknown values inorder to assess prediction performances of the models. Measurement errors could have been due to errors in measurement devices,

ISSN: 2350-0328
International Journal of Advanced Research in Science, Engineering and Technology
Vol. 8, Issue 8 , August 2021

human recording errors, changes in measurement conditions and data integration [14]. The primary use for this tool is to compare the predicted value to the observed value in order to obtain useful information about some of the model parameters. The statistics calculated on the prediction errors serve as diagnostics that indicate whether the model is reasonable for decision making and map production.

To judge if a model provides accurate predictions is verified by:

a. The predictions are unbiased, indicated by a mean prediction error close to 0.
b. The standard errors are accurate, indicated by a root-mean-square standardized prediction error close to 1.
c. The predictions do not deviate much from the measured values, indicated by root-mean-square error and average standard error that are as small as possible.

The ratio between the predicted and the measured values were close to a line with a slope 1:1 and having R^2 close to 1(0.875 – 0.985). The prediction errors were also found to be minimal. The prediction results showed that the mean errors were close to 0, the root mean square error and the average standard error were small and the root mean square-standardized errors were close to 1. The best fitted model parameters and degree of spatial dependency are in Tables 9 and 10 for dry and wet seasons.

Spatial Dependency

The parameters (partial sill, nugget and range) of the best fitted semivariogram were used for the examination of spatial dependency (autocorrelation) between the measured sample points and are presented in Tables 9 and 10 for both seasons respectively. The ratio of the nugget variance to the sill gives the spatial dependence of groundwater quality parameters [16, 17].

Table 9: Model parameters and Degree of spatial dependency for Dry Season

Water para-meter (mg/l)	Fitted model	Range	Nugget (c_n)	Partial sill (σ)	Sill (c) $= c_n + \sigma$	$\left(\frac{c_n}{c}\right)$ %	Degree of Spatial Dependency
Fe	Stable	1533.5	0.00006	0.000013	0.000073	82.19	Weak
Cd	Exponential	24657	0.00	0.000005	0.000005	0.00	Strong
Cr	J-bessel	6418.1	1.7275E-7	0.000002	2.17E-06	7.95	Strong
Cu	Rational Quad.	24657	0.0316	0.0442	0.0758	41.69	Moderate
Pb	Rational Quad.	24657	0.00005	0.0005	0.00055	9.09	Strong

Table 10: Model parameters and Degree of spatial dependency for Wet Season

Water parameter (mg/l)	Fitted model	Range (a)	Nugget (c_n)	Partial sill (σ)	Sill $(c) = c_n + \sigma$	$\left(\frac{c_n}{c}\right)$ %	Degree of Spatial Dependency
Fe	Exponential	5085	0.0002	0.00	0.0002	100.00	Weak
Cd	Circular	24688	0.00	0.000005	5E-06	0.00	Strong
Cr	Exponential	24688	0.00005	0.00049	0.00054	9.259	Strong
Cu	Gaussian	24688	0.06365	0.045628	0.10928	58.25	Moderate
Pb	Rational Quad.	24688	0.00005	0.00049	0.00054	9.26	Strong

The water quality parameters showed relatively moderate degree of spatial dependency which made it possible to represent water quality phenomenon within the study area. Cd, Cr and Pb showed strong spatial dependency, Fe and Cu were of weak spatial dependency in the dry season. In the wet season, Pb was of weak spatial dependency, Cr and Cu showed moderate spatial dependency, while Fe and Cd showed strong spatial dependency.

Spatial Variation Maps

The predicted concentration maps of the studied borehole parameters obtained by using ordinary kriging interpolation method in ArcGIS 10.6 are presented in Figures 10 (a - e) and 11 (a - e) for dry and wet seasons respectively.

ISSN: 2350-0328
International Journal of Advanced Research in Science, Engineering and Technology
Vol. 8, Issue 8 , August 2021

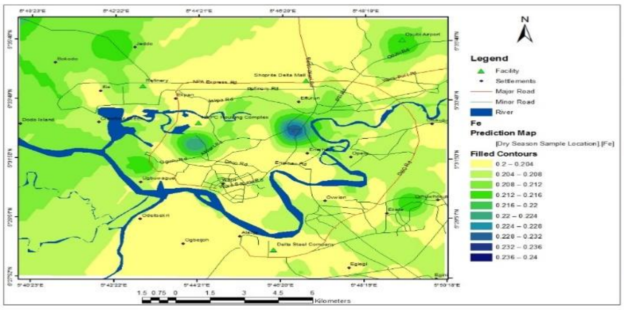


Fig.10c: Fe (DrySeason)

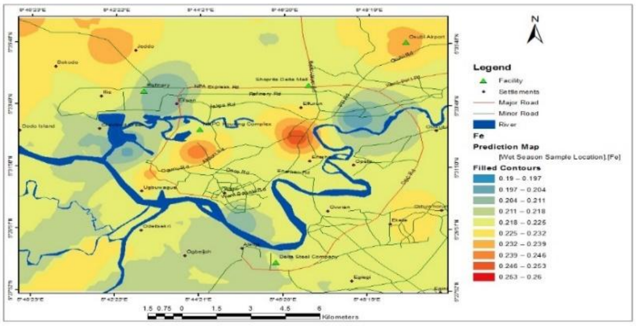


Fig.11c: Fe (Wet Season)

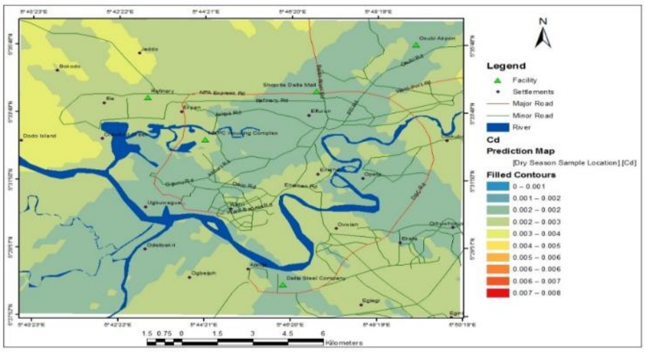


Figure 10d: Cd(DrySeason)

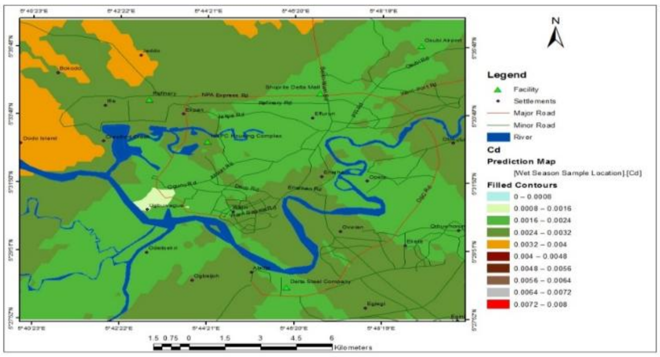


Figure 11d: Cd (Wet Season)

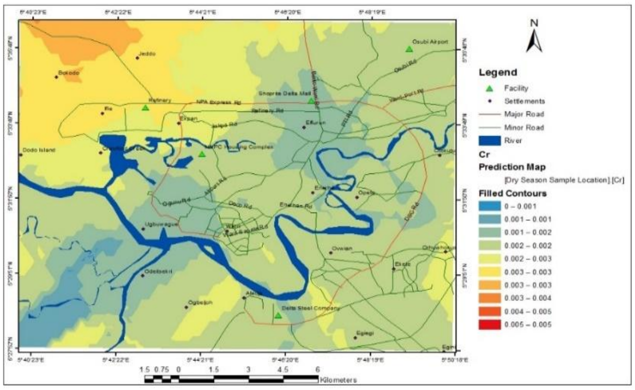


Figure 10e: Cr (DrySeason)

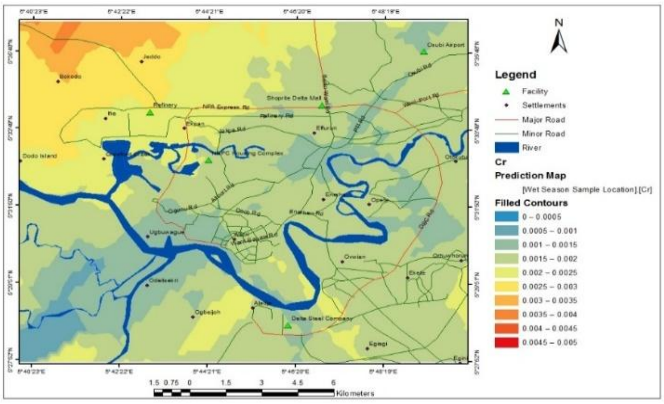


Figure 11e: Cr (Wet Season)

ISSN: 2350-0328
International Journal of Advanced Research in Science, Engineering and Technology

Vol. 8, Issue 8 , August 2021

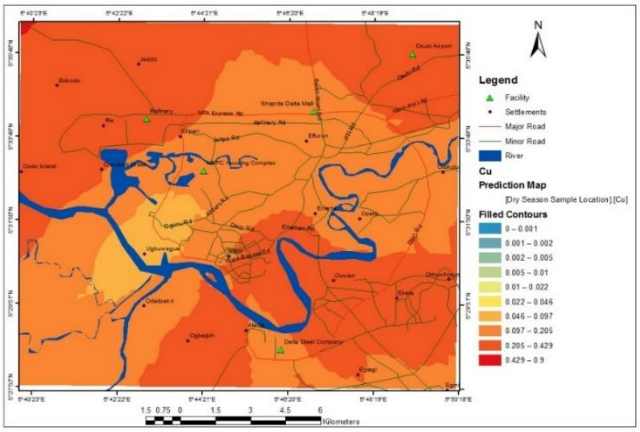


Figure 10f: Cu (DrySeason)

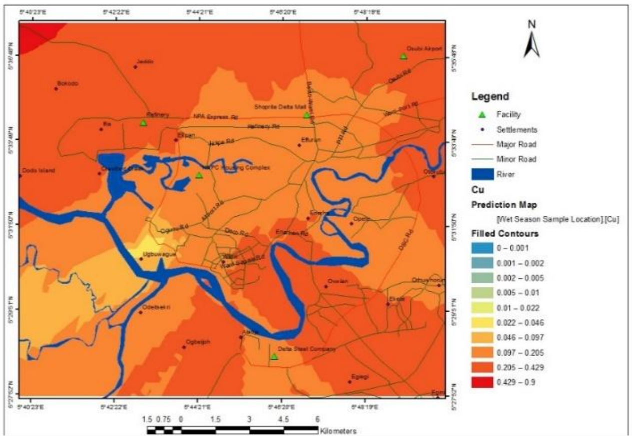


Figure 11f: Cu (Wet Season)

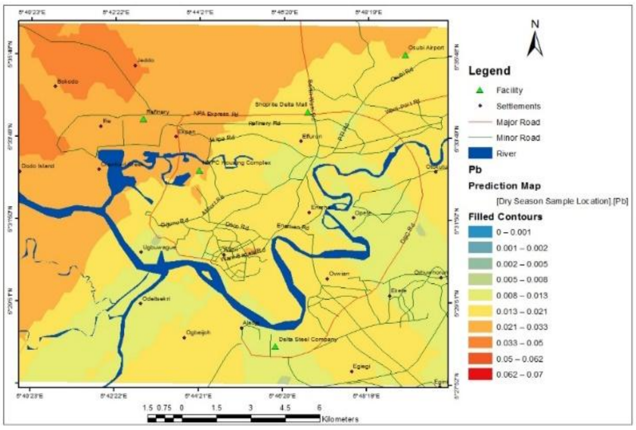


Figure 10g: Pb (DrySeason)

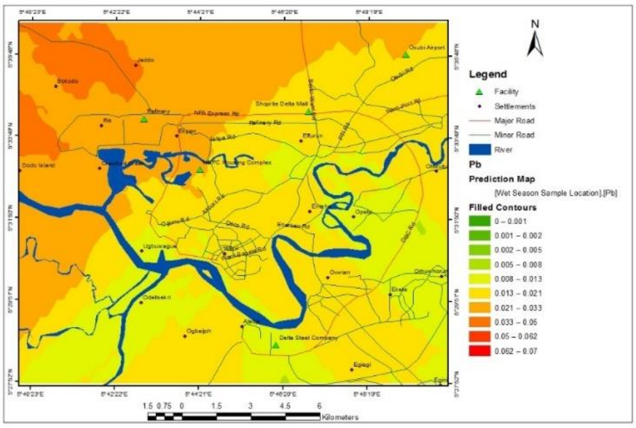


Figure 11g: Pb (Wet Season)

ASSESSMENT OF PREDICTION MAPS

The recommended limit for Iron (Fe) is 0.3mg/l. Spatial variation map of Fe concentration in Figure 10(c) and Figure 11(c) consist of values which are all well below standard limits. It further showed that the concentration distribution is relatively high in many parts of the study area likeUghoton, Ogborode, Warri Port, Warri GRA, Urhobo College Effurun, Ekete, Enerhen, Osubi Road and Orhuwhorun areas while the rest are all of low values following a central distribution pattern. Fe poses a significant health threat as it occurs naturally in soil sediments as well as groundwater and can be found in many types of rocks [18]. In both seasons, the variation for this parameter is significant. The presence of iron in ground water is attributed to the nature of the geological formation, improper waste disposal, industrialization, natural water recharge and water-soil/rock interaction.

Cadmium (Cd) concentrations are all within the recommended limits for both seasons. The Cd values are generally within the permissible limit of 0.003mg/l in its spatial variation map shown in Figure 8(d) and Figure 9(d). Its distribution consists of concentration levels higher than WHO recommended limits for human consumption in both seasons and it is noticeable in DSC Road, DSC Township, Refinery Road, Opete, Warri Port Road, Jeddo and Ogbeijoh routes. The Bokodo and Jeddo areas indicate a sharp increase in Cd levels in the concentrations of 0.007 to 0.008mg/l which is significant. The high Cd levels in these areas could be attributed to effluents containing heavy metals discharged by chemical and petroleum industries in and around those locations.

The Chromium (Cr) values are all within the permissible limit of 0.05 mg/l [19]. The spatial variation shows moderate levels of Cr in the dry season at places around, Airport Road, NNPC Housing Estate, Jakpa Road, Warri Town,

ISSN: 2350-0328
International Journal of Advanced Research in Science, Engineering and Technology
Vol. 8, Issue 8 , August 2021

Ogbeijoh, Aladja, Delta Steel Company, Mofor, Warri Port Road, Osubi Market, Shoprite Delta Mall, Shagholoh and Refinery areas away from the centre in directions north, south west and south east in the study area. This follows similarly for the wet season, that reduced concentrations levels of Cr are located upland north while gradually decreasing in all areas around the study area. Undetectable Cr levels exist in the south western part of the spatial distribution map (Figure 10(e) and Figure 11(e)). Areas with low levels of Cd concentration in the wet season include, Odeitsekri, Ugbuwague, DSC Road, PTI Road, Refinery Road, Osubi Airport, Bokodo and Jeddo areas. Industrial and laboratory effluents around the study area could be a source of Chromium, [20].

Copper (Cu) values do not show significant variation for both seasons. The Cu values are lower than the permissible limit of 2mg/l (WHO, 2011) in all the groundwater sampling locations in dry and wet seasons of the variability map of the study area (Figure 7(f) and Figure 8(f)). Locations with high levels of Cu follow course to include, Ogbeijoh, Delta Steel Company, Egeigi, Egini, Ifie, Refinery, Ekete, Warri Sapele Road, Ovwian, Crawford Creek, Enerhen Road, Otokutu, Osubi Road, Osubi Airport, Dodo Island, Ughoton, Ogborode, Bokodo and Jeddo areas. These values suggest industrial activities within the area which are responsible for the elevated levels of heavy metals in water.

The lead (Pb) values were all below the permissible limit of 0.01mg/l in all the groundwater sampling stations in dry and wet seasons. The spatial distribution of Pb in the study area reveals high levels of Pb in places around Ughoton, Jeddo, Ogborode, Ifie, Edjeba Housing Estate, Refinery, NPA Express Road, NNPC Housing Complex, Ekpan, Jakpa Road areas in the dry season. While in the wet season, increased Pb concentration levels are located around Ogunu Road, Ogbeijoh, Aladja, Egiegi, Enerhen Road, Airport Road, Effurun, PTI Road, Warri Port Road, Otokutu, Refinery Road and Udu Road areas eastwards in the study area. This is depicted in the spatial variational map in Figure 10(g) and Figure 11(g). Pb in groundwater could have resulted from indiscriminate dumping of electronic wastes, oil, batteries and oil exploration and processing activities.

V. CONCLUSION

The concentrations of heavy metals (Fe, Cd, Cr, Cu and Pb) were measured and found to be well below the standard maximum concentrations with concentration values higher in the dry season. This is attributed to the increased amount of groundwater recharge from rainfall, anthropogenic activities resulting from discharge of industrial effluents, effluents from agricultural and domestic wastes, leachates from open dump sites and leakages from septic tanks/soak away pits. Furthermore, leakages from petroleum storage tanks and spills comprise major anthropogenic sources of groundwater contamination. Therefore, the quality of tap drinking water in terms of heavy metals concentration is good in most parts of the study area.

REFERENCES

[1]. N. I.,Dike,A. U., Ezealor andS. J., Oniye (2004). Concentration of Pb, Cu, Fe, and Cd during the dry seasonin river Jakau, Kano Nigeria, Chem Class Journal, 1:78-81.
[2]. H., Musa, I. A., Yakasai,H. H., Musa (2004). Determination of Lead concentration in well and Bore hole water in Zaria, Nigeria. Chem Class Journal 1,14-18.
[3]. Google Maps, (2019). Maplandia.com. Google Maps World Gazetteer. Retrieved from: http://www.maplandia.com/nigeria/delta/warrisouth/ warri/.
[4]. J. E., Agori (2021). Modeling of Spatial and Temporal Distribution of Groundwater Quality Parameters in Warri, Delta State, Nigeria. Unpublished Doctoral Thesis. Federal University of Technology, Owerri.
[5]. O., Izeze and K., Adipere (2018). Statistical and spatial analysis of groundwater quality in Warri anditsenvirons, Delta State, Nigeria. International Journal of Science Inventions Today, 7(3), 401-421.
[6]. I. A., Akpoborie, B., Nfor, A. A. I., Etobro and S., Odagwe (2011). Aspects of the Geology and Groundwater Condition of Asaba Nigeria. Archives of Applied Science Research, 3(2), 537-550.
[7]. C. W., Fetter (1999). Contaminant Hydrogeology. Englewood, New York. Prentice Hall.
[8]. C. S., Nwajide (2006): A guide for Geological Field Trips to Anambra and Related Sedimentary Basins in South Eastern Nigeria. PTDF Fund, University of Nigeria, Nsukka Nigeria. p.68.
[9]. G. T., Amangabara and E., Ejenma (2012). Groundwater Quality Assessment of Yenagoa and Environs Bayelsa State, Nigeria between 2010 and 2011. Researches and Environment, 2(2), 20 - 29.
[10]. O. A., Adejuwon (2012). Rainfall Seasonality in the Niger Delta Belt, Nigeria. Journal of Geography andRegional Planning, 5(2), 51-60.
[11]. APHA, (American Public Health Association) (2012). standard methods of examination of water and wastewater, 22nd Ed. Washington, D.C., American Public Health Association.
[12]. ESRI (2010).ArcGIS Geostatistical Tools for data Exploration, Modeling and Advanced Surface Generation. ESRI White Papers, pp.19.

[13]. K., Marko, S. A. A., Nassir and M. M. E., Amro (2013). Geostatistical analysis using GIS for mapping groundwater quality: Case study in the recharge area of Wadi Usfan, western Saudi Arabia. Arab Journal of Geoscience, 11(1), 1-21.
[14]. G., Bohling (2005). Introduction to Geostatistics and Variogram Analysis. Kansas Geological Survey,Lawrence, 1-20.
[15]. M., Jeihouni,R., Delirhasannia, S. K., Alavipanah, M., Shahabi and S., Samadianfard (2015). Spatial Analysis of groundwater Electrical Conductivity using Ordinary Kriging and Artificial Intelligence Methods (Case Study: Tabriz Plain, Iran). Geofizika 32(5), 191-208.
[16]. R. T., Mehrjardi,M. Z., Jahromi, S., Mahmodi and A., Heidari (2008). Spatial distribution of groundwater quality with geostatistics (case study: yazd-Ardakan plain). World Applied Science Journal 4, 9–17.
[17]. V. G. D., Nayanaka, W. A. U., Vitharana and R. B., Mapa (2010). Geostatistical analysis of soil properties to support spatial sampling in a paddy growing alfisol. Tropical Agricultural Research, 22(1): 34-44.
[18]. WHO (World Health Organization),(2008). Guidelines for drinking water quality, Electronic Resource; Incorporation 1st and 2nd Addenda v. 1 Recommendations; 3rd Edition, Geneva, 515.
[19]. WHO (2011). Guidelines for drinking-water quality; 4th Edn., Geneva, World Health Organization.
[20]. Ndiokwere, C. L. (2004). Chemistry and Environment, Inaugural Lecture Series 73, University of Benin, UNIBEN Press, Pp. 33-37.