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Multivariate and Pollution Assessment of Enugu Industrial Layout, Southeastern Nigeria

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ABSTRACT
This research assesses the heavy metals pollution in the soil and water qualities in Emene and its environs, which is well known for its large industrial activities in South-Eastern Nigeria, using multivariate and pollution load assessment techniques. The sampling was conducted in both water and soils. Sixteen water samples were fetched from an industrial effluent (IEF), surface and groundwater (SW and HDW) and control samples (CTR). At different five industrial sites, a collection of soil samples were made, while two samples which serves as a control were collected far away from the industrial site.. The extent of the sediment pollution was assessed; using pollution load index (PLI). A positive correlation was observed with Fe, As, Pb, Cr, Cu, Zn and Ni. The extracted results of the correlation matrix suggest that the dominant ions in the water (As and Fe, Pb and Fe, Cr and Fe, Cu and Fe, Pb and As, Cr and As, Cu and As, Cr and Pb, Cd and Zn, Ni and Zn, Cu and Cr) were derived from the same source of enrichment. In addition to this, a cluster analysis depicts a set of three clusters from a 13 sampling locations based on the similarities of water quality features. The pollution load index (PLI), showed that all locations have PLI > 1 and were polluted. The index values of the heavy metals for Igeo values shows a range which indicates that the industrial soils are unpolluted with Cu and Ni, in the degree of unpolluted to moderately polluted, it has Cr, Fe and Zn while unpolluted to highly polluted has; Pb and Mn. As and Cd shows a level from unpolluted to very highly polluted.. Based on the average Igeo values of the heavy metals, the industrial soils of the study area are unpolluted with Cr, Cu, Ni, Fe, Pb and Zn; and highly polluted with As, Fe and Cd. The data also indicate that the degree of enrichment of each of the heavy metal reflects its pollution intensity
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INTRODUCTION

It has been established that an exposure to these heavy metals; Lead, Cadmium, Mercury and arsenic has the greatest threat to human health (Suciu et al. 2008; Holmes et al. 2009). It is important of note that organic pollutant can be degraded to harmless molecules whereas metallic pollutants are difficult to remediate from soil, water and air. Lead, Mercury, Cadmium, Copper and Zinc which shows a great level of toxicity are immutable by biochemical reactions (de Vries et al. 2007). (Verma et. al. 2016) shows that Lead and Copper are some of the heavy metals which are regarded as hazardous pollutants of the environment.

Heavy metal and multivariate analyses for the analyzed water and soil samples in the study area were

employed to unravel the degree of contamination and the relationship between parameters and their possible sources of occurrence (Onwuka and Ezugwu 2019). Some reported works established the fact that there is heavy metal pollution in Enugu metropolis (Ogbuagu and Ajiwe, 1998). These industries which are mainly at Emene produce large quantities of liquid wastes. These industries pollution potential can be related directly to the efficiency at which metal can as well be reclaimed from these waste and recycled.. This study aims to assess the physicochemical and heavy metal concentrations in water, soil then escalating the risk potential of physicochemical and heavy metals Via contaminated site which has a long term exposure in Emene and its environs. Multivariate analysis has been employed severally by many researchers Donlagic et al ,2007, Onwuka et al 2004, Ezugwu et al 2019 and Egbueri et al,2020),consistent in their findings they stated that uncontrolled industrial pollution has a major impact on groundwater contamination; their research highlighted that soil and groundwater is high in heavy metal contamination.

LOCATION OF THE STUDY AREA

The area of study lies within latitudes 6°22'N and 6°38'N and longitudes 7°28'E and 7°37'E. The Enugu metropolis comprises of three local government areas, these are; Enugu North, Enugu South and Enugu East (Figure 1). It has a population of 3,590,513 based on 2006 census (Fed. Gov.Gazette, 2007) with an estimated land area of about 372.82/km^2. In the time past, coal mining activity has been the major economic drive of the city, which is the hub of civil servant, traders, artisans and farming activity.

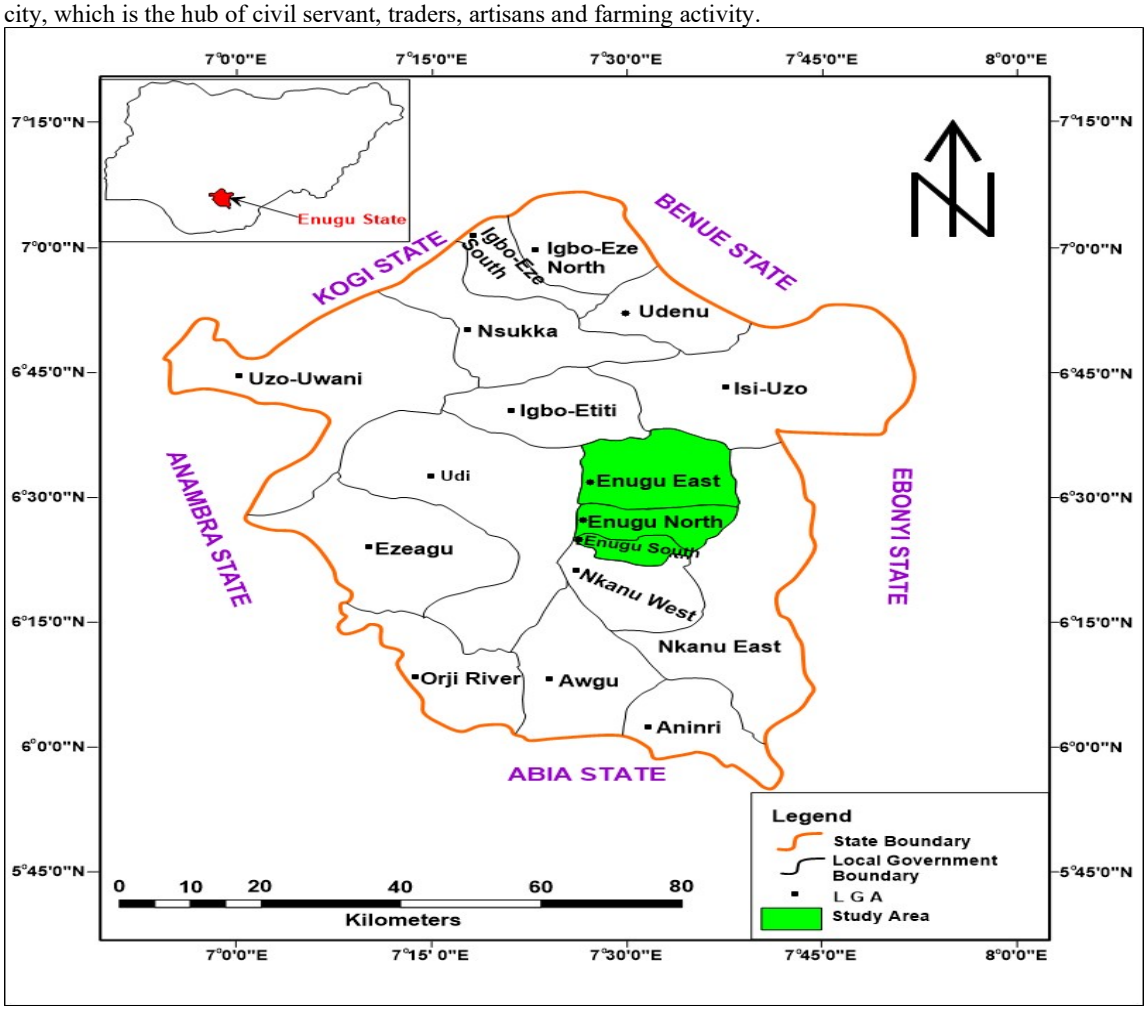

Figure 1: Map of Enugu State showing the study area.

DRAINAGE AND GEOLOGY OF THE STUDY AREA

There are two major river systems within the study area. . The two River systems are; the Ekulu, Nyaba River system which originated close to the base of the escarpment and flows down East into the cross river basin, whereas the second river system consists of the Asata, Mkpume-Olu and Otuku Rivers. The later originates from the dip slope and flows into Anambra basin via West. This buttress the fact that Udi plateau constitutes a

watershed which separates the two river systems that drains the coal field. During the rain, this river hardly fills its channel and discharge decreases significantly as soon as the rain ends. The flow is shallow but rapid. Sharp bends are observed along the river course. The bend nearer the ridge shows a sharp lateral juxtaposition of fine sandstones against dark grey shales.

The study area and environs lie predominantly on Enugu Shale, which is light to dark grey, greatly fractured, and contains bands of clay Ironstone. At some depths, Enugu Shale is weathered to a dirty brown lateritic regolith which is porous and varies in thickness up to a maximum of 20m, depending on the topography of the area (Fig.2).

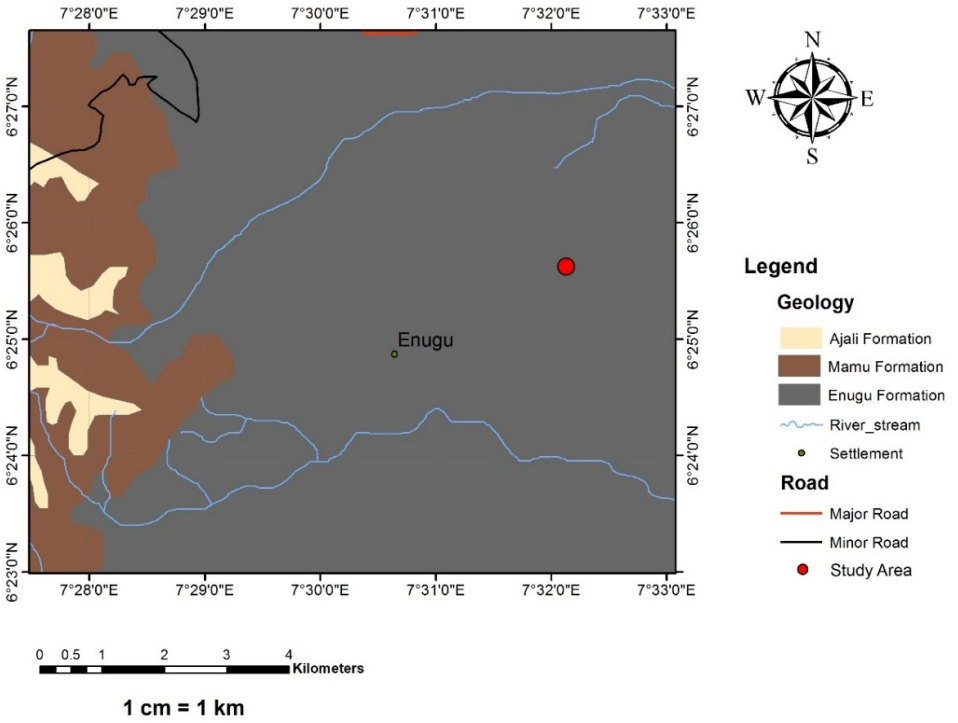

Fig.2 Geologic Map of the Study Area and Environs

METHODOLOGY

For the present study, groundwater and soil samples were taken from each of the following industries:
Area 1. Plastic
Area 2. Soap
Area 3. Asbestos
Area 4. Pharmaceutical
Area 5. Palm Cannel
Control samples were taken from hand dug wells and soils located away from these industrial areas.

SOIL SAMPLING

A total of seven soil samples were collected from the study area during May 2018.Where five soil samples were collected from Enugu State Industrial Layout while two samples were collected from control sites. At every sampling point, a random selection of soil samples are made, from the surface (0–15cm soil layer) using a small hand trowel. The soil samples collected from the factory outlet were found to be wet and in slurry condition. The samples collected from these mentioned five industries above were kept in a clean polyethylene bags and well labelled before taking to the laboratory for analysis. 1kg powdered form of the samples was collected after subjecting them to a room temperature.

WATER SAMPLING

A total of sixteen water samples were collected from the study area during May 2018.Where five water samples were collected from Enugu State Industrial Layout; eight samples from surface and groundwater and three samples from control sites. A polyethylene bottles which was soaked overnight in 15% nitric acid were used to collect the water samples. The bottles were now washed with deionized water and exposed at room temperature

for drying. . The containing bottles were washed and rinsed severally from the water source before the sample collection. A sample of water is taken after a pumping period of 10 mins has elapsed. . In order to protect the quality of the sample and avoid unusual changes, the samples where brought in the laboratory in an icebox and stored in the refrigerator at (4ºC) before analysis. . The collection, preparation and preservation of samples all followed the report and procedures of earlier studies and in standard as listed by American Public Health Association (APHA, 1995)

SAMPLE ANALYSIS

Samples were subjected to physicochemical analysis at Simuchi Analytical Laboratory, Nsukka, Enugu state, Nigeria.

Water Analysis

The analysis of the water samples for various physiochemical parameters were carried out in line with the standards and recommendation by APHA (1998). At the point of sampling, some basic parameters of the groundwater like Temperature (ºC), Turbidity, pH, and Electrical conductivity (EC) were all determined using the digital portable water analyzer kits whereas other parameters were determined in the laboratory via analysis. Some variables like the total alkalinity and calcium hardness were determined based on complexometric EDTA titration methods which involve Eriochrome black T. (EBT) and murexide (ammonium purpurate) indicator respectively. The Magnesium concentration was calculated using the total alkalinity and calcium hardness.

In using the phenolphthalein and methyl orange as an indicator, the Bicarbonate concentrations were estimated through titrimetric method. The total dissolved solid (TDS) were measured after subjecting the filtered sample in a hot oven at 180+/- 2oC and allowing it to evaporate. . At the evaporation of the whole sample, the evaporation dish were allowed to cool before determining the final weight and this was computed with its initial weight. . The estimation of heavy metals which includes Manganese, Lead, iron, Nickel, Chromium, Cadmium, Arsenic, and Zinc were carried out using Flame Atomic Absorption Spectrometer, (FAAS-210VGP). The estimation of the major cations (Na^+ and K^+) was done by Single channel emission, Flame Photometer (JENWAY -PFP7).

In using UV-Visible spectrophotometer type (JASCO V-530) via colorimetric method, the Nitrate (NO_3^-), sulphate (SO_4^{2-}) and phosphate (PO_4^-) were determined. The chloride ions analysis were done using ion selective electrodes (Jenway -304 chloride and Jenway 924-305 fluoride) respectively. In this study, it involved the precision of results which was evaluated by the relative standard deviation of the results of the triplicate measurements, which each sample were used for the analysis of different parameter of ground water samples.

Pollution Load Index (PLI) of heavy metals in soils

Pollution Load Index (PLI) was developed by Tamlinson et al., (1980) to measure the degree of soil pollution for each metal in a single site. Pollution Load Index provides simple but comparative means for assessing a site quality. Pollution Load Index is calculated using Tamlinson et al., (1980) which is given as

$$PLI = [(CF1) \times (CF2) \times (CF3) \ldots\ldots\ldots (CFn)]^{1/n} \quad (1)$$

Where n is the number of selected metals for the assessment of PLI and CF is the contamination factor defined by $CF = C_{metal} / C_{background / control}$; C_{metal} is the concentration of pollutant in the soil or sediments and $C_{background / control}$ is the background value for the metal.

PLI < 1, denotes perfection;

PLI = 1, denotes that only baseline levels of pollutants are present, and

PLI > 1, indicates deterioration in quality of the environment / site.

In order words, the PLI for a single site is the nth root of n number multiplying the contamination factor (CF values) together. The CF is the quotient obtained as

$$CF = C_{metal\ concentration} / C_{control\ point\ concentration\ of\ the\ same\ metal} \quad (2)$$

$$And;\ PLI = nth\ \sqrt{CF1 \times CF2 \times CF3 \times CFn} \quad (3)$$

Where n is the number of metals studied and CF is contamination factor.

Contamination Factor (CF)

Contamination factor (CF) was developed by Hakanson (1980). It is used to evaluate the level or degree of deterioration or otherwise in the quality of environmental media such as soils or sediments. The contamination factor of a particular metal in an environment is the ratio of the concentration of such as metal in the sample to the concentration of the metal in the control or background sample. Therefore, contamination factor values indicate the individual impact of each metal on the sample. Table 1 shows the degree of contamination that could be assumed by metals in an environmental media.

$$CF = C_{metal} / C_{background / control} \quad (4)$$

C_{metal} is the concentration of pollutant in the soil or sediments and $C_{background / control}$ is the background value for

the metal.

Table 1. Classification of contamination factor indices (Tomlinson et al., 1980)

Contamination Factor (CF) Indices	**Degree of Contamination**
CF < 1.0	Low contamination
1 ≥CF ≤3	Moderate contamination
3 ≥CF ≤ 6	Considerable contamination
CF > 6	High contamination

Geo-accumulation index

Geo-accumulation index was introduced by Muller (1969) (Table 2) and it has been widely used since the late 1960's for assessment and quantification of heavy metals in pollution studies. Geo-accumulation assessment is by comparing the level of heavy metals obtained at a site to the background level in the environment. Although it was originally used for bottom sediments contamination assessment, but has recently gained general acceptability for soil contamination studies (Lu et al., 2009; Srinivasa et al., 2010). Index of geo-accumulation (Igeo) is expressed as follows:

$$Igeo = Log_2[Cn] / 1.5Bn \quad 5$$

Where: Cn is the concentration of the metal in the sample, Bn is the geochemistry background / control value of the metals and 1.5 is introduced to minimize the effect of possible variations in the background value which may be attributed to natural/lithological variations in the soil sediments. According to Huu et al., (2010), seven contamination classes are used to define the degree of metal pollutants in soils based on the increasing value of the index of geo-accumulation as follows:

Table 2. Geo-accumulation indices classes of heavy metals (Muller, 1969)

Igeo Index Value	**Pollution Intensity**
< 0	Practically unpolluted
0 – 1	Unpolluted to moderately polluted
1 – 2	Moderately polluted
2 – 3	Moderately to highly polluted
3 – 4	Highly polluted
4 – 5	Highly to very highly polluted
>5	Very highly polluted

RESULTS AND DISCUSSION

WATER SAMPLES

This study shows that the metal concentrations on water samples also depict a powerful geochemical tool for monitoring the impact of anthropogenic activity. The geochemical data analysis for the analyzed water samples are presented in the tables below:

Physico-chemical Parameters

Table 3: Physico-chemical parameters of analyzed water

Industrial Effluent Samples										
Parameters	pH	Total alkalinity	Color	EC **µs/cm**	TDS	DO	BOD	COD	TOC	TSS
Plastic (IEF 1)	7.4	53	96.9	87	114	140.8	25.6	140.8	0.34	0.2
Soap (IEF 2)	6.5	65	138.1	116	14	195.2	36	195.2	2.24	0.2
Asbestos (IEF 3)	8.3	77	52.2	292	1674	145.6	8.8	145.6	0.33	0.2
Pharmaceutical (IEF 4)	7.1	147	122.6	114	1299	212.8	23.2	212.8	1.20	0.2
Palm Cannel (IEF 5)	7.3	13	137.1	666	276	165.6	19.2	165.6	0.51	-
Surface and Groundwater Samples										
Ekulu River (SW 1)	6.4	100	44	104	43	91.2	27.2	91.2	0.03	-
Otuku River (SW 2)	6.7	80	29	105	19	89.6	24.8	89.6	0.06	0.2
Mkpume Olu (SW 3)	5.4	40	89	47	21	70.4	33.6	70.4	0.27	0.2
HDW 1	6.6	60	194	49	20	96.8	5.6	96.8	0.03	0.2
HDW 2	5.9	40	45	641	153	961	8.0	96	0.04	-
HDW 3	6.2	80	86	96	43	56.8	42.4	56.8	0.13	-
HDW 4	5.5	60	47	94	37	50.4	11.2	50.4	0.06	-
HDW 5	5.9	40	107	320	60	71.2	28.8	71.2	0.14	-
Control Water Samples										
CTR 1	7.5	120	41	89	45	103.2	4.8	103.2	0.12	0.2
CTR 2	7.1	80	20	112	20	110.4	35.2	110.4	0.04	-
CTR 3	6.4	60	82	95	136	58.4	44	58.4	0.24	-
Regulatory Bodies										
WHO 2008	6.5 – 8.5	400		1000	500	6.4				
NWQS 2007	6.5 – 8.5	100		1250	500	4	30	80		25

Table 4: Major and minor ions of analyzed water

Industrial Effluent Samples									
Parameters	Ca^{2+}	Mg^{2+}	Na^{+}	K^{+}	Cl^{-}	HCO_3	SO_4^{2-}	NO_3	PO_4
Plastic (IEF 1)	8.0	25.13	152.5	8.06	284	0.11	53	1.18	3.47
Soap (IEF 2)	9.5	72.51	440	22.5	731.3	0.13	147	1.49	17.6
Asbestos (IEF 3)	6.9	26.9	254	19.13	177.6	0.28	77	0.59	2.13
Pharmaceutical (IEF 4)	7.0	41.2	250	11.51	451.5	0.28	65	1.31	9.45
Palm Cannel (IEF 5)	8.7	59.33	360	16.77	646.1	0.28	13	1.32	9.64
Surface and Groundwater Samples									
Ekulu River (SW 1)	0.96	6.18	35	0.25	71	0.22	30	0.028	2.40
Otuku River (SW 2)	0.86	2.47	15.0	0.78	35.5	0.23	20	0.076	3.41
Mkpume Olu (SW 3)	0.79	2.06	10.6	0.30	33.5	0.01	10.5	0.080	1.48
HDW 1	0.79	2.88	17.5	0.05	35.5	0.01	10.3	0.084	0.83
HDW 2	0.63	2.47	10.3	9.05	106.5	0.07	10.5	0.066	1.20
HDW 3	1.82	5.36	27.5	0.13	71	0.01	10.4	0.074	0.55
HDW 4	0.83	1.24	7.5	1.02	35.5	0.01	20	0.065	0.46
HDW 5	67.5	2.06	12.5	0.82	35.5	0.14	20	0.068	0.46
Control Water Samples									
CTR 1	50	9.06	0.76	0.33	71	0.12	20	0.02	0.83
CTR 2	27.5	4.94	1.01	2.74	71	0.02	10.6	0.017	1.11
CTR 3	1.05	10.71	0.63	6.15	213	0.03	40	0.063	1.29
Regulatory Bodies									
WHO 2008	75	150	200	55	200	150	200	10	-
NWQS 2007	75	100	200	-	250		100	50	0.2

SOIL SAMPLES

The present study shows that the metal concentrations of top soil can be used as a powerful geochemical tool for monitoring the impact of anthropogenic activity. The physiological properties like Ca, Na, Mg, K, SO_4 and PO_4 of soil sample were done and the results are tabulated in Table 5.

Table 5: Major, minor and heavy metal content of the analyzed soil samples

Industrial Soil Samples												
Parameters	Ca^{2+}	Mg^{2+}	Na^{+}	K^{+}	SO_4^{2-}	PO_4^{2-}	Fe^{3+}	Zn	Cu	As	Ni	Pb
Plastic (SS 1)	87	7.21	0.23	2.76	0.233	4.34	3.61	0.290	4.96	1.378	0.197	0.072
Soap (SS 2)	70	7.42	0.79	2.28	0.297	22.14	1.451	0.382	3.216	0.294	0.163	0.077
Asbestos (SS 3)	202	14.6	0.58	6.1	1.838	99.45	1.234	0.936	2.626	0.374	0.376	0.012
Pharmaceutical (SS4)	225	16.07	0.80	3.11	0.809	32.19	3.78	0.536	5.919	0.981	0.186	0.037
Palm Cannel (SS 5)	105	7.83	0.88	2.86	0.492	32.84	1.852	0.400	4.077	0.273	0.284	0.087
Control Soil Samples												
CTR 1	82	14.32	0.22	4.84	0.624	19.91	0.71	0.044	1.65	0.090	0.007	0.008
CTR 2	89	6.99	0.06	1.91	0.418	7.57	1.44	0.032	0.79	0.088	0.091	0.006

Note: All parameters measured in mg/L

POLLUTION ASSESSMENT

POLLUTION LOAD INDEX

Pollution index greater than 1.0 (PLI > 1.0) shows that average metal concentrations are above the permissible level; PLI < 1.0 indicated average level of metals are below standards but does not necessarily mean that there is no anthropogenic source or other enrichments above background concentrations (Srinivasa et al., 2010). The pollution load index (PLI), showed that all locations have PLI > 1 and were polluted (Table 6).

Table 6. Pollution load index of sample areas

Sites ID	PLI	Sites ID	PLI	Sites ID	PLI	Sites ID	PLI	Sites ID	PLI
SS 1	1.27	SS 2	1.07	SS 3	1.16	SS 4	**0.32**	SS 5	1.10
SS 6	**0.67**	SS 7	1.79						

CONTAMINATION FACTOR (CF)

From the CF (Table 7), Pb has the highest average CF values of (67.80) from all locations, followed by Fe (56.45), Zn (50.28), As (33.72), Cu (32.68) and Ni (24.84). Nickel has the least CF value of 24.84. Iron (Fe) has moderate contamination in nine locations and considerable contamination in two other locations. Copper has considerable contaminations in industrial soils. Zinc has low contamination at control samples, moderate contamination at Asbestos (SS 3), Pharmaceutical (SS 4) and Palme Kernel (SS 5) industrial sites and considerable contamination at Plastic (SS 1) and Soap (SS 2).Lead CF ranged from 6.4 to 18.8. All locations recorded very high contamination. The CF values of Ni indicate that Pharmaceutical (SS 4) and Asbestos (SS 3) were moderately contaminated, Palme Kernel (SS 5) soils considerably contaminated while Plastic (SS 1) and Soap (SS 2) have very high contaminations. Lead has the highest CF value in the study, followed by Fe in most of the areas, Zn, As and Ni while Cu was the least (Table 7). The most contaminated locations were Plastic, Soap, Asbestos, Pharmaceutical, Palme Kernel and control samples in decreasing order. Heavy metal CF rank was: Pb > Fe>Zn > As >Ni>Cu.

Table 7. Contamination factors of the heavy metals in the soil samples

Heavy metals	**Sample Sites**							**Average CF value**	**Degree of contamination**
	SS 1	**SS 2**	**SS 3**	**SS 4**	**SS 5**	**CTR 1**	**CTR 2**		
Ni	1.48	2.77	1.33	0.71	1.00	1.15	0.32	1.25	Moderate
Zn	5.41	8.86	15.10	3.98	0.87	2.23	0.12	5.22	High
As	6.92	7.79	1.23	0.57	0.42	1.02	0.31	2.61	Moderate
Pb	11.75	7.98	4.61	4.01	7.98	9.86	2.63	6.97	High
Cu	1.23	2.07	0.63	0.40	0.71	0.85	1.26	1.02	Moderate
Fe	5.98	8.25	11.40	7.25	10.16	1.64	1.39	6.58	High

Geo-accumulation index

The ranges of Igeo index values of the heavy metals indicate that the industrial soils are unpolluted with Cu and Ni, unpolluted to moderately polluted with Cr, Fe and Zn, unpolluted to highly polluted with Pb and Mn, unpolluted to very highly polluted with As and Cd. Based on the average Igeo values of the heavy metals, the industrial soils of the study area are unpolluted with Cr, Cu, Ni, Fe, Pb and Zn; and highly polluted with As, Fe and Cd. The data also indicate that the degree of enrichment of each of the heavy metal reflects its pollution intensity. The geogenic factors of Fe (83.72%) in the soils indicate that Fe mainly derived from the underlying rocks of the Enugu Shale and that it is highly polluted in the soils. As and Cd which were enriched through anthropogenic means also indicated high pollution intensity. The continuous discharge of untreated industrial

effluents may be the source of enrichment and accumulation and the subsequent high pollution status in the industrial soils of the study area. The rest of the elements show no pollution at the various sites. This might be due to the little or absence of anthropogenic activity and horizontal spread of metal pollutants in these areas. On the average, the pollution intensity of the heavy metals in the industrial soils from the study area is in the order Fe>As>Cu> Ni > Pb> Zn (Fig 8).

Table 8. Geo-accumulation index of the heavy metals

Heavy metals	Range of Igeo index values		Average Igeo values	Pollution intensities
	Min.	Max.		
Fe	0.00	10.91	4.25	Highly polluted
As	0.00	8.23	3.52	Highly polluted
Cu	-4.24	-0.65	-1.58	Practically unpolluted
Ni	-4.77	-0.97	-1.52	Practically unpolluted
Pb	-7.25	3.67	-0.36	Practically unpolluted
Zn	-2.97	0.62	-0.01	Practically unpolluted

STATISTICAL INTERPRETATION

Correlation Matrix in the Water Samples

Considerable high correlation was found between EC and pH (R = 0.78), DO and Turbidity (0.60), TOC and TDS (R = 0.66), TOC and Turbidity (R= 0.61), DO and Turbidity (R= 0.60), TSS and Turbidity (R = 0.70). Other parameters also showed fair to negative correlation as summarized in (Table 9). Positive high correlation was observed between $NO_3^-$and Na^+ (R = 0.65), K^+ and Mg^{2+} (0.97), SO_4^{2-} and Mg^{2+} (R = 0.74), SO_4^{2-} and K^+ (R= 0.75), PO_4^- and NO_3^- (R= 0.84). Whereas other parameters also indicated fair to negative correlation as summarized in (Table 9). Considerable high correlation was found between As and Fe (R = 0.73),Pb and Fe (0.72), Cr and Fe (R = 0.83), Cu and Fe (R= 0.67), Pb and As (R= 0.87), Cr and As (R = 0.55), Cu and As (R = 0.87), Cr and Pb (R = 0.75), Cd and Zn (R = 0.96), Ni and Zn (R = 0.97), Cu and Cr (R = 0.69). Other elements also showed fair to negative correlation as summarized in (Table 9, 10 and 11).

Table 9. Correlation matrix of physical parameters of the water samples from the study area

PARAMETERS	pH	EC	TDS	DO	COD	BOD	Turbidity	TOC	TSS
pH	1.00								
EC	0.78	1.00							
TDS	-0.55	-0.12	1.00						
DO	-0.50	-0.78	0.30	1.00					
COD	-0.02	0.13	0.01	-0.02	1.00				
BOD	-0.18	-0.61	-0.44	0.43	0.12	1.00			
Turbidity	-0.71	-0.76	0.16	0.60	-0.14	0.08	1.00		
TOC	-0.64	-0.23	0.66	0.22	-0.21	-0.51	0.61	1.00	
TSS	-0.18	-0.45	-0.48	0.36	0.11	0.32	0.70	0.15	1.00

Table 10. Correlation matrix of chemical parameters of the water samples from the study area

	Ca^{2+}	Na^+	Mg^{2+}	K^+	Cl^-	HCO_3^-	SO_4^{2-}	NO_3^-	PO_4^-
Ca^{2+}	1.00								
Na^+	-0.20	1.00							
Mg^{2+}	-0.10	0.23	1.00						
K^+	-0.04	-0.01	0.97	1.00					
Cl^-	-0.64	0.21	0.16	0.07	1.00				
HCO_3^-	-0.42	0.28	0.37	0.26	0.47	1.00			
SO_4^{2-}	-0.29	0.13	0.74	0.75	0.47	0.17	1.00		
NO_3^-	-0.07	0.65	0.39	0.24	-0.30	0.12	-0.13	1.00	
PO_4^-	0.20	0.22	0.34	0.29	-0.44	-0.13	-0.27	0.84	1.00

Table 11. Correlation matrix of heavy metals of the water samples from the study area

	Fe	Mn	As	Pb	Zn	Cd	Cr	Ni	Cu
Fe	1.00								
Mn	-0.03	1.00							
As	0.73	0.00	1.00						
Pb	0.72	0.02	0.87	1.00					
Zn	0.48	-0.21	0.32	0.09	1.00				
Cd	0.36	-0.22	0.09	-0.15	0.96	1.00			
Cr	0.83	-0.06	0.55	0.75	-0.05	-0.15	1.00		
Ni	0.44	-0.24	0.16	-0.08	0.97	1.00	-0.06	1.00	
Cu	0.67	0.05	0.87	1.00	0.11	-0.15	0.69	-0.08	1.00

Hierarchical Cluster Analysis (HCA)

- Hierarchical cluster analysis (HCA) was classified the thirteen sampling stations into three statistically significant clusters at (Dlink/Dmax) ∗ 25 < 5 in which resulted a dendrogram (Figure 3).
- HCA categorized thirteen samples into three distinctive clusters which were described based on pollution magnitude as slightly polluted and polluted.
- Stations HDW 5, SW 2, HWD 1, HDW 4 and HDW 3 formed clusters 1 indicating slightly polluted.
- While cluster 2 comprised stations SW 3, IEF 1, SW 1, IEF 2 and HDW 2, as well as stations IEF 3, IEF 5 and IEF 4 formed cluster 3 revealing polluted.

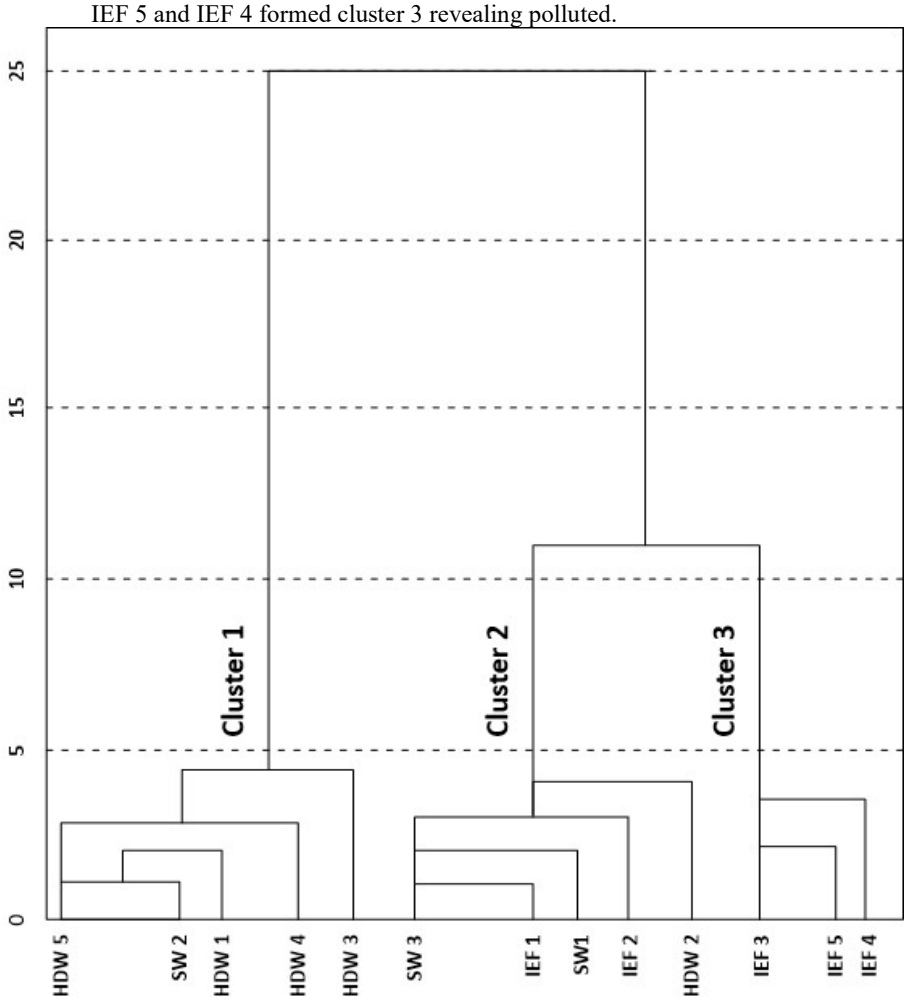

Figure 3: Dendrogram of cluster analysis of the water quality data.

ASSESSMENT OF SOIL CONTAMINATION

Heavy metal contamination in the surface environment is associated with more than one metal. In most cases pollution index of soils is used to identify multi element contamination resulting in increased overall metal toxicity (Jung, 2001). Generally, PLI can be computed by averaging the ratios of metal concentration in sampled soils to the assumed permissible level of metals. Out of the 7 sites visited in the study area, 5 representing 71.43% are progressively deteriorating in varying degrees, 2 representing 28.57% ranged from been perfect to having only baseline levels of pollutant (Table 12). Pollution index greater than 1.0 (PLI > 1.0) shows that average metal concentrations are above the permissible level; PLI < 1.0 indicated average level of metals are below standards but does not necessarily mean that there is no anthropogenic source or other enrichments above background concentrations (Srinivasa et al., 2010). The pollution load index (PLI), showed that all locations have PLI > 1 and were polluted.

Table 12. Pollution load index of sample areas

Sites ID	PLI	Sites ID	PLI	Sites ID	PLI	Sites ID	PLI	Sites ID	PLI
SS 1	1.27	SS 2	1.07	SS 3	1.16	SS 4	**0.32**	SS 5	1.10
SS 6	**0.67**	SS 7	1.79						

From the CF (Table 13), Pb has the highest average CF values of (67.80) from all locations, followed by Fe (56.45), Zn (50.28), As (33.72), Cu (32.68) and Ni (24.84). Nickel has the least CF value of 24.84. Iron (Fe) has moderate contamination in nine locations and considerable contamination in two other locations. Copper has considerable contaminations in industrial soils. Zinc has low contamination at control samples, moderate contamination at Asbestos (SS 3), Pharmaceutical (SS 4) and Palme Kernel (SS 5) industrial sites and considerable contamination at Plastic (SS 1) and Soap (SS 2).Lead CF ranged from 6.4 to 18.8. All locations recorded very high contamination. The CF values of Ni indicate that Pharmaceutical (SS 4) and Asbestos (SS 3) were moderately contaminated, Palme Kernel (SS 5) soils considerably contaminated while Plastic (SS 1) and Soap (SS 2) have very high contaminations. Lead has the highest CF value in the study, followed by Fe in most of the areas, Zn, As and Ni while Cu was the least (Table 13). The most contaminated locations were Plastic, Soap, Asbestos, Pharmaceutical, Palme Kernel and control samples in decreasing order. Heavy metal CF rank was: Pb > Fe>Zn > As >Ni>Cu.

Table 13. Contamination factors of the heavy metals in the soil samples

Heavy metals	**Sample Sites**							**Average CF value**	**Degree of contamination**
	SS 1	**SS 2**	**SS 3**	**SS 4**	**SS 5**	**CTR 1**	**CTR 2**		
Ni	1.48	2.77	1.33	0.71	1.00	1.15	0.32	1.25	Moderate
Zn	5.41	8.86	15.10	3.98	0.87	2.23	0.12	5.22	High
As	6.92	7.79	1.23	0.57	0.42	1.02	0.31	2.61	Moderate
Pb	11.75	7.98	4.61	4.01	7.98	9.86	2.63	6.97	High
Cu	1.23	2.07	0.63	0.40	0.71	0.85	1.26	1.02	Moderate
Fe	5.98	8.25	11.40	7.25	10.16	1.64	1.39	6.58	High

Soil quality of the study area was measured using the *I*geo index of classification proposed by Muller (1981) (Table 14). The ranges of Igeo index values of the heavy metals indicate that the industrial soils are unpolluted with Cu and Ni, unpolluted to moderately polluted with Cr, Fe and Zn, unpolluted to highly polluted with Pb and Mn, unpolluted to very highly polluted with As and Cd. Based on the average Igeo values of the heavy metals, the industrial soils of the study area are unpolluted with Cr, Cu, Ni, Fe, Pb and Zn; and highly polluted with As, Fe and Cd. The data also indicate that the degree of enrichment of each of the heavy metal reflects its pollution intensity. The geogenic factors of Fe (83.72%) in the soils indicate that Fe mainly derived from the underlying rocks of the Enugu Shale and that it is highly polluted in the soils. As and Cd which were enriched through anthropogenic means also indicated high pollution intensity. The continuous discharge of untreated industrial effluents may be the source of enrichment and accumulation and the subsequent high pollution status in the industrial soils of the study area. The rest of the elements show no pollution at the various sites. This might be due to the little or absence of anthropogenic activity and horizontal spread of metal pollutants in these areas. On the average, the pollution intensity of the heavy metals in the industrial soils from the study area is in the order Fe>As>Cu> Ni > Pb> Zn.

Table 14. Geo-accumulation index of the heavy metals

Heavy metals	Range of Igeo index values		Average Igeo values	Pollution intensities
	Min.	Max.		
Fe	0.00	10.91	4.25	Highly polluted
As	0.00	8.23	3.52	Highly polluted
Cu	-4.24	-0.65	-1.58	Practically unpolluted
Ni	-4.77	-0.97	-1.52	Practically unpolluted
Pb	-7.25	3.67	-0.36	Practically unpolluted
Zn	-2.97	0.62	-0.01	Practically unpolluted

CONCLUSION

This research assesses the heavy metals pollution in the soil and water qualities in Emene and its environs, which is well known for its large industrial activities in South-Eastern Nigeria, using multivariate and pollution load assessment techniques.

The sampling was conducted in both water and soils. A total of sixteen water samples were collected from industrial effluents (IEF), surface and groundwater (SW and HDW) and control samples (CTR). Soil samples were collected from five industrial sites (SS) and two samples were collected far away from industrial area and they served as control samples. The extent of the sediment pollution was assessed; using pollution load index (PLI). A positive correlation was observed with Fe, As, Pb, Cr, Cu, Zn and Ni.

The extracted results of the correlation matrix suggest that the dominant ions in the water (As and Fe, Pb and Fe, Cr and Fe, Cu and Fe, Pb and As, Cr and As, Cu and As, Cr and Pb, Cd and Zn, Ni and Zn, Cu and Cr) were derived from the same source of enrichment. Furthermore, cluster analysis classified 13 sampling locations into three clusters based on similarities of water quality features. The pollution load index (PLI), showed that all locations have PLI > 1 and were polluted.

The ranges of Igeo index values of the heavy metals indicate that the industrial soils are unpolluted with Cu and Ni, unpolluted to moderately polluted with Cr, Fe and Zn, unpolluted to highly polluted with Pb and Mn, unpolluted to very highly polluted with As and Cd. Based on the average Igeo values of the heavy metals, the industrial soils of the study area are unpolluted with Cr, Cu, Ni, Fe, Pb and Zn; and highly polluted with As, Fe and Cd. The data also indicate that the degree of enrichment of each of the heavy metal reflects its pollution intensity.

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