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Spatial Distribution and Seasonal Variations of Heavy Metals in Soils of Warri and Environs, Southwestern Nigeria.

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ABSTRACT

The concentration and distribution of heavy metals (Cd, Pb, Cr, As, Ni, Zn, Fe and Cu) lead, in soils of Warri and environs were examined using Atomic Absorption Spectrophotometer, in the rainy and dry seasons. A total of forty-eight soil samples were collected from parks, commercial areas, main roadside, from residential areas, and from industrial areas, as well as from control sites. The range of mean heavy metal concentrations during the rainy season were: Pb: >0.01 – 0.21mg/kg, Cd: >0.01 – 0.01, Cr: >0.01 - 2.61, As: >0.01, Ni: >0.01 – 0.17, Cu: >0.01 – 7.21, Fe: 0.44 – 1348.66, and Zn: >0.01 – 21.12. The range of mean heavy metal concentrations during the dry season were: Pb: >0.01 – 1.11mg/kg, Cd: >0.01 – 5.92, Cr: >0.05 – 6.12, As: 0.001- 0.01, Ni: >0.01 – 0.34, Cu: >0.01 – 8.12, Fe: 0.87 – 1451.02, and Zn: >0.01 – 19.58.The mean concentrations of heavy metals obtained in all the soil samples in the study area showed an increasing order of As>Cd>Pb>Ni>Cr>Zn>Cu>Fe in both rainy and dry season. The concentrations of heavy metals studied in soil of all sites in the dry season were slightly higher than those of the rainy season. Hierarchical cluster analysis (HCA) was employed in order to further ascertain the sources of heavy metal in soils of the study area, and it revealed that the heavy metals in all the sampled media had a common origin and were associated with anthropogenic activities in the study area. Pearson's correlation of heavy metals in the samples showed strong relationships among metals suggesting a similar distribution pattern and a combination of natural and anthropogenic sources. Spatial distribution maps of the study area showed that patterns of heavy metals were associated with several factors which include industrial activities such as gas flaring, high traffic density, and the geology of the study area. While measured concentrations are generally within international limits, there is cause for concern since the concentrations of heavy metal in some soil samples were elevated near some industrial areas. Therefore, regular monitoring of the soils is essential to prevent excessive build-up of the toxic heavy metals in the soils and water resources of the study area.

Introduction

Contamination or pollution of soils by heavy metals such as mercury, cadmium, lead, copper, zinc and selenium, constitutes a major global threat to the environment and the quality of human health [1]. Heavy metals are naturally present in different concentrations in rocks, soil, surface water, groundwater and stream sediments [2]. However, the concentration of heavy metals in soils has greatly increased due to anthropogenic activities and this poses a threat worldwide [3]. Natural sources include volcanic eruptions, wildfires and weathering of parent rocks, while anthropogenic sources include industrial effluents, sewage disposal, urban storm, water runoff, leaching of heavy metals from refuse disposed at open waste dump sites. Other anthropogenic sources of heavy metals as identified by [4] include mine tailings, indiscrimate disposal of e-waste , leaded gasoline and paints, application of fertilizers, pesticides, wastewater irrigation, and spillage of petrochemicals. More so, considerable amounts of heavy metal may enter the environment through precipitation and atmospheric deposition.

These anthropogenic sources of heavy metals, especially from atmospheric deposition, usually accumulate easily in the topsoil of the study area, and constitute a threat as they, accumulate in the food chain, are toxic to plants and animals, degrade the ecosystem and cause adverse health effects.

These heavy metals are considered to be dangerous environmental pollutants because they are persistent, bioaccumulative, have reduced biodegradability, and are soluble hence their mobility increases when released into the environment [4].

Since more than twenty years ago, Warri and environs has experienced rapid urbanization and development. This has therefore led to increased industrialization, increase in the use of agrochemicals, general environmental degradation and consequently the accumulation of heavy metals in the environment. Heavy metal pollution in the Niger Delta Basin has been linked to different onshore and offshore operations in the petrochemical industry and their related activities. These activities which may contaminate or pollute the soils include blow out during drilling operations, leakage of wellhead, improper disposal of petroleum wastes and other industrial activities. The elevated level of heavy metals in soils of the Niger Delta Basin as a result of improper release of waste from refinery process have been examined by [6], [7], [8], [9] and [10]showed that Nigeria's crude oil contains heavy metals in varying proportion. Gas flaring around and within the study area may releases heavy metals into soil. The concern is heightened in the study area because of some activities in auto-mechanic workshops. Drilling muds are known to contain heavy metal. Studies by [11] showed that Nigeria's crude oil contains heavy metals in varying proportion. Gas flaring around and within the study area may releases heavy metals into soil. The concern is heightened in the study area because of some activities in auto-mechanic workshops. These activities include poor disposal of used engine oil, local oil spills, batteries and tyres, which may have continued over a long period of time, thus posing a serious environmental concern because of the hazard associated with them [12].

Therefore, it is important that the sources, concentration and spread patterns of heavy metals in soils, stream sediments, water resources and other environmental media is known as this will aid in sustainable environmental management programme globally [13]. The main objective of this study was to determine the concentrations and distribution of heavy metals in soils of Warri and environs, as this will aid in the quantification of potential risks they may pose to the environment at elevated levels.

The area under study is Warri and its environs in Delta State, Niger Delta Basin of Southwestern Nigeria (Figure 1). It is located within latitudes 5.29°N and 5.34°N and longitudes 5.41°E and 5.49°E. The climate of Warri and Environs is mainly tropical with alternating wet and dry season. The dry season occurs annually from November to March, while the rainy season usually occurs from April to October. However during the dry season, it rains occasionally, also a brief period without rainfall occurs during the wet season in August known as August break. Mean annual temperatures range from about 220C to 340C, while mean annual rainfall is between 1,501 mm and 2000 mm; mean evapotranspiration is 1117 mm [14], [15], with high humidity [16]. Warri and Environs lies within a geological area known as the Niger Delta Basin which is situated on the continental margin of the Gulf of Guinea in Southern Nigeria. Both the solid and superficial geology of the study area are shown on the Nigerian Geological Survey map.

The map indicates that the studied area is underlain by Benin Formation, which is overlain by superficial deposits of alluvium of a Quaternary to Recent age known as the Sombreiro-Warri Deltaic Plain sands. The Benin Formation is a continental Eocene to Recent deposit which comprises of loose sands with intercalations of lenses of shale and clay which increase towards the base, with a thickness of up to 2000 metres [17],[18] [19]. The Benin formation is the major aquifer in the studied area, with an appreciable groundwater storage and recharge of over $6.63 \times 10^8 m^3$ per annum [20].

Methodology

Soil samples were taken from different locations to cover industrialized, agricultural, housing areas and main roadsides. Control soil samples were also collected from areas that are majorly residential area with low traffic volume industrial activities. A total of forty-eight soil samples, were collected for three months each during both seasons. A Garmin model GPS device was used to determine the geographical coordinates of each sampled site. In order to obtain representative sampling, a regular sampling grid network composed of cells was adopted to sample the soils in the study area. To achieve this, the base map was divided into squared grids, however this was not strictly adhered to due to inaccessibility in some locations. Each cell of the defined sampling grid was tagged alphanumerically with codes which were consequently used for sample identification in the laboratory.

The soil samples were obtained at a depth of 0 - 15 cm from each site using a clean stainless steel soil auger. The soil auger was washed and rinsed with distilled water after each sampling in order to reduce the likelihood of sample cross-contamination. Soil samples were collected from the middle and all edges of each grid and mixed properly to give a composite sample mixture which was kept in labelled polythene sample bags for analysis. Heavy metals analyzed in all soil and sediment samples are cadmium, lead, chromium, arsenic, nickel, zinc, iron and copper. Wet Oxidation Method was adopted to extract the heavy metals from samples through digestion. The samples were air dried at room temperature, and then loosened using a ceramic pestle and mortar, after which they were sieved using a 2 mm mesh sieve in order to remove coarse materials and other debris. Afterward, 5g of the dried fine soil and sediment samples were grinded and blended with an agate mortar until a fine powder which could pass through a 0.15 mm polyethylene sieve was obtained. Then about 2g of this powder was taken, and transferred into a $250cm^3$ acid washed conical flask, this was digested with 1ml of perchloric acid ($HClO_4$) and 3ml of nitric acid (HNO_3) for 10 minutes at room temperature. The digested mixture was heated on a hot plate in a fume cupboard at 40^0C until the digestion was completed. After the mixture had been cooled at room temperature, it was filtered using Whitman No.1 filter paper into a 50 ml flask. The filtrate was then stored in polythene bottles ready for analysis. The same procedures were carried out for the blank samples. The sample solution, the standard and the blanks were aspirated respectively into the air-acetylene flame of Atomic Absorption Spectrophotometer (AAS) for heavy metal analyses using different heavy metals cathode lamps. Varian Spectra Model 220 (Fast Sequential) AAS was used for the analyses. All samples were analyzed in duplicate and during the analysis, and it was ensured that the instruments were well calibrated and operated according to the specifications of the manufacturer. Standard reference materials as well as blank samples were included in each batch of analyses for quality assurance and quality control (QA/QC) procedures.

Statistical analyses of all the data obtained from all sampled sites in the present study were carried out with IBM Statistical Package for the Social Sciences (SPSS) 20.0 software. Multivariate statistical analyses were done to further identify the sources of the heavy metals in soils and stream sediments of the study area, using Hierarchical Cluster Analysis (HCA) and Pearson's correlations. Pearson's significant correlation analysis, which was used to find out association among heavy metal concentrations in the study area, was also determined using the SPSS 20.0 software. The range and mean values of different physico-chemical parameters and heavy metals was calculated using Excel statistical functions. More so, all the mean concentrations of obtained results were compared against known standards.

Spatial distribution maps of heavy metals in soils of the study area were produced using the Arc GIS software, version 9.3.

Results and Discussion

Heavy metal concentrations in soil

The concentration of lead in the rainy season ranged from less than 0.001 mg/kg to 0.21 mg/kg with a mean value of 0.0296 mg/kg. The concentrations of lead in the dry season were slightly higher than those of the rainy season, with values ranging from 0.001 mg/kg to 1.11 mg/kg. A mean value of 0.1692 mg/kg was obtained in the dry season. The highest value recorded during the study was within the vicinity of the Warri Refinery and Petrochemical Company. It is likely that these increased levels of Pb in that vicinity is caused by atmospheric deposition via gas flaring in the study area. These concentrations of Pb recorded in this study are similar to those recorded by [21], [22] in their study on heavy metal analysis of soil samples within the same region. However, the mean concentration of lead is also slightly higher than those recorded at the control site. Lead concentration in most of the study areas were generally below [23] standard. This therefore implies that the concentration of lead in soils of Warri and Environs does not constitute a threat. Lead can be inhaled in dust from Pb based paints, or waste gases from leaded gasoline. High levels of lead in humans is known to pose health risk, such as anaemia, colic, headache, central nervous system and gastrointestinal tract disorder, hypertension and an increased risk of miscarriage in pregnant women [24], [25].

The concentration of cadmium in the soils within the study areas ranged from less than 0.01mg/kg to 0.01 mg/kg in the rainy season and 0.01 mg/kg to 5.92 mg/kg in the dry season. A mean value of 0.002 mg/kg and 0.616 mg/kg was recorded in the rainy and dry seasons respectively which are slightly higher than the values recorded at the control site. According to [26], soil cadmium concentrations generally greater than 0.5mg/kg are considered to be an evidence of soil pollution. The highest value during the study was observed along roads with high traffic density. The high concentration of cadmium in some parts of the study area could be attributed to wear and tear from the automobiles on the urban roads of Warri, lubricating oils, vehicle wheels and metal alloys used for hardening of engine parts. Overall, the concentration of Cd in soils of the study area poses no significant environmental concern. Cadmium is also a non-essential heavy metal which can be very toxic even at low concentration. Elevated concentrations of cadmium have been reported to cause attention deficit hyperactivity disorder (ADHD) and other learning difficulties in children [27].

The concentration of chromium in the rainy season ranged from less than 0.001 mg/kg to 0.21 mg/kg with a mean value of 0.0296 mg/kg. The concentrations of chromium in the dry season were slightly higher than those of the rainy season, with values ranging from 0.005 mg/kg to 6.12 mg/kg. A mean value of 1.3288 mg/kg was obtained in the dry season. The highest value during the study was recorded at Premium Steels and Mines, Aladja, which was formerly Delta Steel Company (DSC). The concentration of Cr in the environment has been reported to increase steadily because of its use in glass, metal, beauty, chemical and leather industries [5]. Chromium could be atmospherically deposited and may be attributed to leachate from municipal and industrial waste dump sites. Although there is no risk of Cr contamination universally, it can percolate into the soil, water or the atmosphere and might accumulate excessively in the environment [5].

The concentration of arsenic in the rainy season had values ranging from less than 0.001 mg/kg to 0.0.005 mg/kg with a mean concentration of 0.0018 mg/kg and 0.0064mk/kg in the rainy and dry seasons respectively. These mean concentrations of arsenic are higher than those recorded at the control site. The concentrations of As obtained from this study are comparable to those recorded by [21],[22] in their study on heavy metal analysis of soil samples within the same region.

The concentration of Nickel ranged from less than 0.001 mg/kg to 0.17 mg/kg with a mean value of 0.0172 mg/kg in the rainy season. Nickel concentrations in the dry season were slightly higher, with values ranging from less than 0.001 to 0.34 mg/kg. A mean value of 0.852 mg/kg was obtained in the dry season. Nickel concentrations in soils of the study area were generally within that of the control sites and below standard limits. Further, the concentration range reported in this study was similar to concentration range values reported in a similar study [21]. This implies that Ni in soils of the study area does not pose a threat to humans and the environment at large.

Copper had relatively low values ranging from 0.001 mg/kg to 0.17 mg/kg with the control site recording concentration less than 0.001 mg/kg. High values of copper are attributed to the presence of electronic and automobile wastes containing electrical and electronic parts, such as copper wires, electrodes and copper pipes and alloys from corroding vehicle scraps which corrode and gradually leach into the sol. Within the study area the low levels of copper recorded may be attributed to the activities of scavengers, who go about picking up metal scrap and selling them off to recycling companies at a profit. These levels of Cu recorded in this study were similar to those recorded by [21] but were however lower than those recorded by [28]. The maximum value of copper concentration recorded in the study area were below the guideline values for soil (20 - 30 mg/kg) [3], and those set by [23].

The concentration of iron in the rainy season ranged from less than 0.44 mg/kg to 1348.66 mg/kg with a mean value of 485.5954 mg/kg. The concentration of iron in the dry season was higher than those of the rainy season, with values ranging from 0.87 mg/kg to 1451.02 mg/kg. A mean value of 499.971 mg/kg was recorded in the dry season. The highest concentration of iron during the study was recorded at Iyara. This was expected, considering its proximity to Rubber Plantation, which is a metal scrap yard littered with several auto mechanic workshop. Further, the topsoil in Warri comprises of "Coastal Plain Sand", which is a member of the Benin Formation. The soil is without a lateritic cover which characterizes the tropics, hence which was reflected by low Fe content of 0.44 mg/kg at the control site.

The concentration of zinc in top soil ranged from less than 0.001 mg/kg to 21.12 mg/kg in the rainy season, with a mean concentration 5.269 mg/kg. Higher values were obtained in the dry season than those of the wet season with concentrations ranging from 0.001 mg/kg to 19.58 mg/kg with a mean value of 6.076 mg/kg. This was considerably higher than the control site which had values less than 0.001 mg/kg. Elevated levels of zinc at some sample locations may be from the use of fertilizers and pesticides at these locations [29]. Zinc oxide is a component of paint, so the high zinc levels in the soils of the study areas could be as a result of the activities of the spray painter and also vehicle body paints. Zinc is also a component of automobile exhaust and part of additives to lubricating oils [4] and so its high concentration could also be attributed to these. Other increased sources of Zn content in some of the samples may have been from traffic sources, especially automobile tyres and emissions. Zn is also used as a vulcanization agent in automobile tyres. High levels of zinc cause anaemia and skin irritation in humans and are phytotoxic to plants.

Studies show that zinc is usually adsorbed to the surface of soil, and this is greatly increased when the soil is alkaline as observed at most of the sampling sites [29]. It is likely that the concentration of zinc will reduce with depth in the study area just like other heavy metals, and this greatly reduces its potential to pollute the water in the Benin Formation, which is the major aquifer in the study area. From the results, the mean concentration of zinc is lower at the control site when compared to results obtained from other sites in the studied area as the control station was far away from the anthropogenic sources of pollution. This buttresses the obvious that human activities contribute significantly to the accumulation of heavy metals in the studied area.

Correlation Matrix

The correlation matrix of heavy metals in soils of the study area during the rainy and dry season is shown in Table 5 and 6. Pearson's correlation of heavy metals in soil during the rainy season showed significant correlations among some paired metals. Correlations are considered significant when the p-value is less than 0.05 level of significance. Strong positive correlations signify that each paired elements have common contamination sources. Strong positive correlation were seen among Ni/Cr (0.735), Cu/Cr (0.726). Moderate positive correlation were observed with Pb/ Cd (0.597), Ni/Cu (0.503), Fe/ Zn (0.671) and Cu/Cr (0.693)

In the dry season the following correlations were observed for soils: Cadmium had a positive perfect correlation with Chromium with a value of 1.00 and a p-value of 0.000. Copper had a moderate positive correlation of 0.693 with both Cadmium and Chromium with a p-value of 0.000.

Iron had a moderate positive correlation with Zinc, with a correlation value of 0.684 and a p-value of 0.000. The only significant correlation between metals of soil in the dry season was seen with Iron which had a moderate positive correlation with Chromium of 0.672 and a p-value of 0.

Clustering Analysis

Cluster Analysis (CA) was applied to further assist in the identification of pollutant sources. CA has been reported to be useful in the explanation of spatial distribution of heavy metals in sediments [30]. CA is often carried out to help classify elements of different sources on the basis of their similarities and to identify homogeneous variables having similar properties [31]. Cluster multivariate analysis of heavy metal concentrations of soil samples collected during the study showed the heavy metal source apportionments in the soil samples. From the dendogram depicted in Figure 2, two cluster groups were identified, based on the various sources of heavy metals in the soil samples. They were; crustal or geogenic source (Iron) and anthropogenic sources (Cadmium, Arsenic, Nickel, Lead, Chromium, Copper and Zinc). A natural source was suggested because of its separate clustering from the other heavy metals.

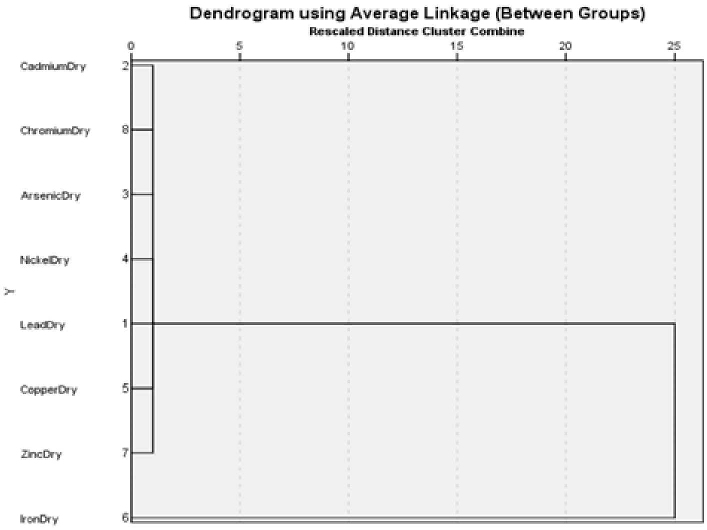

Figure 2. Hierarchical dendogram of heavy metals in in soil samples in the study area.

Table 1. Average heavy metal concentration of soil samples in the study area during the rainy season (mg/kg).

Location	Lead	Cadmium	Arsenic	Nickel	Copper	Iron	Zinc
Ekpan	.0200	.0015	.0010	.0155	.3030	1118.1050	5.1895
Refinery	.2070	.0055	.0010	.0315	3.0615	646.0050	13.1280
Ubeji	.0495	.0025	.0015	.0095	6.6025	423.4700	10.0575
NPA	.0165	.0015	.0015	.1010	.0815	1235.9050	21.1240
Jakpa	.0130	.0020	.0020	.0010	.0175	1044.1450	1.8560
NNPC H/E	.0010	.0025	.0020	.0010	.1385	1187.6650	2.1300
Ejeba	.0075	.0020	.0025	.0010	4.3830	654.3200	15.1080
Ogunu	.1320	.0035	.0010	.0010	.0010	23.7070	.9710
Aladja	.0230	.0015	.0025	.1690	7.2075	977.9900	10.1625
Udu Rd	.1070	.0015	.0020	.0010	.6875	54.6890	3.3150
Ugbomro	.0380	.0020	.0025	.0020	.1295	8.5105	.1360
Esiri Rd	.0015	.0015	.0015	.0015	1.4985	491.2400	7.8875
PTI Road	.0065	.0020	.0015	.0020	.2165	77.9965	3.3285
Ugborikoko	.0015	.0020	.0015	.0025	1.1885	2.7170	.0025
Iyara	.0155	.0030	.0015	.0100	.0010	1348.6600	8.3900
Ovwian	.0095	.0015	.0015	.0225	.4275	1.7695	.0395
Main Mkt	.0055	.0010	.0020	.0010	.0010	1.3240	.0015
Ekete	.0025	.0015	.0010	.0020	.0165	.7615	.0015
Okere Mkt	.0015	.0010	.0020	.0055	.1975	21.7670	3.1570
Lower Erejuwa	.0160	.0020	.0020	.0035	.0160	1268.0600	14.8670
Ogidi St Ogunu	.0015	.0015	.0025	.0010	2.2035	.4360	.0015
Enerhen Road	.0015	.0015	.0015	.0150	.0195	1.0520	.0510
Urhobo College	.0015	.0020	.0020	.0100	.0010	3.0840	.2780
Okere Airport	.0305	.0060	.0025	.0020	.1390	1060.9100	0.381

Table 2. Average metal concentration of soil samples in the study area during the dry season (mg/kg).

Location	Lead	Cadmium	Arsenic	Nickel	Copper	Iron	Zinc
Ekpan	.0455	.2280	.0050	.0215	.4600	1131.5350	5.6350
Refinery	.4150	.6765	.0055	.0675	5.2800	677.7250	14.0150
Ubeji	.0660	.6280	.0075	.0250	7.2850	436.3300	11.1600
NPA	.0345	.0055	.0075	.3400	.1300	1244.3650	19.5800
Jakpa	.0280	.0075	.0060	.0020	.1400	1078.0150	2.0350
NNPC H/E	.0035	.6950	.0070	.0020	.4550	1196.6100	2.4500
Ejeba	.0160	3.5550	.0080	.0020	5.5350	676.0250	16.7400
Ogunu	.6000	.1230	.0065	.0010	.0020	28.3700	1.4450
Aladja	.3500	5.9150	.0070	.2600	8.1200	991.1200	12.6150
Udu Rd	.5565	.6900	.0035	.0030	.8135	66.7350	4.0150
Ugbomro	.5510	.0720	.0110	.0040	.3550	10.0550	.2165
Esiri Rd	.0065	.0065	.0045	.0050	1.9950	503.2800	7.9700
PTI Road	.0045	.5395	.0075	.0050	.5650	85.4350	3.9400
Ugborikoko	.0045	.0945	.0085	.0085	2.7800	3.1800	.0055
Iyara	.1135	.5280	.0055	.0615	.0020	1451.0200	8.7650
Ovwian	.0115	.0075	.0070	.0830	.6750	1.9600	.0690
Main Mkt	.0085	.0060	.0055	.0080	.0020	3.6150	.0045
Ekete	.0075	.0065	.0050	.0080	.1150	1.0500	.0035
Okere Mkt	.0055	.0280	.0045	.0100	.4590	28.0000	4.1150
Lower Erejuwa	1.1125	.5460	.0065	.0130	.1085	1285.6550	15.2800
Ogidi St Ogunu	.0065	.0060	.0075	.0085	4.0600	.8700	.0035
Enerhen Road	.0055	.0065	.0055	.0200	.1050	3.9050	.0885
Urhobo College	.0075	.0065	.0060	.0675	.0020	5.5000	.4450
Okere Airport	.1000	.4060	.0055	.0125	.3675	1088.9500	15.2350

Table 3. Descriptive statistics of heavy metals concentration in soils during the rainy season (mg/kg).

Parameter	N	Minimum	Maximum	Mean	Std. Deviation	WHO, 1996
Lead	24	0.001	1.11	0.1692	0.28368	85
Cadmium	24	0.01	5.92	0.616	1.34238	0.8
Chromium	24	0.005	6.12	0.616	1.3288	100
Arsenic	24	0.001	0.01	0.0064	0.00159	-
Nickel	24	0.001	0.34	0.0443	0.08521	35
Copper	24	0.001	8.12	1.6588	2.48537	36
Iron	24	0.87	1451.02	499.971	540.6725	-
Zinc	24	0.001	19.58	6.0763	6.44827	50

Table 4. Descriptive statistics of heavy metals concentration in soil during the dry season (mg/kg).

Parameter	N	Minimum	Maximum	Mean	Std. Deviation	WHO, 1996
Lead	24	0.001	1.11	0.1692	0.28368	85
Cadmium	24	0.01	5.92	0.616	1.34238	0.8
Chromium	24	0.005	6.12	0.616	1.3288	100
Arsenic	24	0.001	0.01	0.0064	0.00159	-
Nickel	24	0.001	0.34	0.0443	0.08521	35
Copper	24	0.001	8.12	1.6588	2.48537	36
Iron	24	0.87	1451.02	499.971	540.6725	-
Zinc	24	0.001	19.58	6.0763	6.44827	50

Table 5. Pearson correlation matrix of heavy metal concentrations of soils in Warri and environs in the rainy season.

	Pb	Cd	As	Ni	Cu	Fe	Zn	Cu
Pb	1							
Cd	.597**	1						
As	-.340	-.084	1					
Ni	.036	-.103	.111	1				
Cu	.175	.048	.212	.503*	1			
Fe	-.034	.302	.071	.334	.096	1		
Zn	.196	.248	-.006	.467*	.404	.671**	1	
Cr	.015	-.038	.392	.735**	.726**	.291	.339	1

**. Correlation is significant at the 0.01 level (2-tailed) ./

*. Correlation is significant at the 0.05 level (2-tailed).

Table 6. Pearson correlation matrix of heavy metal concentrations of soils in Warri and environs in the dry season.

	Pb	Cd	As	Ni	Cu	Fe	Zn	Cu
Pb	1							
Cd	.134	1						
As	.077	.158	1					
Ni	-.024	.398	.134	1				
Cu	-.014	.693**	.245	.238	1			
Fe	.151	.283	-.079	.358	.055	1		
Zn	.247	.444*	-.002	.492*	.395	.684**	1	
Cr	.134	1.000**	.158	.398	.693**	.283	.444*	1

**. Correlation is significant at the 0.01 level (2-tailed).

*. Correlation is significant at the 0.05 level (2-tailed).

Spatial distribution of heavy metals in soil

Knowledge of the spatial distribution of a contaminant is important for site evaluation and any subsequent risk assessment [32]. Contamination of soil by heavy metals is a spatial phenomenon, as are the risk associated with it, so it is important that geostatistical techniques such as kriging and geographical information software such as ArcGIS are employed in mapping the concentration of heavy metals across the entire study area [33], [34]. Mapping of the distribution of heavy metals in the study area was considered important as it allows an immediate appreciation of the change in the concentrations of the heavy metals with space and enables identification of areas that may contain hazardous concentrations [32]. Furthermore, spatial distribution maps can help to pinpoint parts of the study area that require remediation, and this will enable land owners undertake a cost-effective and targeted remediation programme.

In order to identify patterns in the spatial distribution of the concentration of the heavy metal contaminants of concern in the present study, it was essential to present the data in form of a map. The approximate location of each of the sampling points was measured by a Garmin GPS device. The maps of the spatial distribution of the heavy metals Pb, Cd, Cr, As, Ni, Cu, Fe, and Zn were generated by interpolating data from the study area using kriging. ArcGIS software was used to produce spatial distribution maps and identify the possible sources of heavy metals in Warri and environs.

Spatial distribution maps of the aforementioned heavy metals in Warri and environs are presented in Figure 3. The maps enable possible linkages between anthropogenic activities and heavy metal concentration in all the sampled sites to be established. Increased concentrations of Pb, Cu, and Zn were seen around industrial buildings, road junctions and near major roads with large density of traffic. It is possible that dust derived from the flaring of gas at Warri refinery and Petrochemical Company may have contributed to increased concentrations of heavy metals, in the soil especially Pb, Cu, and Zn [35], through atmospheric deposition. The deposition of heavy metals through atmospheric deposition is considered to significantly contribute in urban soil pollution. Higher values of heavy metals in soil were generally observed in the northern part of the study area, when compared to considerably lower values in the southern part.

Generally, the spatial patterns of heavy metals such as Pb, Cu, and Zn in Warri and environs were identified to be associated with several factors which include industrial activities, road traffic, and the geology of the study area.

Conclusion and Recommendation

The concentrations of the heavy metals in soils of the study area showed that there was no substantial accumulation in the study area. The mean concentrations of heavy metals obtained in all the samples in the study area showed an increasing order of As>Cd>Pb>Ni>Cr>Zn>Cu>Fe in both rainy and dry season. The concentrations of heavy metals investigated in soils of all sampled locations in the dry season were slightly elevated when compared to those of the rainy season. This was attributed to the transport and dilution of heavy metals from the top soil during the rainy season.

Hierarchical cluster analysis (HCA) was employed in order to further investigate the sources of heavy metal at all sampled sites in the study area, and it revealed that the heavy metals in all the soil samples had a common origin and were associated with anthropogenic activities in the study area. Pearson correlation analysis of the heavy metals in the soils during the rainy season showed significant correlations among the metals. Cluster analysis identified two cluster groups based on the various sources of heavy metals in the soil samples. They were; crustal or geogenic source (Iron) and anthropogenic sources (Cadmium, Arsenic, Nickel, Lead, Chromium, Copper and Zinc).

Spatial distribution maps of heavy metal distribution in soils of the study area showed that patterns of heavy metals were associated with several factors which include industrial activities such as gas flaring, untreated effluent discharge, high traffic density, and the geology of the study area.

While measured concentrations are within international limits, there is cause for concern, as it is likely that prolonged deposition of heavy metals from atmospheric sources such as gas flaring, vehicular emission and other sources may result to excessive accumulation of heavy metals on the surface soils thus causing contamination [36]. The present work has shown that human activities significantly contribute to heavy metal contamination of the soils of Warri and Environs.

The concentration of heavy metals determined in this study may signify an early phase in the accumulation of heavy metals in soils of Warri and Environs, which may eventually result to environmental contamination or pollution. Based on the findings of the present study, it is recommended that the concentrations of heavy metals in the soils should be continuously monitored to check on their levels, best practices should be employed by industries, and gas flaring should be stopped.

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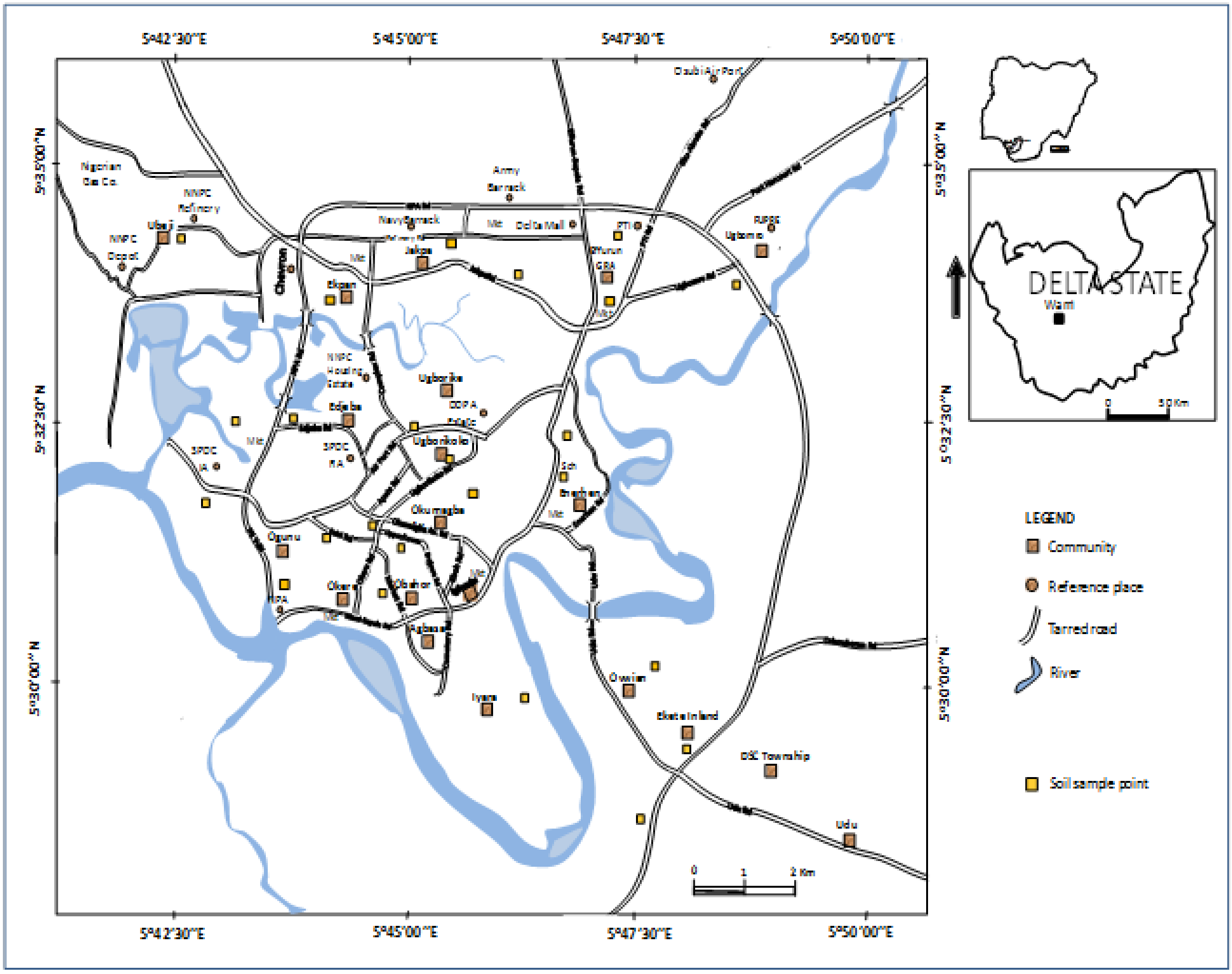

Figure 1. Map of the study are showing sampling points.

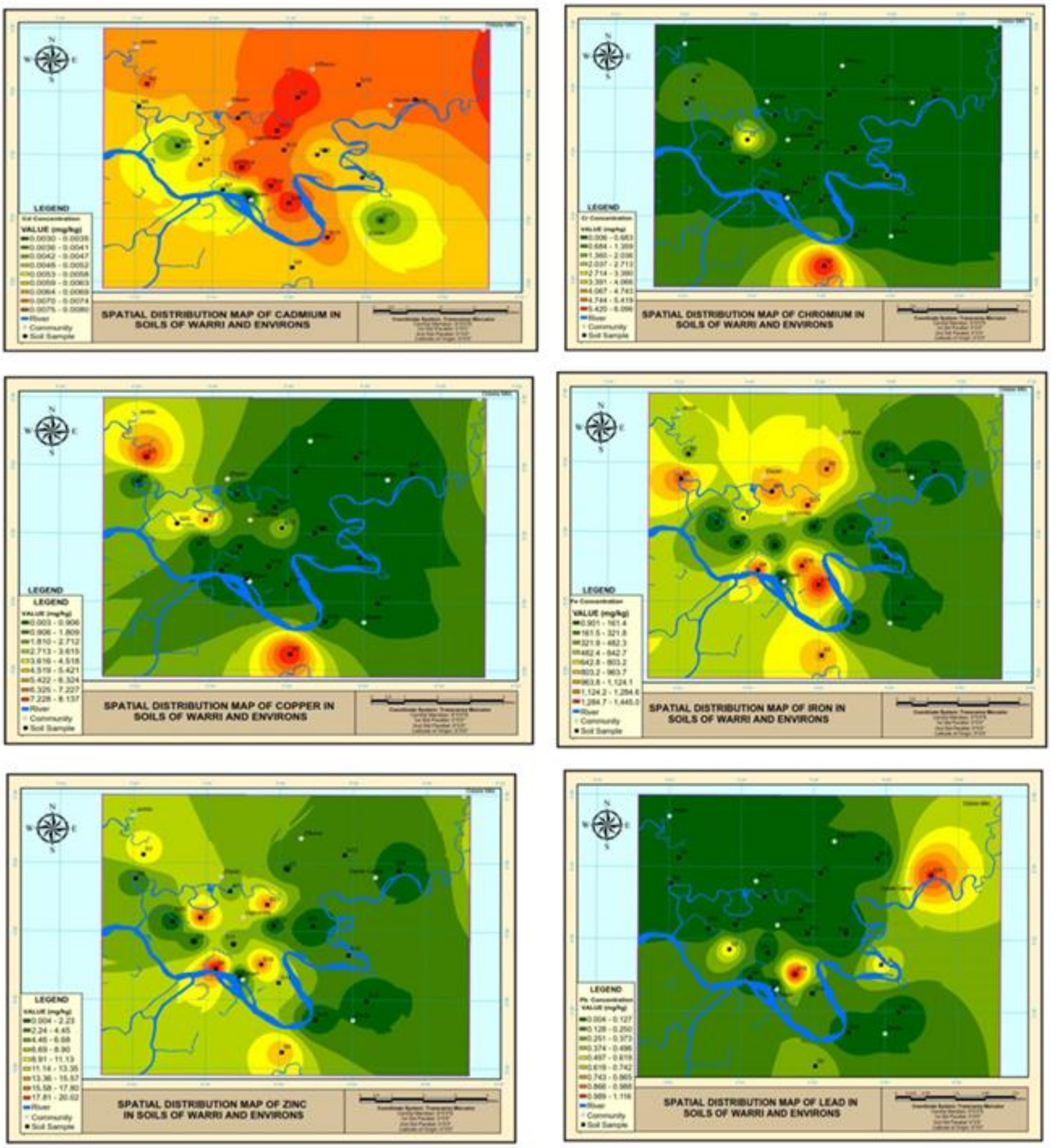

Figure 3. Spatial distribution maps of some heavy metals in soils of Warri and Environs.