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Pollution Indices, Potential Ecological Risks and Spatial distribution of Heavy Metals in soils around Delta State, Nigeria

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Abstract The study investigated the pollution indices and potential ecological risks of heavy metals (HM) occurrence in the soil affected by municipal waste from selected parts of Delta state southern, Nigeria. The heavy metal concentrations were analyzed using Atomic Absorption Spectrometry (AAS). Heavy metals analyzed for this study are Zn, Cr, Cu, Pb, Cd, Co, Ni, and As. Findings obtained from a heavy metal risk assessment indices such as potential ecological risk assessment (ERI), index of geoaccumulation (Igeo), degree of contamination (Cdeg), and Nemerow Pollution (PNI) showed that human activities such as automobile mechanics, dumping of solid waste, and agricultural activities are the major source of heavy metals pollutionin soil within the study area. Findings obtained from Igeo are contrary to findings obtained from ERI which revealed soil samples were unpolluted, implying that the anthropogenic activities within the area had little influence on the ERI. Observation from Cdeg indicated a low contamination degree in the soil. Results from PNI showed that 36.4 %, 27.3 %, and 13.6% of analyzed soil samples were classified to be clean, slightly clean, and moderately polluted respectively. Deduction from Principal Component Analysis PCA analysis and Pearson correlation matrix suggested that anthropogenic activities within the study area have led to the occurrence of heavy metals in soil.

Keywords Heavy Metals · Soil · Multivariate Techniques · Risk Assessment · Nigeria

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1 Introduction

In some parts of the world especially in developing nations, unregulated waste generation and indiscriminate dumping and disposal constitute global challenges occasioned by increasing world population and rapid urbanization. The absence of strict adherence to waste management legislation, poor urban design, and insufficient effort by government agencies have all contributed to inappropriate waste disposal across urban areas in Nigeria (Backsion et al., 2006; Omene et al., 2015; Eyankware et al., 2016). Human activities generate waste and these undesirable materials that are disposed of as waste, with no further value to the original users. Obasi et al. (2015) and Igwe et al. (2020, 2021) noted that widespread and indiscriminate dumping of these wastes remains a major source of heavy metal pollution and a serious concern confronting humans. The quantity and content of waste generated in any given location are determined by social traits, economic strength, population size, consumption patterns, and the nature of services provided to the general public (Eyankware, 2019). According to studies, the soil is the primary recipient of the heavy metals (HM) constituents of municipal wastes and significantly high heavy metal concentrations could lead to soil pollution (Benedicta et al., 2017; Eyankware & Ephraim, 2021; Eyankware & Obasi, 2021; Islam et al., 2015; Obasi et al., 2015; Turhan et al., 2020; Ulakpa & Eyankware, 2021). Mine tailings and municipal wastes (waste from human activities, small industries, and commercial activities) were identified as major sources of HMs in the soil (Ezemokwe et al., 2016; Igwe et al., 2020; Karim et al., 2014; Singh et al., 2011; Wei & Yan, 2010). Similarly, hazardous waste (paint, varnishes, batteries, expired medications, insecticides), ashes from heating systems, and the organic fraction, which has a high accumulation capacity, are also common sources of heavy metals (Agidi et al., 2022; Akakuru et al., 2021a, b; Onyeanwuna et al., 2024; Omoko et al., 2023; Opara et al. 2023a, b). HMs harm soil ecosystems for a long time and hinder soil enzymes (Akakuru et al., 2023a, b). Heavy metals are a big problem due to their toxicity and long-term persistence in the soil (Islam et al., 2015; Yakovlev et al., 2020). HMs are not biodegradable, unlike organic pollutants (Eyankware & Obasi, 2021). They have the potential to accumulate in the soil and enter the food chain via vegetable consumption growing near contaminated soil (Abdusalam, 2009; Igwe et al., 2020). HM contamination of soil can lead to the decomposition of soil biology, changes in soil physicochemical characteristics, possible dangers, and other negative consequences on the soil ecosystem. HM contamination of soil has indeed been found to have negative effects on human health, animals, soil productivity, and vegetation diversity and abundance, according to Ogunbanjo et al. (2016), Riyad et al. (2015), Papa et al. (2010), and Smith et al. (1996). Enrichment factor (EF), contamination factor (Cf), degree of contamination, index of geoaccumulation (Igeo), pollution load index (PLI), and other traditional methods have been developed and used to assess the pollution status of HMs in soil over the last few decades (Islam et al., 2014; Islam et al., 2015). Each method takes a unique approach to both the estimation and interpretation of outcomes. Risk assessment is a powerful instrument in environmental health and is very significant in hazard evaluation, control, and management, hence ecological risks assessment is a part of the current study in soil pollution investigations (Fairbrother et al., 2007; Igwe et al., 2020; Kumar et al., 2018; Sahito et al., 2016). It shows that heavy metals tend to have negative effects on the environment (Ogunbanjo et al., 2016). HMs around urban and rural wastes have the potential to harm ecosystems and human health, and they are a major source of worry for human and environmental health, particularly in areas near dumpsites. HMs can enter the food chain in significant amounts through plants (vegetable and other arable crops) and animal grazing since they are taken up by plants (vegetable and other arable crops) as stated by Zhao et al. (2010). As a result, eating vegetables produced on dumpsite soils with high metal concentrations could put people at risk for serious health impacts from heavy metals. To the best of our knowledge, no previous research had examined the pollutant features and potential ecological effects of HMs on soil within the study area. Hence this study was carried out to ascertain the impact of heavy metals on soil using various heavy metals indexes such as geoaccumulation (Igeo), contamination factor (Cf), degree of contamination (Cdeg), and Nemerow pollution (NP)

1.1 Location and Physiography

The study area is located in the western portion of the Niger Delta. It covers an area of more than 15,000 km^2 and is one of the top oil-producing states in Nigeria (Olobaniyi et al., 2007). The research region, which has a high average annual precipitation of about 1900 mm and an elevation of 280 m, is roughly located between Latitude 5°18'N-5°3-0'N and Longitude 5°45'E- 5^{o}59'E, as shown in Fig. 1. With mean annual temperatures varying between 220C and 340C, rainfall varying from 1,501 mm to 1850 mm, and mean evapotranspiration of 1117 mm (FME, 2001; Chizoba et al., 2023; Asuquo et al., 2024; Eyankware & Akakuru, 2022; Oli et al., 2022; Urom et al., 2021), the climate is generally warm. Olobaniyi et al. (2007) point out that the study region ranges in elevation from heights of less than 6 meters above sea level (mSL) in the lowlands that border the water to more than 280 m above mSL in the plateau that marks the state's northern border (Fig. 1). The vegetation in the research area ranges from rain forest in the northernmost parts of the state to a saline water marsh in the coastal area next to the sea (Olobaniyi et al., 2007).

1.2 Geologic Setting

The study area is located in the Niger Delta Basin. Previous authors (eg., Burke et al., 1971; Evamy et al., 1978; Hoque & Nwajide, 1984; Murat, 1972; Nwajide, 2013) have given a summary of the geologic setting of the Niger Delta Basin. The previous studies documented three major tectonic phases for the southeastern Nigerian sedimentary basins. The origin of the basins commenced with the break-up of the African and South American continents during the Early Cretaceous (Murat, 1972). The pre-Santonian sediments of the Benue Trough and the upper Cretaceous Anambra Basin, respectively, evolved and were deposited as a result of the first and second tectonic phases, whereas the Paleocene to Recent sediments of the Niger Delta Basin were created by the third tectonic event. The Niger Delta Basin covered the eastern flank of the Abakaliki Anticlinorium, where the Afikpo Sub-basin unconformably overlies the pre-Santonian strata (Igwe et al., 2013; Igwe, 2015; Obasi et al., 2022; Usman et al., 2022; Igwe & Okoro, 2021).The Niger Delta Basin developed a

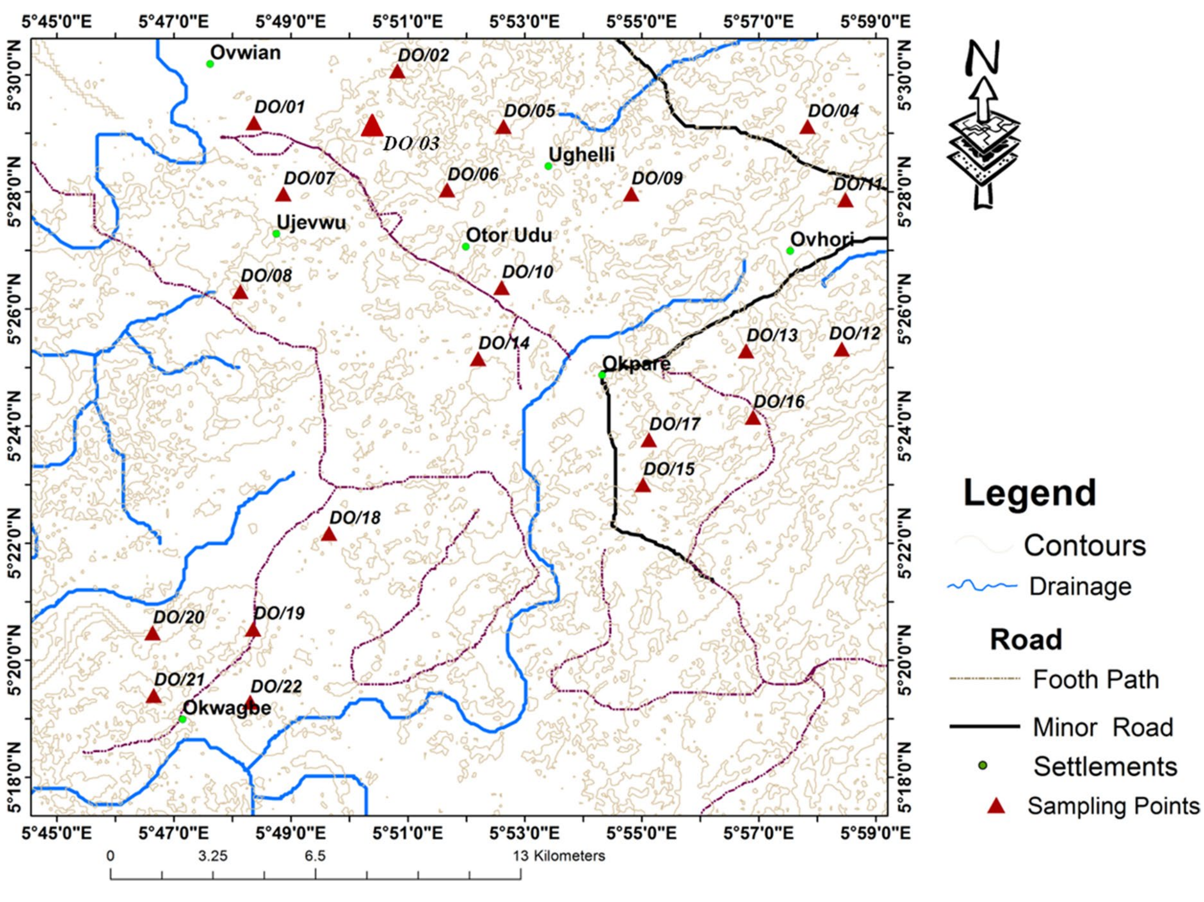

Fig. 1 Topographic Map of the study area showing sampling points

continuous variety of formations from the Cretaceous to the Quaternary upwards, and developed three diachronous lithological formations namely Akata Formation, Agbada Formation, and Benin Formation, respectively since the Eocene time (Corredor et al., 2005; Lonergan et al., 2013).

The Agbada Formation is overlain by the Akata Formation, which is made up of continuous shale and roughly 10% sandstone (Orji & Egboka, 2015). In the subsurface, the Agbada Formation lies on top of the Akata Formation. It is made up of a parallel alternating succession of shale and sandstone varying in age from the Eocene in the north to the Pliocene/ Pleistocene in the south, and recently in the delta surface. The Ogwashi-Asaba Formation and the Ameki Formation, both of Eocene-Oligocene age, are its lateral analogs at the surface. The primary rock outcrops in the Asaba Capital Territory are part of the Ogwashi-Asaba Formation. The Benin Formation, which is Miocene to Recent in age and conformably overlies the Agbada Formation, is a continental Miocene-Recent formation. The formation is mostly sand, with a small amount of shale/clay. They're also badly sorted, with lignite streaks and wood fragments, and are sub-angular to well-rounded. The Benin Formation is found just west and northwest of Asaba town and extends into Agbor town (Akpoborie et al., 2011). The Benin Formation is obscured by the newer Holocene deposits of the Sombreiro-Warri Deltaic Plain, the Mangrove Swamp, and Freshwater Swamp wetlands to the west and south of Abraka, as well as Sapele, Warri, and Ughelli (Eyankware & Ephraim, 2021) Fig. 2.

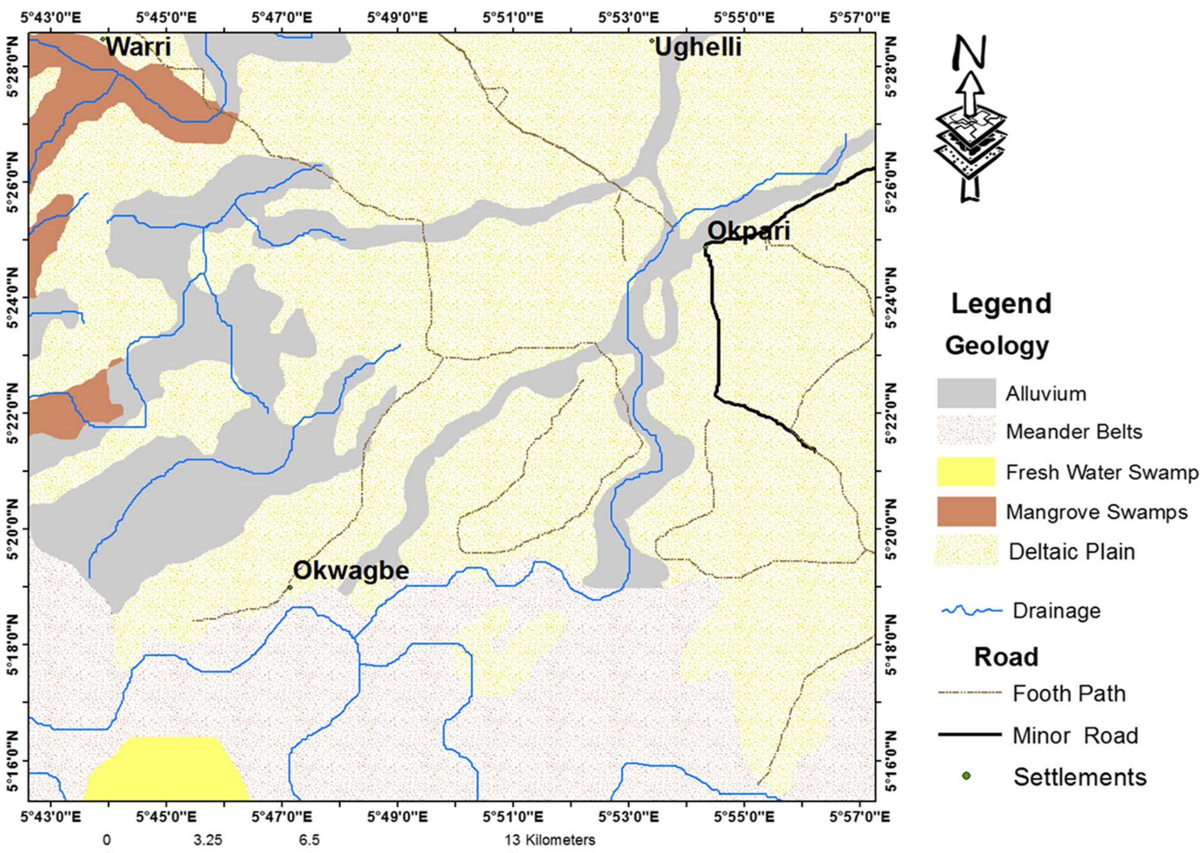

Fig. 2 Geology Map of the study area

2 Materials and Method

A total of twenty-two (22) soil samples were collected at 20 km intervals in Delta State, Nigeria. Control samples were specifically gathered from towns including Ughelli, Okpare, Ujevwu, and Okwagbes. Each sampling point yielded a minimum of three composite soil samples. A steel Auger was used to collect soil samples from a depth of 0–15 cm into transparent plastic bags. In the laboratory, samples were air-dried for several days by spreading them out on transparent plastic on a bench. They were then sieved at 2 mm and repackaged in clear plastic bags until they could be analyzed. 20 g sieved air-dried soil samples were placed in 250 cm^3 conical flasks that had been thoroughly cleaned, and 100 cm^3 of 0.5 M nitric acid was added. A mechanical shaker was used to mechanically shake the flasks for at least 30 minutes. The materials were then filtered through ashlessWhatman filter paper 40 into 100 cm^3 plastic bottles. Some control samples were tested for background target analytes before being spiked with known levels of Arsenic (As), Cobalt (Co), chromium (Cr), cadmium (Cd), copper (Cu), lead (Pb), Nickel (Ni), and zinc (Zn) and going through the entire process to assess the extraction procedure's recovery rates. The percent recoveries were determined by the differences between the baseline concentrations and the concentrations of the spiked samples. In the preparation of solutions used to spike the samples for cadmium, general-purpose reagent cadmium nitrate with a minimum purity of 99 percent was utilized. In the production of solutions used in the spiking of samples for lead, copper, and zinc, an analytical grade of lead nitrate salt and analytical grade granules of copper and zinc were utilized. A reagent blank for each metal was likewise created and run through the whole process before being used in the sample determination. Analysis-grade metals and metal salts were used to create calibration curves. Using a Varian Techtron AA6 atomic absorption spectrophotometer and associated metallic hollow cathode lamps, the concentrations of cadmium, copper, lead, and zinc were determined. The fuel was acetylene gas, and the support was air. In every case, an oxidizing flame was used. The concentrations of four metals were calculated using calibration curves. To zero the instrument, a reagent blank was employed. The aspiration of standard solutions was then performed, followed by the aspiration of soil sample extracts.

2.1 Soil Pollution Indexes Calculation

The occurrence of heavy metal in soil was computed using the following: potential ecological risk index, geoaccumulation index (Igeo), contamination factor, and Nemerow pollution.

2.2 Data Analysis

To obtained Pearson correlation analysis, Principal Component Analysis (PCA), data were analyzed using the SPSS statistical package.

2.2.1 Potential Ecological Risk Index

The Potential Ecological Risk Index (PERI) is a tool used to assess the potential risk posed by heavy metals in the environment, particularly in soil and sediment. It evaluates the toxicity and concentration of various contaminants to determine their likely impact on ecological systems. By integrating factors such as contamination levels and ecological sensitivity, PERI helps in identifying areas at high risk and prioritizing remediation efforts. The potential ecological risk index was first proposed by Hakanson (1980) as presented in equation 1:

$$E_r^i = C_f^i * T_r^i = T_r^i * {}^{C_i}/_{C_b} \quad (1)$$

where E_r^i denotes the potential ecological risk index of metal i^{th}; T_r^i is the toxic response factor of the ith metal. In this study, the T_r^i of Zn, Cr, Pb, Cu, Ni, and Cd are 1, 2, 5, 5, 5 and 30, respectively (Islam et al., 2015; Weihua et al., 2010). The C_f^i values of each heavy metal are obtained from (Eq. 1).To quantitatively express E_r^i, five criteria grades were employed: $E_r^i < 40$, $40 \le E_r^i < 80$, $80 \le E_r^i < 160$, $160 \le E_r^i < 320$ and ≥ 320 signifying low, moderate, considerable, high and very high risk, respectively (Hakanson, 1980; Ogunkunle & Fatoba, 2013; Riyad et al., 2015). The potential ecological risk index for various heavy metals in the soil is determined as the sum of the single potential ecological risks factor. It represents the sensitivity of various biological communities and possible risks caused by heavy metals. The potential ecological risk index of all the measured heavy metals was computed using (Equation 2)

$$RI = \sum_{i}^{n} E_r^i \tag{2}$$

2.2.2 The Geoaccumulationindex (Igeo)

The Geoaccumulation Index (Igeo) is a quantitative measure used to assess the degree of heavy metal pollution in soils and sediments. It compares current concentrations of metals to pre-industrial levels to determine the extent of anthropogenic influence. By categorizing pollution into various classes, ranging from unpolluted to extremely polluted, Igeo helps in identifying the severity of contamination and guiding environmental management practices. The formula for the Igeo calculation is presented in Equation 3:

$$I_{geo} = \log_2\left({}^{c_n}/_{kB_n} \right) \tag{3}$$

As proposed by Muller (1979)

Where Cn is the measured concentration (µgg-1) of element n, and Bn is the geochemical background concentration (mg/kg) see equation 3.

2.2.3 Contamination factor (C_{deg})

The Contamination Factor (C_deg) is a metric used to evaluate the extent of contamination by comparing the concentration of a particular pollutant in the environment to a baseline or reference value. It quantifies the degree of contamination for individual elements, indicating how much a pollutant exceeds its natural or pre-industrial concentration. By assessing C_deg, environmental scientists can identify hotspots of contamination and assess the potential ecological and health risks associated with specific pollutants. Equation 4 is the C_deg formula:

$$C_{deg} = \sum_{i=1}^{n} C_f^i \tag{4}$$

As proposed by Devanesan et al. (2017); Ogundele et al. (2020)

2.2.4 Nemerow Pollution

The Nemerow Pollution Index is an integrated measure used to assess the overall pollution level of an environment by combining multiple pollution indices. It takes into account both the average pollution level and the maximum pollsution level of various contaminants, providing a comprehensive assessment of environmental quality. This index is particularly useful for identifying areas with significant pollution issues and prioritizing them for remediation efforts. NP can be calculated using Equation 5:

$$NP = \sqrt{ {}^{(p_{ave}^1 + p_{max}^2)}/_{2} } \tag{5}$$

As proposed by Ogundele et al. (2020)

Pave and Pmax are the average and maximum values of single pollution index (SPI) for all heavy metalssee equation 5. The NP indices of each metal was calculated and classified into 5 grades: NPs < .7, 0.7 ≤ NP ≤ 1.0, 1.0 ≤ NPs ≤ 2.0, 2.0 ≤ NPs ≤ 3.0 and NPs > 3.0 indicating safety, precaution, slightly polluted, moderate polluted and serious polluted domain, respectively (Cheng & Zhu, 2007; Ogunkunle & Fatoba, 2013).

2.2.5 Principal Component Analysis

In the PCA, component loading entailed reducing a large dataset of many variables into a smaller number of linear combinations in the component that accounted for an appropriate fraction of the total data variance and easily associated the variables to the sources or processes via equation 6.

$$\sigma^2 = \frac{1}{N} \sum_{i=1}^{N} \left(X_N \_ N \right)^2 \tag{6}$$

3 Result and Discussion

The concentrations of heavy metals such as zinc, chromium, copper, lead, cadmium, nickel, and arsenic in mg/kg., there minium, maximum, and average values are presented in Table 1. Table 2, was

Table 1 Concentration (mg/kg) of heavy metals in soil samples within the study area

Sample site	Latitude	Longitude	Znmg/kg	Crmg/kg	Cumg/kg	Pbmg/kg	Cdmg/kg	Comg/kg	Nimg/kg	Asmg/kg
DO/01	$5^0$29’	$5^0$48.5’	32.48	12.43	10.31	4.07	0.74	9.01	2.47	0.000
DO/02	$5^0$30’	$5^0$50.9’	16.47	17.09	7.82	1.97	0.38	11.07	1.03	0.0020
DO/03	$5^0$29’	$5^0$49’	13.11	8.37	9.07	4.28	3.40	6.78	1.18	0.000
D0/04	$5^0$29’	$5^0$58’	19.47	11.03	4.38	4.02	0.38	13.96	3.11	0.0001
DO/05	$5^0$29’	$5^0$52’	22.36	4.93	6.39	3.48	0.94	10.15	3.04	0.000
DO/06	$5^0$28’	$5^0$51’	17.61	10.01	13.40	5.28	1.53	8.07	0.99	0.003
DO/07	$5^0$28’	$5^0$49’	11.38	8.48	9.29	1.77	0.27	6.11	1.82	0.000
DO/08	$5^0$26	$5^0$48’	30.88	15.09	5.38	6.31	1.61	4.38	2.71	0.000
DO/09	$5^0$28’	$5^0$54’	23.47	21.49	4.51	4.20	2.47	7.27	1.36	0.003
DO/10	$5^0$28’	$5^0$52’	17.34	9.13	7.37	2.54	0.62	9.39	2.29	0.020
DO/11	$5^0$28’	$5^0$58’	14.28	10.77	6.31	2.99	0.47	7.86	1.11	0.000
D0/12	$5^0$25’	$5^0$58’	12.93	4.26	19.29	1.38	1.03	6.69	4.09	0.0001
DO/13	$5^0$25’	$5^0$56’	9.47	7.33	8.37	3.44	1.28	9.04	4.27	0.0003
DO/14	$5^0$25’	$5^0$52’	14.62	9.15	7.21	1.93	4.01	9.35	4.01	0.0000
DO/15	$5^0$23’	$5^0$55’	28.38	12.48	11.37	3.34	1.13	5.86	2.38	0.0002
DO/16	$5^0$24’	$5^0$57’	15.04	10.11	9.01	2.07	0.93	7.97	3.03	0.0010
D0/17	$5^0$23’	$5^0$55’	9.37	5.23	5.52	4.88	0.37	11.08	1.19	0.0000
DO/18	$5^0$22’	$5^0$49’	11.38	4.99	6.27	2.17	1.39	13.97	2.37	0.0001
DO/19	$5^0$20’	$5^0$48’	16.93	11.12	14.37	2.05	0.33	6.86	3.01	0.0002
DO/20	$5^0$20’	$5^0$46’	20.17	8.21	18.11	4.13	3.91	8.11	2.99	0.0001
DO/21	$5^0$19’	$5^0$46’	10.93	6.37	26.36	1.94	1.92	10.63	4.18	0.0000
DO/22	$5^0$19’	$5^0$48’	16.34	11.18	9.31	3.22	0.38	11.37	3.25	0.0001
Min			9.37	4.26	4.38	1.38	0.27	4.38	0.99	0.00
Max			32.48	21.49	26.38	6.31	4.01	13.97	4.27	0.02
Aver			17.76	10.20	10.42	3.29	1.40	8.88	2.54	0.0020

Table 2 The value of control site

Control sites	Zn	Cr	Cu	Pb	Cd	Co	Ni	As
Ughelli	9.11	12.07	4.86	1.05	0.95	6.88	2.47	0.0001
Okpare	12.37	9.54	9.65	3.64	2.58	5.91	1.03	0.0000
Ujevwu	8.28	16.77	6.01	4.22	2.42	9.36	1.59	0.0010
Okwagbe	9.37	10.02	4.53	1.74	1.55	4.20	3.09	0.0002
Min	8.28	9.54	4.53	1.05	0.95	4.2	1.03	0.001
Max	12.37	16.77	9.65	4.22	2.58	9.36	3.09	0.001
Aver	9.96	12.45	6.53	2.65	1.88	6.65	2.05	0.00

used as control site at Ughelli, Okpare, Ujevwu, and Okwagbe.

3.1 Potential Ecological Risks Assessment

The potential ecological risk index was developed by Hakanson (1980) a Swedish scientist. It had been employed to evaluate the adverse effects of the contaminants on the environment and human and reflects the toxicity and ecological sensitivity of the concentration of contaminants (Hakanson, 1980; Suresh et al., 2012; Weihua et al., 2010). Originally, it was used as an evaluation tool for sediment pollution in aquatic environments. It had been successfully used for risk assessment of soils, dust, and air (Qingjie et al., 2008; Eyankware et al., 2023; Suresh

Table 3 Results of Ecological Risk Index

Ti*PI								∑ Ti*PI
Zn	Cr	Cu	Pb	Cd	Co	Ni	As	
0	20.18632	1971.589	839.234	125491.7	6536.667	227.0888	0	135086.4
5.88E-05	14.07362	2056.058	308.108	31191.67	4124.118	116.348	0.058857	37810.43
0	5.486535	1167.937	776.392	606333.3	22600	81.63673	0	630964.8
3.48E-06	10.73771	743.2523	352.152	63650	5200.784	443.0163	0.008886	70399.95
0	5.51174	484.6569	444.744	136300	9353.922	314.8571	0	146903.7
9.43E-05	8.813805	2063.6	1415.04	336600	12105	81.52347	0.084857	352274.1
0	4.82512	1211.988	328.866	19912.5	1617.353	113.4714	0	23189
0	23.29896	1248.988	678.956	423295.8	6913.529	121.1204	0	432281.7
0.000126	25.21852	1491.075	378.84	432250	17604.8	100.8898	0.116571	451850.9
0.000619	7.91571	1035.202	374.396	65616.67	5707.647	219.4194	1.308571	72962.56
0	7.68978	1045.518	377.338	58554.17	3621.765	89.02653	0	63695.5
2.31E-06	2.75409	1264.237	532.404	59225	6755.588	279.2051	0.011686	68059.2
5.07E-06	3.470755	943.8785	575.856	183466.7	11344.31	393.8857	0.0366	196728.1
0	6.68865	1014.946	278.306	322470.8	36758.33	382.5867	0	360911.7
1.01E-05	17.70912	2183.04	759.516	157258.3	6491.961	142.3143	0.0136	166852.9
2.69E-05	7.60272	1401.402	373.014	80212.5	7266.765	246.4194	0.086571	89507.79
0	2.450255	444.1477	538.752	75233.33	4019.216	134.5429	0	80372.44
2.03E-06	2.83931	481.3431	272.118	125679.2	19037.55	337.8459	0.006771	145810.9
6.05E-06	9.41308	2458.375	589.17	28187.5	2219.412	210.7	0.0172	33674.59
3.6E-06	8.279785	2287.432	1495.886	672845.8	31088.33	247.4378	0.008543	707973.2
0	3.481205	2583.28	1022.768	155200	20009.41	453.402	0	179272.3
2.92E-06	9.13406	1601.32	599.564	50983.33	4235.882	377.0663	0.009286	57806.31

et al., 2012; Ogunkunle & Fatoba, 2013; Iqbal & Shah, 2014; Riyad et al., 2015; Osipova et al., 2016). The results from Table 3 revealed that the entire samples within the study area are above 600, this implies that the soils have very high ecological risk. Soil pollution by heavy metals represents a threat to the environment and food security due to the fast growth of industry and agriculture, and the disruption of natural ecosystems by anthropogenic pressure linked to the growth of human populations (Sarwar et al., 2017). Environmental pollution and human exposure associated with heavy metals are attributed to different anthropogenic activities that include mining, industrial production, and the use of metal-containing compounds in domestic and agricultural settings (Tchounwou et al., 2012).

3.2 Index of Geoaccumulation

The index of geoaccumulation (Igeo) was proposed by Muller (1979) to verify the degree of the contamination of elemental concentrations in the sediment, water, dust and soil and it had been widely employed in assessing their pollution status worldwide (Hazzeman et al., 2017). The classifications of (Igeo) and their respective interpretations are Igeo ≤ 0 (practically unpolluted), 0 <Igeo ≤ 1 (unpolluted to moderately polluted), 1 <Igeo ≤ 2 (moderately polluted), 2 <Igeo ≤ 3 (moderately to strongly polluted), 3 <Igeo ≤ 4 (strongly polluted),4 <Igeo ≤ 5 (strongly to extremely polluted), and Igeo ≥ 5 (extremely polluted) see Table 2, (Olujimi et al., 2014; Qing et al., 2015; Wei & Yan, 2010). From the results of the geoaccumulation index (Table 4), it revealed that the entire sample vales are within 0 to 2, which indicates that they samples are unpolluted. This is contrary to the result of the potential ecological risk index, which revealed that the soils are greatly polluted. Generally, the Igeo demonstrated that the greater part of the heavy metals have not unequivocally affected the soils within the study area.

Table 4 Results of Geoaccumulation Index

Zn	Cr	Cu	Pb	Cd	Co	Ni	As	Geoaccumulation
0.069839	0.037418	0.11937	0.012252	0.278453	0.079773	0.005311	0	0.602416
0.035414	0.051446	0.090541	0.00593	0.142989	0.098012	0.002215	1.2E-05	0.426559
0.028189	0.025196	0.105013	0.012884	1.279377	0.060029	0.002537	0	1.513226
0.041865	0.033204	0.050712	0.012101	0.142989	0.123599	0.006687	6.02E-07	0.411158
0.048079	0.014841	0.073984	0.010476	0.35371	0.089866	0.006537	0	0.597493
0.037865	0.030133	0.155146	0.015894	0.57572	0.07145	0.002129	1.81E-05	0.888356
0.024469	0.025527	0.10756	0.005328	0.101598	0.054097	0.003913	0	0.322493
0.066399	0.045425	0.06229	0.018995	0.605823	0.03878	0.005827	0	0.843539
0.050466	0.064691	0.052217	0.012643	0.92943	0.064367	0.002924	1.81E-05	1.176757
0.037285	0.027484	0.08533	0.007646	0.233298	0.083137	0.004924	0.00012	0.479225
0.030705	0.032421	0.073058	0.009001	0.176855	0.069591	0.002387	0	0.394017
0.027802	0.012824	0.223341	0.004154	0.387576	0.059232	0.008794	6.02E-07	0.723725
0.020363	0.022065	0.096909	0.010355	0.481648	0.080039	0.009181	1.81E-06	0.720562
0.031436	0.027544	0.083478	0.00581	1.508913	0.082783	0.008622	0	1.748587
0.061023	0.037569	0.131643	0.010054	0.425205	0.051883	0.005118	1.2E-06	0.722496
0.032339	0.030434	0.104318	0.006231	0.349947	0.070565	0.006515	6.02E-06	0.600357
0.020148	0.015744	0.063911	0.01469	0.139226	0.0981	0.002559	0	0.354378
0.024469	0.015021	0.072595	0.006532	0.52304	0.123688	0.005096	6.02E-07	0.770442
0.036403	0.033475	0.166377	0.006171	0.124175	0.060737	0.006472	1.2E-06	0.433811
0.04337	0.024715	0.209679	0.012433	1.471284	0.071805	0.006429	6.02E-07	1.839714
0.023502	0.019176	0.305198	0.00584	0.722472	0.094116	0.008988	0	1.179292
0.035135	0.033655	0.107792	0.009693	0.142989	0.100668	0.006988	6.02E-07	0.436921

3.3 Degree of Contamination (C_{deg})

The contamination factor reflects the pollution characteristics of the studied area. It indicates a single pollution index of a given metal in an environmental media. The contamination factor was quantified as the ratio of the heavy metal concentration to the background concentration of the corresponding metal (Ogundele et al., 2017). The $C_{deg}$of contamination may be classified based the scale ranging from <8 to >32: < 8, 8–16, 16–32 and > 32 indicates low degree, moderate, considerate and very high degree of contamination, respectively (Oli et al., 2022; Ogundele et al., 2017; Devanesan et al., 2017). The results of the degree of contamination as presented in Table 5 reveals that the entire samples were less than 8, indicating that they have low contamination degree. This results are in conformity with the results of thegeoaccumulation index of the samples within the area but dissimilar with the potential ecological risk index assessment done within the locality.

3.4 Nemerowpollution(PNI)

PNI (Nemerow 1974) is another numerical index that incorporates multiple factors into single factor. The NPI value, on the other hand, represents the combined water quality level of various pollution parameters. In terms of empirical validity, using an integrated water quality index to evaluate an intrinsic groundwater risk assessment is preferable to merely examining the concentrations of one or two specific contaminants (Eyankware et al., 2022a, b; Akakuru et al., 2023a, b, c, d). The PNI calculates the relative pollution contribution of each parameter in a water sample. The parameter(s) responsible for the quality status will be identified this manner.

PNI value of ≤ 0.7 indicates that the water is clean, PNI value of 0.7< PNI ≤ 1.0 implies slightly clean, PNI value of 1.0< PNI≤ 2.0 implies slightly polluted, PNI value of 2.0< PNI≤ 3.0 implies moderately polluted, while PNI value of > 3.0 implies heavy pollution (Table 5). From the results in Table 5, it shows that 36.4% of the entire sample

Table 5 Results of Contamination Factor, Pollution Load Index and Nemerow pollution

Zn	Cr	Cu	Pb	Cd	Co	Ni	As	Cdeg	PNI	**PNI**
0.232	0.1243	0.396538	0.0407	0.925	0.265	0.017643	0	2.001181	0	0.700276
0.117643	0.1709	0.300769	0.0197	0.475	0.325588	0.007357	0.00004	1.416997	2.33E-06	0.379718
0.093643	0.0837	0.348846	0.0428	4.25	0.199412	0.008429	0	5.02683	0	3.070192
0.139071	0.1103	0.168462	0.0402	0.475	0.410588	0.022214	0.000002	1.365837	9.49E-07	0.376777
0.159714	0.0493	0.245769	0.0348	1.175	0.298529	0.021714	0	1.984826	0	0.867103
0.125786	0.1001	0.515385	0.0528	1.9125	0.237353	0.007071	0.00006	2.951055	8.12E-06	1.40175
0.081286	0.0848	0.357308	0.0177	0.3375	0.179706	0.013	0	1.0713	0	0.273652
0.220571	0.1509	0.206923	0.0631	2.0125	0.128824	0.019357	0	2.802175	0	1.465527
0.167643	0.2149	0.173462	0.042	3.0875	0.213824	0.009714	0.00006	3.909103	1.00E-05	2.237207
0.123857	0.0913	0.283462	0.0254	0.775	0.276176	0.016357	0.0004	1.591952	1.07E-05	0.583019
0.102	0.1077	0.242692	0.0299	0.5875	0.231176	0.007929	0	1.308897	0	0.446483
0.092357	0.0426	0.741923	0.0138	1.2875	0.196765	0.029214	0.000002	2.404161	7.72E-07	0.958718
0.067643	0.0733	0.321923	0.0344	1.6	0.265882	0.0305	0.000006	2.393654	2.07E-06	1.170267
0.104429	0.0915	0.277308	0.0193	5.0125	0.275	0.028643	0	5.80868	0	3.61798
0.202714	0.1248	0.437308	0.0334	1.4125	0.172353	0.017	0.000004	2.400079	2.47E-06	1.042873
0.107429	0.1011	0.346538	0.0207	1.1625	0.234412	0.021643	0.00002	1.994342	3.03E-06	0.858982
0.066929	0.0523	0.212308	0.0488	0.4625	0.325882	0.0085	0	1.177219	0	0.358618
0.081286	0.0499	0.241154	0.0217	1.7375	0.410882	0.016929	0.000002	2.559353	7.16E-07	1.269567
0.120929	0.1112	0.552692	0.0205	0.4125	0.201765	0.0215	0.000004	1.44109	1.04E-06	0.342822
0.144071	0.0821	0.696538	0.0413	4.8875	0.238529	0.021357	0.000002	6.111397	4.12E-06	3.539408
0.078071	0.0637	1.013846	0.0194	2.4	0.312647	0.029857	0	3.917521	0	1.766295
0.116714	0.1118	0.358077	0.0322	0.475	0.334412	0.023214	0.000002	1.451419	1.05E-06	0.381744

Table 6 Ecological Risk Index set limit in Soil (Hakanson, 1980)

S/No	Range	Remarks
1	$R_i \; or \; E_r^i$	Ecological Pollution Degree
2	$E_r^i < 40 \; or R_i < 150$	Low Ecological Risk
3	$40 \le E_r^i < 80 \; or 150 \le R_i < 300$	Moderate Ecological Risk
4	$80 \le E_r^i < 600 \; or 300 \le R_i < 600$	Considerable Ecological Risk
5	$160 \le E_r^i < 320 \; or \; 600 \le R_i$	Very high Ecological Risk

are had a value <0.7, indicating that the samples are clean, 18.2% of the entire sample have had a value <1, indicating that the sample is slightly clean, 27.3% of the entire samples had values <3, implying that the samples are moderately polluted, while 13.6% of the samples are >3, implying that the samples are heavily polluted. Anthropogenic factors could be to responsible for the high levels of pollution seen in this study. This finding contradicts a study conducted in Nigeria by Egbueri and Mgbenu (2020), Eyankware et al., (2022a) Tables 6 and 7.

Table 7 Geoaccumulation Index scale (Igwe et al., 2020; Igwe et al., 2022; Hazzeman et al., 2017)

I_{geo}values	I_{geo}Class	Designation of sediment quality
>5	6	Very highly polluted
4-5	5	Highly populated
>3-4	4	Moderate to highly polluted
2-3	3	Moderately polluted
>1-2	2	Moderated to unpolluted
0-2	1	Unpolluted
0<	0	Background concentration

3.5 Pearson Correlation Matrix

The correlation matrix is a useful tool for assessing the correlations between two variables. In most cases, the correlation coefficient is between -1 and +1. The relationship is considered to have a negative slope or be anti-correlated if the r-value is close to -1. The relationship is said to have a positive slope or be correlated when the value of r is near +1. The points are considered to be uncorrelated if the value is zero (Omoko et al., 2023; Onyeanwuna et al., 2024; Akakuru et al., 2023a, b). The correlation matrix (Table 8) showed that there was a positive correlation between Zn and Cr (0.560), and Zn and Pb (0.491). From Table 8, there exists a weak correlation amongst elements and the majority of the elements are not correlated implying that there is no relationship between the two variables. In other words, as one variable moves one way, the other moves in another unrelated direction. This also suggests that anthropogenic sources are the major source of heavy metals in soils (Anegbe et al., 2018; Ugbome et al., 2018).

3.6 Principal Component Analysis (PCA)

PCA is a based classification method that seeks to explain the variation of a large number of interconnected variables (Eyankware & Akakuru, 2022; Akakuru et al., 2021a, 2021b). It demonstrates how variables are linked, which reduces the dataset's complexity. PCA extracts eigenvalues and eigenvectors from the original data's covariance matrix. Principal components (PCs) are the uncorrelated (orthogonal) variables obtained by multiplying the original correlated variables with the eigenvectors (loadings). The eigenvalues of the PCs assess their associated variance, the loadings indicate the original variables' participation in the PCs, and the transformed observations are referred to as scores. In PC1, 62.5% of the variables in the components have loadings, they include Zn (0.718), Cr (0.777), Cu (0.570), Pb (0.697), and Ni (0.620). PC2 has a loading of 37.5% among variables Cu (0.579), Cd (0.697) and Co (0.615). For PC3. 12.5% of the variables have loading As (0.671). The result of this PCA confirms previous results and it further reveals that the continued anthropogenic activities within the locality have greatly affected the soil in the area (Akpoveta et al., 2010; Osakwe, 2014; Osakwe et al., 2012). Soil contamination with heavy metals draws a genuine concern given their negative consequences for the living biota. The diligent and non-biodegradable nature of weighty metals facilitates their collection in the climate. Soil is getting the gigantic measure of toxins from different sources. Past basic cutoff points, HMs give a perilous effect on human well-being as they ruin the ordinary working of the living frameworks. The huge amount of waste created should be dealt with appropriately keeping in thought the natural estimates associated with land treatment. The raised heavy metal levels in the horticultural soils rely upon the attributes of the dirt and the pace of use by the provider with its essential fixation (Eyankware & Ephraim, 2021; Agidi et al. 2022; Akakuru et al. 2022b) Table 9.

3.7 Spatial Distribution of Heavy Metals in Soil Within the Study Area

3.7.1 Zinc (Zn)

Zn concentrations in soil range from 9.37 to 32.48 mg/kg in the research area, with an average value of

Table 8 Pearson correlation matrix

	Zn	Cr	Cu	Pb	Cd	Co	Ni	As
Zn	1							
Fe	0.025488							
Cr	0.560*	1						
Cu	-0.16975	-0.33752	1					
Pb	0.491*	0.272765	-0.3171	1				
Cd	0.026617	-0.00129	0.202242	0.167255	1			
Co	-0.3282	-0.26215	-0.16555	-0.17461	-0.1986	1		
Ni	-0.08498	-0.38656	0.421162	-0.35799	0.153029	0.105209	1	
As	0.017426	0.084328	-0.1274	-0.07929	-0.12653	0.031307	-0.15348	1

*Moderate Correlation

Table 9 Table PCA

	Communalities	Component		
		1	2	3
Zn	.639	.718	.314	.158
Cr	.618	.777	.014	.120
Cu	.669	-.570	.579	-.092
Pb	.523	.697	.193	.022
Cd	.501	-.018	.697	-.123
Co	.510	-.358	-.615	.056
Ni	.605	-.620	.330	.334
As	.557	.118	-.305	-.671
	Eigenvalues	.743	1.206	-.196
	Variance (%)	34.11195	19.35694	8.905483
	Cumulative var. (%)	29.885	48.468	64.617

17.76 mg/kg. The highest concentration of Zn was observed in NW, and NE parts of the study area as shown in Fig. 3a. About the WHO standard based on their standard for soil (Table 10), the Maximum Permissible Addition (MPA), of Zinc in the study area is relatively low, though low hazardous. The relatively high concentrations of Zn in the aforementioned area are linked to disposed of refused coupled with the geochemical content of the riverine region in the study area (Oli et al., 2022; Obasi et al., 2022; Usman et al., 2022; Omoko et al., 2023)

3.7.2 *Chromium (Cr)*

Cr concentrations in soil range from 4.26 to 21.49 mg/kg in the study area, with a mean of 10.20 mg/kg (see Table 1). Findings from Fig. 3c, it was observed that a highest concentration of Cr in soil was in the SW and SE axis of the study area. Jankiewicz and Ptaszynski

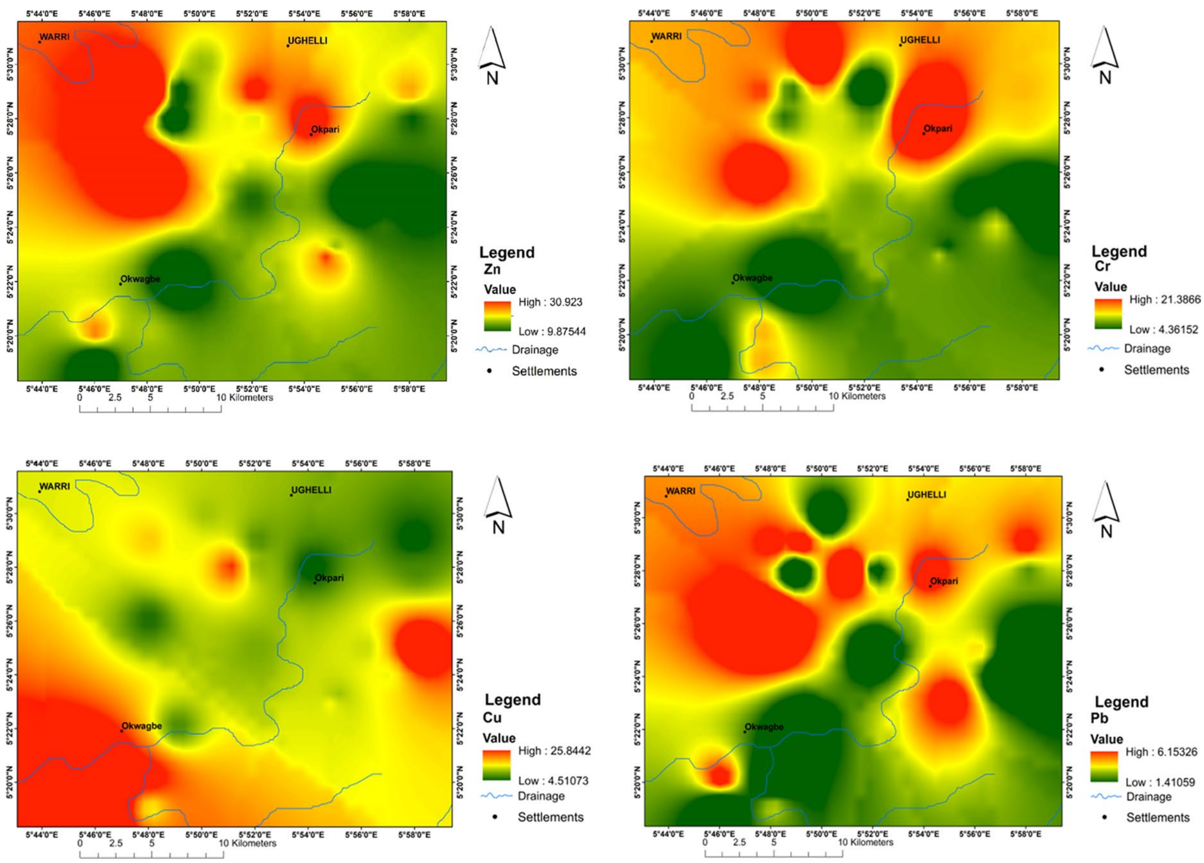

Fig. 3 Spatial distribution of Zn, Cr, Cu, Pb, Ni, As, Co, Cd, Geo accumulation index, PLI, PN, and ERI (Ti*Pi) respectively

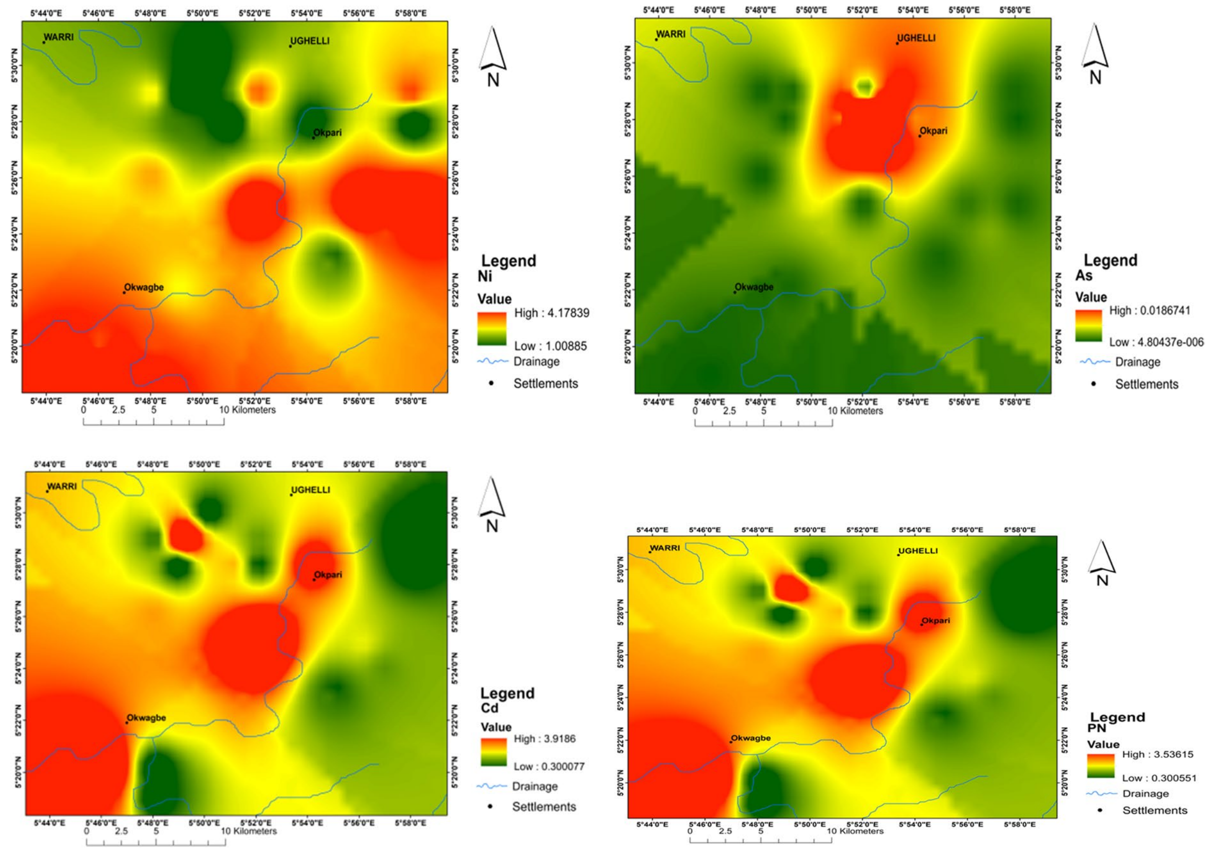

Fig. 3 (continued)

(2005) found that the concentration of Cr in the soil varies greatly and is dependent on the nature of the parent geological materials from which the soil was generated. Furthermore, anthropogenic activities such as mining, especially near active mines, may considerably increase Cr concentrations in soil. When plants take HMs from the soil and ingest them, they can cause kidney and liver damage in humans (Harendra et al., 2017) .In comparison with RGTS, chromium element which is moderately hazardous has all its concentration in the soil above MPA.

3.7.3 Copper (Cu)

Cu concentrations in soil vary from 4.38 to 26.36 mg/kg in the study area, with a mean value of 10.42 mg/kg (see Table 1). From Table 1 and Fig. 3c, it was observed that a high concentration of Cu was observed at sample locations DO/06, 12, 19, 20, and 21. SW, and SE respectively. This could be attributed to geological parent material which is the most important natural source of Cu in soil. Similarly, Cu is one of the few metals that can be found in nature as an uncombined mineral. On the other hand, Cu is introduced into the soil, it can get tightly linked to organic and geological components, making it difficult to spread. Cu's excess effect could be felt in nearby places where there is a high concentration of Cu or in plant products that have absorbed a high concentration of Cu and are carried to other locations. Cu in the soil can be linked to copper ores mining and processing, according to Igwe et al. (2021); Zhuang et al. (2009). Cu is a major contributor to pollution in the environment, affecting environmental quality and ecosystem resources. Some metal pollutants, such as Cu, may escape during ore mining or processing and be distributed over considerably longer distances, harming soil sediment quality (Eyankware et al., 2022a). By comparing the concentration

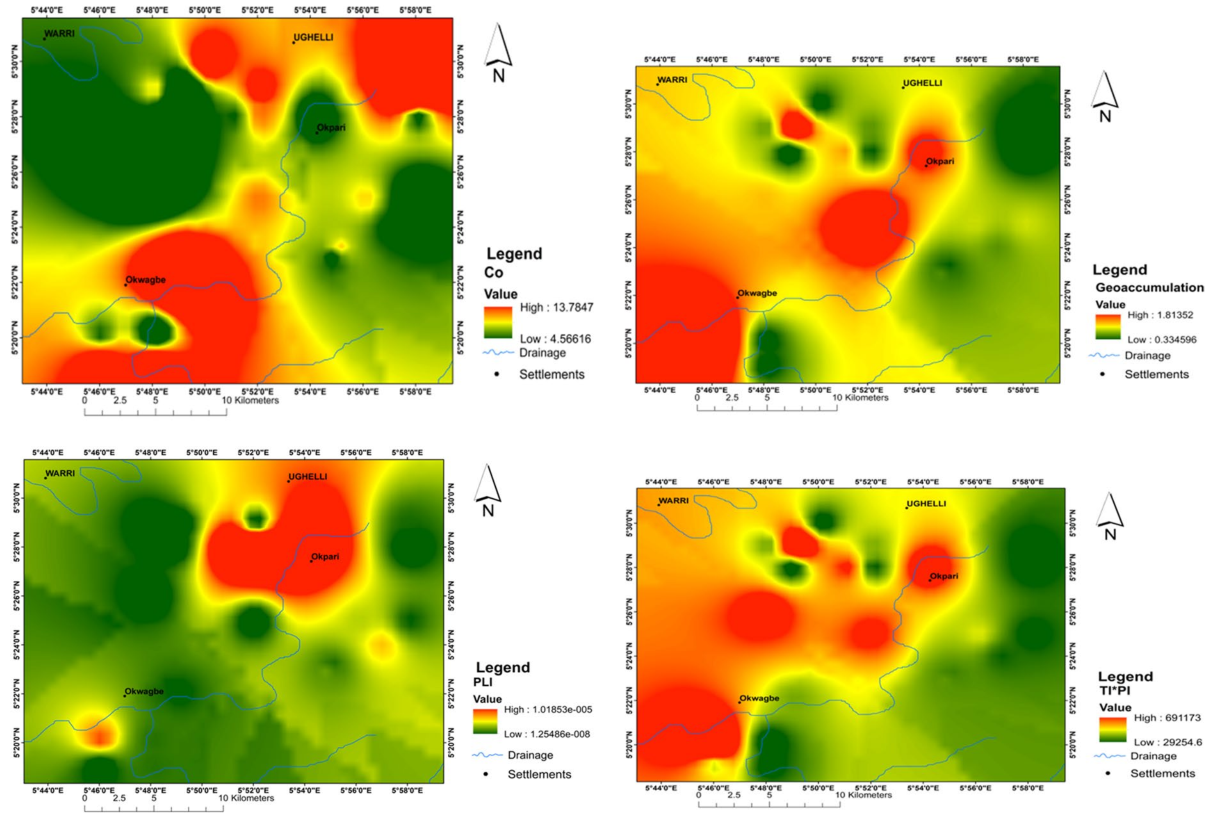

Fig. 3 (continued)

Table 10 WHO heavy metal standard for soil

Heavy metal	Target Value of soil (mg/kg)
Zn	50
Cr	100
Cu	36
Pb	85
Ni	35
As	4.5
Co	24
Cd	0.8

of Cu in the study area with the RGTS, it was observed that all the soil sample collected have their concentration above the MPA. Although Cu is rated moderately hazardous by Akakuru et al (2022a) yet caution is still highly demanded.

3.7.4 Lead (Pb)

Pb is a non-essential element that is hazardous, and its effects have been studied more thoroughly than those of other trace metals (Egbueri & Mgbenu, 2020; Eyankware et al., 2022a; Igwe et al., 2021; Raikwar et al., 2008; SON, 2015). To understand the ease of accessibility of Pb in soil, the pH of all the soil samples whose Pb contents were studied was measured. With a pH of 6–8 (near-neutral soils), Pb is tightly bonded to soil particles and may not be available for plant uptake. The concentration of Pb for this study ranges from ranges between 1.38 to 6.31 mk/kg with an average value of 3.29mk/kg as shown in Table 1. From Fig. 3d, it was observed that NW, NS, and a selected part of SW, could be attributed to refuse disposal in the environment which is often used as a landfill or littered on the ground. The concentration of Pb in the study area is observed to be below the MPA when compared with the WHO.

3.7.5 Nickel (Ni)

Ni concentrations in soil range from 0.99 to 4.27 mg/kg in the study area, with a mean value of 2.54 mg/kg (Table 1). The highest concentration of Ni was observed in SE, SW, and selected parts of NE see Fig. 3e. Ni can also be found in soils in a variety of forms, including adsorption of complex formation on organic cation surfaces or inorganic cation exchange surfaces, inorganic crystalline minerals or precipitates, water-soluble, free-ion, or chelated metal complexes in soil solution, and inorganic crystalline minerals or precipitates. The concentration of Nickel in the study area is about 50% above the MPA limit. However, Ni is rated moderately hazardous.

3.7.6 Arsenic (As)

As is a naturally occurring substance that can be found throughout the earth's crust. As is a highly toxic metalloid that is widely distributed on the Earth's surface and in its hydrosphere (Emilie et al., 2017; Igwe et al., 2022). It is a well-known poison, and even a small amount of arsenic trioxides, such as 0.1 g, can be extremely harmful to the environment. Although persistent arsenic poisoning as a result of occupational exposure is well-known, high arsenic toxicity is now rare (WHO, 1981). As has been known to be a human carcinogen at high doses for over a century, and it is now widely established that ingestion of inorganic arsenic can induce skin, lung, and leukemia cancer, while inhalation can cause respiratory tract cancer (Jarup, 1992; Kotoky et al., 2008). Long-term exposure can result in skin illnesses such as blackening and swelling of the palms and torso (Opara et al., 2022, 2023a). Because of the potential for harmful human effects, excessive arsenic concentrations in the natural geochemical environment have been a serious concern in recent years (Thornton, 2016). Concentrations in soil range from 0.00 to 0.02 mg/kg in the study area, with a mean value of 0.002 mg/kg (Table 1). It was observed that sample location DO/10 had the highest As concentration in the soil (see Table 1), This could be attributed to biochemical activities that lead to the ingestion of detrital organic carbon (Eyankware et al., 2020; 2022b). The values of As in the study area are very low and are all less than the MPA limit of RGTS.

3.7.7 Cobalt (Co)

Cobalt is a naturally occurring element that resembles iron and nickel in characteristics. Small levels of cobalt occur naturally in soil (Igwe et al., 2021). Within the study area, Co concentrations vary from 4.38 to 13.97 mg/kg, with a mean of 8.88 mg/kg (see Table 1). HMs such as Co, which are emitted by lead-zinc mining under particular conditions, can stimulate, transfer, and build up in various target media such as soil, impacting plants, animals, and humans directly or indirectly, according to Igwe et al. (2021).

3.7.8 Cadmium (Cd)

Cadmium is an element found in mineral soils that occurs naturally (Igwe et al., 2022; Segura et al., 2006). The concentration of Cd in soil ranges from 0.27 to 4.01 mk/kg with an average value of 1.40 mk/kg. The highest concentration of Cd was observed in SW, SE, and selected parts of NE, this could be attributed to geogenic sources. According to Agidi et al. (2022) and Li et al. (2015), Cd concentration depends on geologic parent materials, however, soil cadmium concentrations are normally less than 1 mg/kg, which is in line with the WHO's 0.8 mg/kg permitted limit. Cd has about 59% of its concentration above the MPA limit of RGTS. Moreso, it is rated to be highly hazardous.

4 Conclusion

This study carried out assessment of soils impacted by municipal wastes within some parts of Delta State in Nigeria for heavy metals concentration, pollution indices including potential ecological risk (ERI).Geochemical analysis revealed concentration of heavy metals in soil Zn, Cr, Cu, Pb, Cd, Co, Ni, and As with value ranges of 9.37 to 32.48, 4.26 to 21.49, 4.38 to 26.38, 1.38 to 6.31, 0.27 to 4.01, 4.38 to 13.97, 0.99 to 4.37, and 0.00 to 0.02 respectively. The estimated value obtained from the heavy metal index suggested that ERI, Igeo, Cdeg, and PNI range from 23189 to 707973.2, 0.322493 to 1.83971, 1.0713 to 6.11397, and 0 to 1.7 x 10-5 respectively. Findings from heavy metals index such as ERI suggested that estimated values obtained from ERI were above 600, this implies that analyzed soil is of very high ecological risk. Estimated results from Igeo revealed that analyzed soil samples fell within the category of unpolluted (Igeo class 1), deduction from Cdeg revealed that analyzed soil samples fell within <8>32 which implies that soil samples can be classified to be low contamination. This is in line with the results obtained from Igeo. Finally, results from PNI suggested that analyzed soil samples fell within clean, slightly clean, and moderately polluted, with a percentage value of 36.4, 27.3, and 13.6 % respectively. Results obtained from PCA and Pearson correlation revealed that the occurrence of heavy metals in soil is attributed to human activities.HM pollutants, as well as their degradation in soil ecosystems are known to be typically linked to human activities such as the industrial revolution, the use of agrochemicals on farmland, energy generation, and fuel processing, mining, and steel production, and waste disposal, all of which pose a threat to all forms of life.The outcome of this study is an indication of the influence of anthropogenic activities on the study area which has heavily impacted on the quality of soil. It is important to note that the polluted soil has interference with the water resources and if not checked could pose serious threat on humans and other living plants and animals within the ecosystem. The presence of these metals in soil could endanger human and aquatic life, and they could contaminate surface water, groundwater, and the food chain. As a result, measures should be made to prevent its accumulation in certain locations, as the harmful effects of heavy metal fallout pose a serious threat to human life.

Data Availability The datasets generated during and/or analyzed during the current study are available from the corresponding author on reasonable request.

Declarations

Compliance with Ethical Standards This research work is carried out in compliance with transparency, moral values, honesty, and hard work. No human participation or animals are involved in this research work.

Conflict of Interest The authors declare that they have no competing interests.

Ethical Approval As per the literature review, this is neither a repetition of any work nor copied key data from other's work. The methodology, findings, and conclusions made here belong to original research work as per our knowledge and belief.

Informed Consent Every step of processing for publication informed to all co-authors of this paper at the earliest, and everything is carried out with collective decision and consent.

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