



Studies of heavy metal in soil at Omoku, River State, Nigeria, using Pollution Indices and Potential Ecological Risk

ABSTRACT

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Competing Interests.

The authors declare no competing interests.

This study used Atomic Absorption Spectrometry (AAS) to measure the levels of heavy metals (HM) in soil affected by oil spills in a few locations in River State, Southern Nigeria, in order to investigate the ecological dangers and pollution status of HM. This study examined the heavy metals iron (Fe), arsenic (As), lead (Pb), mercury (Hg), barium (Ba), vanadium (V), nickel (Ni), copper (Cu), zinc (Zn), and chromium (Cr). The study analyzed the outcomes of a heavy metal risk assessment index, which encompassed the level of contamination, the Geo-accumulation index (Igeo), and the prospective ecological risk assessment (ERI). Findings from the showed that Nemerow Pollution (PNI), Potential Ecological Risk Index (PERI), Degree of Contamination (Cdeg) ranges from 12.64 to 28.26, 2.40 to 518.48, and 17.63 to 32.44 respectively. Results obtained from the study are considered to be fairly above the international standard at some locations. Deduction from the study suggested that human activities such farming, oil spillage, solid waste disposal, and automobile workshop were identified to be the primary contributors of heavy metal pollution in the soil (Cdeg) and PNI. As seen by the uncontaminated soil samples and the negligible effect of local human activity on the ERI, the Igeo results run counter to the ERI results. The Cdeg observation indicated that the soil was not very polluted.

Keywords: Index, Oil Spillage, Pollution, soil, heavy metal

1. Introduction

Due to fast urbanization and population growth, unchecked waste production and negligent disposal are serious environmental problems, especially in emerging nations as stated by Eyankware et al., (2024). A lack of strict waste management legislation, poor urban planning, and a lack of effort by government authorities have all been blamed for the inappropriate disposal of waste, especially in Nigerian major cities (Omene et al., 2015; Akinseye et al., 2023; Eyankware et al., 2016). These abandoned waste, which are frequently the consequence of human activity, are regarded as trash or waste because their original owners can no longer use them. Obasi et al. (2015) and Igwe et al. (2020, 2021) pointed out that irresponsible and widespread waste disposal has greatly increased heavy metal contamination in soil, and water resources, which is a major health risk to people. The amount and composition of waste produced in any area are influenced by several factors, including population size, consumption patterns, social characteristics, economic strength, and available public services

(Eyankware, 2019). Elevated concentrations of heavy metals (HMs) are a major concern because soil, which is the primary recipient of these metals from municipal waste, can become contaminated (Odesa et al., 2024a; Eyankware & Ephraim, 2021; Eyankware & Obasi, 2021; Islam et al., 2015; Obasi et al., 2015; Turhan et al., 2020; Ulakpa & Eyankware, 2021). Sources of heavy metals in soil in an area include oil spills, municipal waste from human activities, small industries, and commercial operations (Ezemokwe et al., 2016; Igwe et al., 2020; Karim et al., 2014; Singh et al., 2011; Wei & Yan, 2010). Additionally, ashes from heating systems, hazardous waste (e.g., paint, batteries, insecticides), and the organic fraction, which accumulates metals, are common sources of contamination (Obasi et al., 2022).

Heavy metals pose serious problems because of their toxicity and long-term stability. Similarly, heavy metals do not biodegrade like organic pollutants do (Eyankware & Obasi, 2021). When vegetables are cultivated in soil

and make their way into the food chain (Odesa et al., 2024b; Igwe et al., 2020). Furthermore Eyankware & Ephraim, (2021); Onwe et al., (2024) were of the view that heavy metal contamination of soil can have detrimental effects on ecosystems, change physicochemical characteristics, and damage soil biology. It has been demonstrated that this type of contamination has a detrimental impact on soil production, animal and human health, and flora diversity (Ogunbanjo et al., 2016; Riyad et al., 2015; Papa et al., 2010; Ulakpa et al., 2021). The pollution load index (PLI), enrichment factor (EF), contamination factor (Cf), degree of contamination, and index of geoaccumulation (Igeo) are some of the heavy metal indexes that have been used over the past few decades to assess the pollution status of heavy metals in soil (Islam et al., 2014; Islam et al., 2015). Different methods are used in interpreting the level of heavy metal pollution in soil. Examining, regulating, and managing these environmental risks all depend heavily on ecological risk assessment (Onwe et al., 2022; Ulakpa et al., 2020; Igwe et al., 2020; Kumar et al., 2018; Sahito et al., 2016). Ogunbanjo et al. (2016) stated that heavy metals are generally considered harmful to the environment, particularly in the vicinity of dumpsites and other urban and rural waste sites. Both human health and ecosystems are seriously at risk from these toxins. Additionally, Eyankware and Obasi (2021) pointed out that plants can absorb heavy metals from contaminated soils and introduce them into the food chain, thereby harming the end users which are human. Despite the recognition of these issues, no studies have yet investigated the specific characteristics of pollutants and the ecological effects of heavy metals on soil in the study area. Therefore, this study aims to assess the impact of heavy metals on soil using indicators such as Nemerow Pollution Index (NP), Contamination Factor (Cf), Degree of Contamination (Cdeg), and Geoaccumulation Index (Igeo).

Location, accessibility, Climate, vegetation and topography

The study area is in Port Harcourt, River State, Nigeria, and is situated between latitudes 4°47' N–4°49' N and longitude 6°58' N–7°01' E, as shown in Fig. 1. As illustrated in Fig. 1, the research area comprises a network of major and small roads. The research area experiences both the rainy and dry seasons and is located in a tropical environment. The research area's

typical rainfall, according to Nwankwor et al. (2016), is between 1000 and 2000 mm. They also noted that the rainy season lasts from mid-April to early November, with July and October seeing the most significant rainfall. The research area has temperatures between 26° and 28°C, and the vegetation is normally found in mangrove swamp forests, though there has been significant human alteration due to farming, lumbering, and exploration; in many cases, grassland has taken its place. According to Nwankwor et al. (2016), it is further distinguished by hazy, dry, and dusty winds that originate from the Arabia-Eurasia high pressure band and are known as the Tropical Continental Air Mass or the North-East Trade winds. According to Edokpa and Nwagbara (2017), the Niger Delta's coastline region experiences an average monthly wind speed pattern of 0 to 3 m/s, with periods of lower and higher trend seen during the night and evening. The research area's topography is moderate, with an average elevation of roughly 18 meters above sea level. Imposing hills that rise above the surrounding environment are conspicuously absent. After rain, flooding is frequently encouraged by the area's low-relief features and topography. Many creeks with a dendritic drainage pattern meander across the study area, and some of their tributaries discharge their water into the Atlantic Ocean.

Geology/hydrogeology

The research area is isolated from the sea by a sizable belt of brackish/saline mangrove swamps, especially along the coast (Oteri and Atolagbe 2003). Salinity-related water supply issues are limited to the saline mangrove swamp and the sandy islands and barrier ridges that surround it along the coast. Three groups of the Niger Delta Formation were identified by Short and Stauble (1967): Akata, Agbada, and Benin (Fig. 1). With thin shale/clay interbeds, the Benin Formation, a system of many aquifers in the delta, is mostly composed of massive, very porous sands and gravels. Despite the hopeful findings of drilling several boreholes into the Benin Formation aquifers, many of them have been abandoned due to high salinity (Oteri and Atolagbe 2003). The Benin Formation, formed during the continental period of the Niger Delta, has a sediment thickness of around 2100 meters, according to Weber and Daukoru (1976). The Benin Formation is mostly composed of sandstone, sands, and gravel, with clays showing up as lenses, according to Onyeagocha (1980).

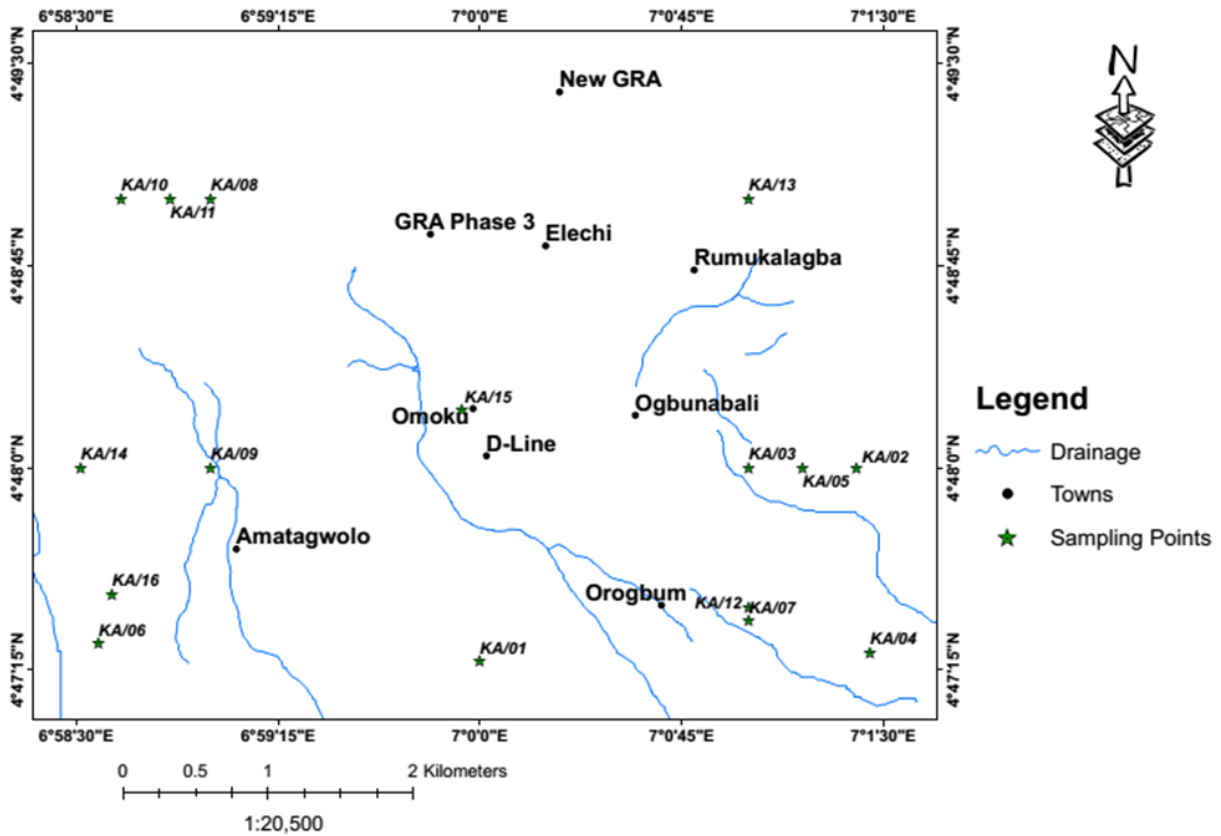


Fig. 1: Topography Map of the study area

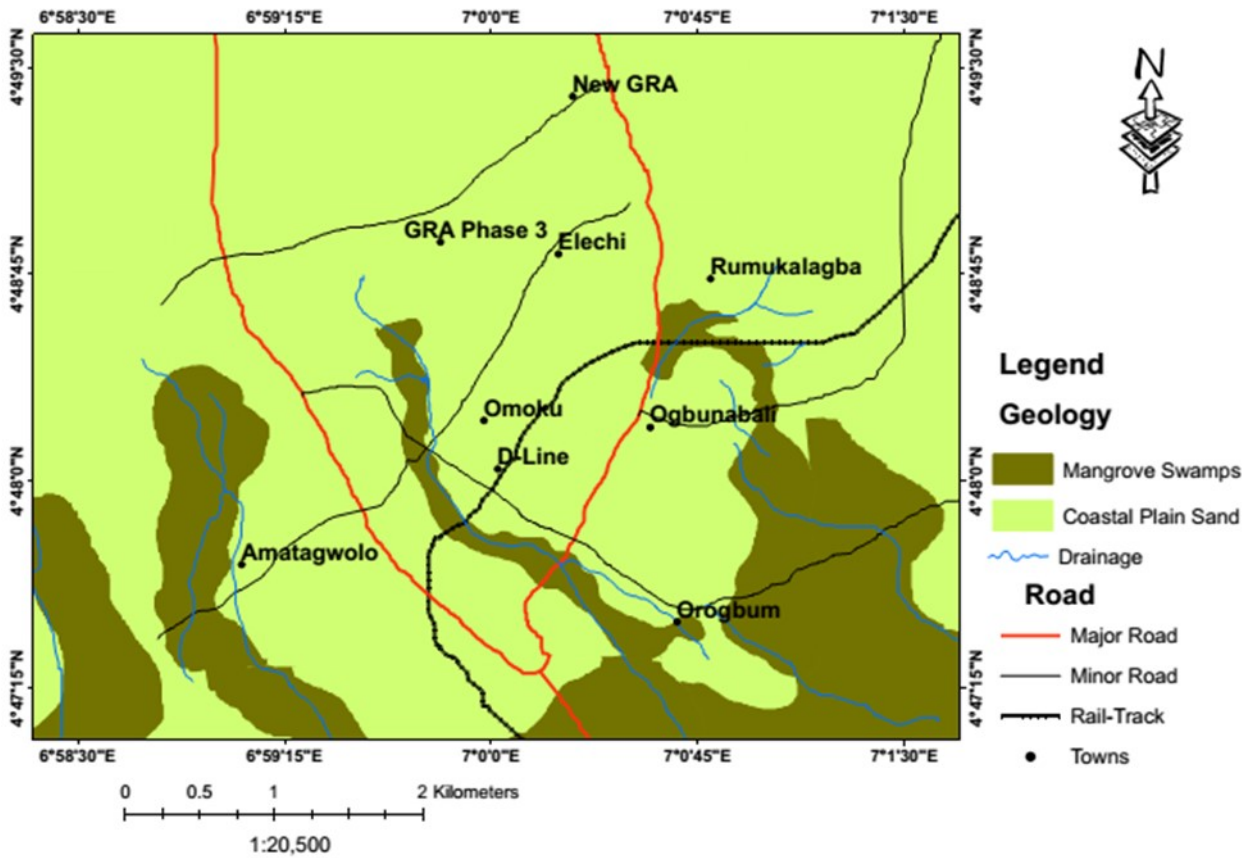


Fig. 2: Geology of Map of the study area.

Sands and sandstones range in thickness, have coarse to fine grains, and are largely unconsolidated. With intercalations of clay and shale, the Benin Formation is primarily composed of continental sand and gravel that are highly resilient and contain fresh water (Oteri 1990). There are multiple aquifers in the Niger Delta Basin, which is composed of sizable, porous sands and gravels. Seawater is covered by a freshwater lens in the unconfined aquifer of the coastal beach ridges. The majority of confined aquifers in the research area have saline water beneath them. Saltwater intrusion has happened in certain Niger Delta zones when freshwater-bearing sands are covered by saltwater-bearing sands. Sands that contain salt water are subsequently spread over these (Oteri and Atolagbe, 2003). In the Niger Delta, saltwater intrusion occurs into aquifers that are not confined as well as those that are. The unconfined aquifers of coastal beach ridges or sandy islands inside the saline mangrove belt contain freshwater lens float above the salt water-bearing sands (Oteri 1990). The Benin Formation's confined aquifers were further separated into two main areas based on the depth of occurrence of saline water sands: areas where saline water sands are encountered at shallow depths beneath freshwater sands, and areas where saline water sands are encountered at shallow depths beneath both freshwater and saline water sands in succession (Oteri and Atolagbe 2003).

Sixteen (16) soil samples were taken at 10 km intervals around certain oil spill locations in River State, Nigeria. Soil samples from a depth of 0 to 15 cm were collected using a steel auger and placed in clear plastic bags. Samples were spread out on clear plastic on a bench in the lab and allowed to air dry for a few days. Before they could be examined, they were wrapped in clear plastic bags after being sieved at a size of 2 mm.

After properly cleaning 250 cm³ conical flasks, 20 g sieved air-dried soil samples were added, and 100 cm³ of 0.5 M nitric acid was added. The flasks were shaken mechanically for a minimum of half an hour using a shaker. 100 cm³ plastic bottles were then filled with the ingredients after they had been filtered through ashless Whatman filter paper 40. After testing for background target analysis, a few control samples were spiked with known concentrations of arsenic (As), cobalt (Co), chromium (Cr), cadmium (Cd), copper (Cu),

lead (Pb), nickel (Ni), and zinc (Zn). The extraction process was then run through to evaluate the recovery rates. The variations between the baseline concentrations and the concentrations of the spiked samples were used to calculate the percent recoveries. The general -purpose reagent cadmium nitrate, which must be at least 99 percent pure, was used to prepare the solutions that were used to spike the samples for cadmium. Analytical grade lead nitrate salt and analytical grade copper and zinc granules were used to produce the solutions used to spike samples for lead, copper, and zinc. Before being employed in the sample determination, a reagent blank was also made for each metal and put through the same procedure. Calibration curves were made using analysis-grade metals and metal salts. A Varian Techtron AA6 atomic absorption spectrophotometer and related metallic hollow cathode lamps were used to measure the levels of zinc, lead, copper, and cadmium. Acetylene gas was used as fuel, and air served as support. In each instance, an oxidizing flame was employed. Using calibration curves, the concentrations of four metals were determined. The instrument was zeroed using a reagent blank. The aspiration of soil sample extracts was then carried out after the aspiration of standard solutions.

Soil Pollution indexes calculation

Nemerow pollution, contamination factor, geoaccumulation index (Igeo), and possible ecological risk index were used to calculate the presence of heavy metals in soil.

Data Analysis

The SPSS statistical software was used to analyze the data in order to produce Principal Component Analysis (PCA) and Pearson correlation analysis.

(i). Potential ecological risk index

$$E_r^i = C_f^i * T_r^i = T_r^i * C_i / C_b$$

Equation 1

The potential ecological risk index was first proposed by Hakanson (1980)

where E_r^i denotes the potential ecological risk index of metal i^{th} ; T_r^i is the toxic response

factor of the i th 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 (Weihua et al. 2010; Islam et al. 2015). 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: $E_r^i < 40$, $40 \leq E_r^i < 80$, $80 \leq E_r^i < 160$, $160 \leq E_r^i < 320$ and ≥ 320 signifying low, moderate, considerable, high and very high risk, respectively (Hakanson 1980; Ogunkunle and Fatoba 2013; Riyad et al. 2015). The sum of the individual potential ecological risk factors is used to calculate the potential ecological risk index for different heavy metals in the soil. It symbolizes the vulnerability of diverse biological populations and potential hazards brought on by heavy metals. Equation 2 was used to calculate each measurable heavy metal's possible ecological risk index.

$$RI = \sum_i^n E_r^i \quad \text{Equation 2}$$

(ii). The Geoaccumulation index (Igeo)

$$I_{geo} = \log_2 \left(\frac{C_n}{k B_n} \right) \quad \text{Equation 3}$$

As proposed by Muller, (1979) Where C_n is the measured concentration ($\mu\text{g/g}$) of element n , and B_n is the geochemical background concentration, k is geochemical values (mg/kg) see equation 3.

(iii). Contamination factor (C_{deg})

$$C_{deg} = \sum_{i=1}^n C_f^i \quad \text{Equation 4}$$

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

(iv). Nemerow pollution

$$NP = \sqrt{(P_{ave}^1 + P_{max}^2)/2} \quad \text{Equation 5}$$

As proposed by Ogunde et al. (2020)

P_{ave} and P_{max} are the average and maximum values of single pollution index (SPI) for all heavy metals see equation 5. The NP indices of each metal was calculated and classified into 5 grades: $NP < .7$, $0.7 \leq NP \leq 1.0$, $1.0 \leq NP \leq 2.0$, $2.0 \leq NP \leq 3.0$ and $NP > 3.0$ indicating safety, precaution, slightly polluted, moderate polluted and serious polluted domain, respectively (Cheng & Zhu 2007; Ogunkunle and Fatoba 2013)

v. Principal component analysis

The sum of the individual potential ecological risk factors is used to calculate the potential ecological risk index for different heavy metals in the soil. It symbolizes the vulnerability of diverse biological populations and potential hazards brought on by heavy metals. Equation 2 was used to calculate each measurable heavy metal's possible ecological risk index.

$$\sigma^2 = \frac{1}{N} \sum_{i=1}^N (X_N - N)^2 \quad \text{Equation 6}$$

Results and Discussion

Table 1, shows the concentration of heavy metal in soil across the study area. Table 2. show the results for three important indices used to assess environmental contamination: the Nemerow Pollution Index (NPI), the Potential Ecological Risk Index (PERI), and the Degree of Contamination (Cd) across various sampling sites (KA/01 to KA/16).

Potential Ecological Risks Assessment

The Swedish scientist Hakanson (1980) created the potential ecological risk index. In addition to reflecting the toxicity and ecological sensitivity of the concentration of pollutants, it has been used to assess the negative effects of contaminants on humans and the environment (Hakanson, 1980; Suresh et al., 2012; Weihua et al., 2010). It was initially employed as a method for assessing sediment pollution in aquatic environments. According to several studies (Qingjie et al., 2008; Eyankware et al., 2023; Suresh et al., 2012; Ogunkunle & Fatoba, 2013; Iqbal & Shah, 2014; Riyad et al., 2015; Osipova et al., 2016), it has been effectively applied for risk assessment of soils, dust, and air. The PERI was introduced by Hakanson in 1980 and is calculated using a formula that categorizes

risk into five grades: five criteria grades were employed: $PERI < 40$, $40 \leq PERI < 80$, $80 \leq PERI < 160$, $160 \leq PERI < 320$ and ≥ 320 signifying low, moderate, considerable, high and very high risk, respectively.

The evaluated PERI values show a wide range, from 2.396079 (KA/07) to 518.48 (KA/09). Recent evaluations showed PERI values ranging from 2.396079 to 518.48, with approximately 87.5% of samples falling into the low-risk category. However, two samples KA/01 and KA/10 were classified as moderate to considerable risk, while one sample indicated very high risk. This distribution underscores the necessity for targeted environmental management strategies in areas identified as having higher ecological risks.

Index of Geoaccumulation (Igeo)

In order to check the level of contamination of elements concentrations in sediment, water, dust, and soil, Muller (1979) created the index of geoaccumulation (Igeo), which has been widely used in evaluating their pollution status globally (Hazzeman et al., 2017). The classifications of (Igeo) and their respective interpretations

are $Igeo \leq 0$ (practically unpolluted), $0 < Igeo \leq 1$ (unpolluted to moderately polluted), $1 < Igeo \leq 2$ (moderately polluted), $2 < Igeo \leq 3$ (moderately to strongly polluted), $3 < Igeo \leq 4$ (strongly polluted), $4 < Igeo \leq 5$ (strongly to extremely polluted), and $Igeo \geq 5$ (extremely polluted) (see Table 3), (Olujimi et al., 2014; Qing et al., 2015; Wei & Yan, 2010). All the evaluated samples have negative Igeo values, indicating no significant pollution for Arsenic (As), Barium (Ba), and Vanadium (V). While, Nickel (Ni), Mercury(Hg), Copper (Cu) and Chromium (Cr) have negative Igeo values for all samples except for sample KA/10 which indicate pollution. 12.5%, 68.8% and 50% of the samples have negative Igeo for Fe, Pb and Zn. Meanwhile, 87.5% of the samples indicate positive Igeo values for Iron, this may signifies pollution, and public concern. According to Eyankware et al., (2024), soils with high pH, high organic matter, or high levels of accessible iron are more likely have iron toxicity. Similarly, overconsumption of

iron by humans can cause joint injury, or arthritis. Diabetes. issues relating to the pituitary, thyroid, gallbladder, adrenal glands, or spleen.

Degree of Contamination (Cdeg)

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 Cdeg of contamination may be classified based the scale ranging from <8 to >32 : < 8 , $8-16$, $16-32$ and > 32 indicates low degree, moderate, considerable and very high degree of contamination, respectively (Ogundele et al., 2017; Devanesan et al., 2017).

Nemerow pollution (PNI)

PNI (Nemerow 1974) is an additional numerical index that combines several factors into one. The total soil quality level of all the different pollution factors is represented by the NPI value, however. Compared to simply looking at the concentrations of one or two particular contaminants, employing an integrated soil quality index to establish an intrinsic soil risk assessment has better empirical validity (Eyankware et al., 2022a, b). The PNI determines each parameter's proportional contribution to pollution in a soil sample. This will identify the parameter or parameters that determine the quality status. The findings from the NPI evaluations indicate that the NPI values for various metals range from 12.6413 to 28.2593, placing all sampled sites within the "seriously polluted" category. This high level of pollution suggests significant ecological risks, as elevated NPI values correlate with detrimental impacts on local ecosystems, potentially leading to biodiversity loss and habitat degradation.

Spatial Distribution of Heavy Metals in Soil within the Study Area

Iron (Fe)

Secondary oxides that are absorbed or precipitated onto soil mineral particles and iron-organic matter complexes are the primary source of iron in soils that plants can use (Eyankware, et al., 2024). It is important

Table1: Results of heavy metals within the study area.

Sample Code	Co-ordinate		Iron (Fe) mg/kg	Arsenic (AS) mg/kg	Lead (Pb) mg/kg	Mercury (Hg) mg/kg	Barium (Ba) mg/kg	Vanadium (V) mg/kg	Nickel (Ni) mg/kg	Copper (Cu) mg/kg	Zinc (Zn) mg/kg	Chromium (Cr) Mg/kg
	Latitude	Longitude										
KA/01	4°47' N	7°00' E	60.40	<0.001	1430	<0.001	<0.001	<0.001	14.70	27.70	77.90	10.20
KA/02	4°48' N	7°02' E	6710	<0.001	11.70	<0.001	<0.001	<0.001	11.60	21.30	81.40	7.70
KA/03	4°48' N	7°01' E	5810	<0.001	10.30	<0.001	<0.001	<0.001	10.80	14.60	68.10	13.40
KA/04	4°47' N	7°10' E	4780	<0.001	16.20	<0.001	<0.001	<0.001	9.50	18.30	90.40	8.80
KA/05	4°48' N	7°15' E	6110	<0.001	13.70	<0.001	<0.001	<0.001	18.80	20.20	88.30	10.20
KA/06	4°47' N	6°52' E	8430	<0.001	9.10	<0.001	<0.001	<0.001	8.30	16.40	64.40	6.60
KA/07	4°46' N	7°20' E	4990	<0.001	10.20	<0.001	0.003	<0.001	1.70	14.70	29.90	8.40
KA/08	4°49' N	6°59' E	4830	<0.001	15.20	0.30	0.001	<0.001	10.40	10.90	72.30	6.10
KA/09	4°48' N	6°50' E	N/A	0.846	85	10	0.005	<0.001	35	36	140	100
KA/10	4°50' N	6°50' E	N/A	0.462	530	<0.001	<0.001	<0.001	210	190	720	380
KA/11	4°52' N	6°54' E	8110	<0.001	6.10	<0.001	<0.001	<0.001	3.50	24.60	78.30	6.30
KA/12	4°30' N	7°04' E	6070	<0.001	8.40	<0.001	<0.001	<0.001	6.10	18.70	90.10	8.10
KA/13	4°55' N	7°07' E	6880	<0.001	3.60	<0.001	<0.001	<0.001	6.40	11.60	70.47	11.40
KA/14	4°48' N	6°50' E	8330	<0.001	4.30	<0.001	<0.001	<0.001	2.40	30.20	70.40	9.70
KA/15	4°48' N	6°59' E	6410	<0.001	6.10	<0.001	<0.001	<0.001	3.70	24.40	69.20	4.40
KA/16	4°479' N	6°58' E	8030	<0.001	7.40	<0.001	<0.001	<0.001	4.90	18.60	58.30	6.20
Minimum			60.4	<0.001	3.6	0.3	0.001	0.001	1.7	10.9	29.9	4.4
Maximum			8430	0.846	1430	10	0.005	0.001	210	190	720	380
Average			5877.55	0.002	200.05	5.15	0.003	0.001	31.63889	38.83889	145.5206	54.55

Table 2: Summary of Nenerow Pollution (PNI), Potential Ecological Risks Assessment (PERI), Degree of contamination (Cdeg)

	K A/ 01	K A/ 02	K A/ 03	K A/ 04	K A/ 05	K A/ 06	K A/ 07	K A/ 08	KA / 09	K A/ 10	K A/ 11	K A/ 12	K A/ 13	K A/ 14	K A/ 15	K A/ 16	me an	max	Min
PNI	16.93	22.50	19.48	16.04	20.50	28.26	16.73	16.21	12.64	14.76	27.19	20.36	23.07	27.92	21.49	26.92	20.69	28.26	12.64
PERI	89.42	5.24	4.56	5.26	6.52	4.01	2.40	19.50	518.48	93.75	3.83	4.32	3.40	3.76	3.63	3.41	48.22	518.48	2.40
Cdeg	19.38	24.76	21.44	18.48	23.14	29.96	17.63	18.57	18.85	32.44	29.08	22.58	24.80	29.69	23.22	28.41	23.90	32.44	17.63

Table 3: Results of Igeo values of the study area

Sample	Iron (Fe)	Arsenic (AS) mg/kg	Lead (Pb) mg/kg	Mercury (Hg)	Barium (Ba)	Vanadium (v)	Nickel (Ni) mg/kg	Copper (Cu)	Zinc (Zn)	Chromium (Cr)
KA/01	-2.8973	-12.7207	3.487446	-10.2288	-17.7796	-13.5142	-1.8365	-2.437	0.054733	-3.87832
KA/02	3.898316	-12.7207	-3.44592	-10.2288	-17.7796	-13.5142	-2.17819	-2.81604	0.118138	-4.28396
KA/03	3.690541	-12.7207	-3.62978	-10.2288	-17.7796	-13.5142	-2.28129	-3.36092	-0.13924	-3.48466
KA/04	3.409014	-12.7207	-2.97643	-10.2288	-17.7796	-13.5142	-2.46632	-3.03505	0.269432	-4.09132
KA/05	3.763175	-12.7207	-3.21825	-10.2288	-17.7796	-13.5142	-1.48158	-2.89254	0.235523	-3.87832
KA/06	4.227536	-12.7207	-3.80849	-10.2288	-17.7796	-13.5142	-2.66113	-3.19319	-0.21983	-4.50635
KA/07	3.471043	-12.7207	-3.64386	-10.2288	-16.1946	-13.5142	-4.94871	-3.35107	-1.32675	-4.15843
KA/08	3.424026	-12.7207	-3.06835	-2	-17.7796	-13.5142	-2.33573	-3.78256	-0.05289	-4.62001
KA/09	0	-2.99616	-0.58496	3.058894	-15.4576	-13.5142	-0.58496	-2.05889	0.900464	-0.58496
KA/10	0	-3.86892	2.055495	-10.2288	-17.7796	-13.5142	2	0.341037	3.263034	1.341037
KA/11	4.171705	-12.7207	-4.38554	-10.2288	-17.7796	-13.5142	-3.90689	-2.60823	0.062122	-4.57347
KA/12	3.7537	-12.7207	-3.92396	-10.2288	-17.7796	-13.5142	-3.10544	-3.00385	0.264637	-4.2109
KA/13	3.934412	-12.7207	-5.14636	-10.2288	-17.7796	-13.5142	-3.03617	-3.69277	-0.08988	-3.71786
KA/14	4.21032	-12.7207	-4.89002	-10.2288	-17.7796	-13.5142	-4.45121	-2.31234	-0.09132	-3.95083
KA/15	3.832327	-12.7207	-4.38554	-10.2288	-17.7796	-13.5142	-3.82672	-2.62001	-0.11612	-5.09132
KA/16	4.157403	-12.7207	-4.10683	-10.2288	-17.7796	-13.5142	-3.42146	-3.01159	-0.36339	-4.59655

to remember that iron can exist in two different oxidation states: reduced iron (Fe^{2+}) or oxidized iron (Fe^{3+}). The concentration of Fe for this study ranges from ranges between 60.4 to 8430 mg/kg, with an average value of 5877.55 mg/kg as shown in Table 1. Deductions from Fig.3, suggested that Rumukalagba (KA/13), Ogbunaball (KA/02, 03, and KA/05), and sample locations KA/06, KA/14, and KA/16 that are in red color indicate area with high concentration of Fe within the study area. The high concentration of Fe in soil can be attributed to continuous use of inorganic fertilizers in agricultural fields and other human activities. While areas such as

Amatagwolo, GRA phase 3, and selected parts of Orogbum, and New GRA was observed to have low concentration of iron in soil when compared to other parts of the study area.

Arsenic (As)
It is a substance that is found naturally in all parts of the earth's crust and is a very harmful metalloid that is extensively found in the hydrosphere and on the surface of the Earth (Emilie et al., 2017; Igwe et al., 2022). Arsenic trioxide is a well-known poison that can severely harm the ecosystem at concentrations as little as 0.1 g. According to WHO (1981), substantial arsenic toxicity is now rare, but it is widely acknowledged

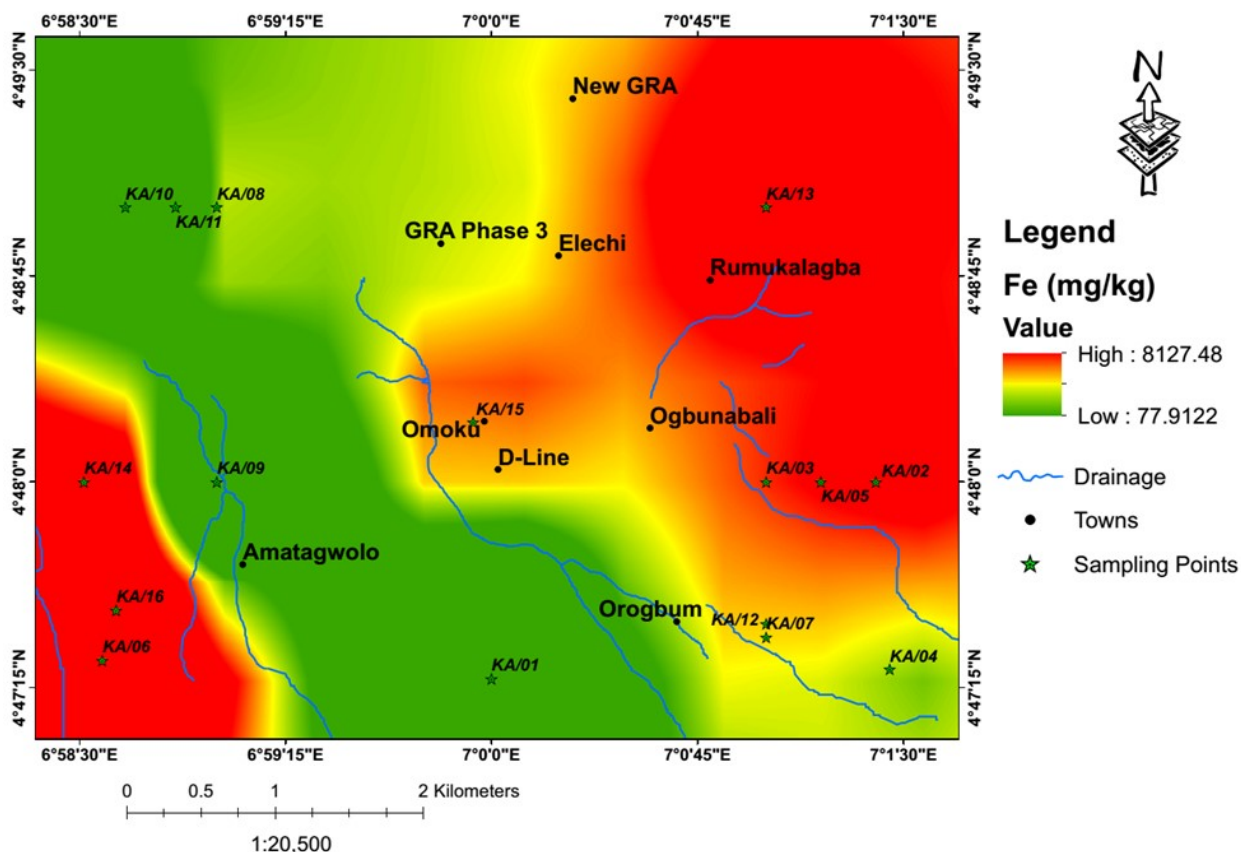


Fig 3: Spatial distribution of Fe within the study area.

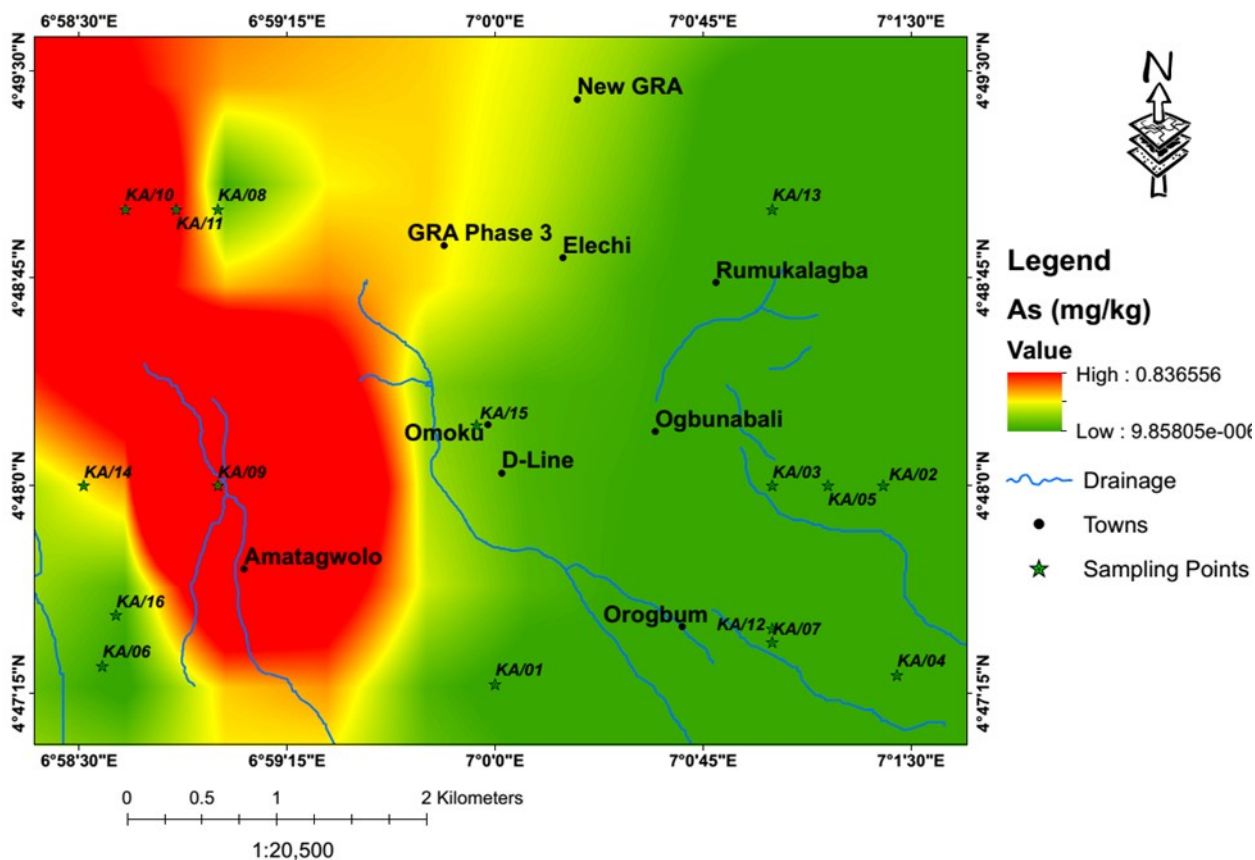


Fig 4: Spatial distribution of As within the study area

that occupational exposure can result in persistent arsenic poisoning. It is now well recognized that ingestion of inorganic arsenic can cause skin, lung, and leukemia cancer, while inhalation can cause respiratory tract cancer. For more than a century, excessive dosages of this substance have been known to cause cancer in humans (Jarup, 1992; Kotoky et al., 2008). Skin conditions like palm and torso edema and blackening can be brought on by prolonged exposure (Opara et al., 2022, 2023a). Excessive quantities of arsenic in the natural geochemical environment have been a major worry in recent years due to the possibility of detrimental human effects (Thornton, 2016). Deduction from the study showed that AS ranges from 60.4 to 8430 mg/kg with an average value of 5877.55 mg/kg, it was observed that the least value of arsenic within the study area was noticed at sampling location SA/01. Further findings from Table 4, suggested that concentration of As where below maximum permissible limit in soil except for sample locations Amatagwolo (KA/08,KA,10, KA/11) and 10.From Fig. 4, it was observed that As in soil increase towards the southwest, and northwest of the study area. Increase in As in soil could be linked to anthropogenic activities within the aforementioned area. Further findings from Fig.4, suggested locations such as New GRA, Rumukalagba, Ogbunaball, Orogum, and selected pars of Omoku has concentration of As in soil.

Lead (Pb)

In comparison to other trace elements, lead's effects have been investigated in greater detail. Pb is a harmful non-essential element (Egbueri & Mgbenu, 2020; Eyankware et al., 2022a; Igwe et al., 2021; Raikwar et al., 2008; SON, 2015). In order to determine how easily accessible lead is in soil, the pH of each soil sample whose Pb content was examined was determined. Pb is firmly bound to soil particles in near-neutral soils with a pH of 6–8, which may prevent it from being absorbed by plants. The concentration of Pb for this study ranges from 0.001 to 0.846 mg/kg as shown in Table 1. It was observed that concentration of Pb within the study area where below permissible limit except for sample location KA/ KA/01 and KA/09 (see Table 4). Findings from Fig.5, revealed that northwest, parts of southwest, and southeast of the study area showed high concentrations of Pb. It could be attributed to

refuse disposal in the environment which is often used as a landfill or littered on the ground.

Mercury (Hg)

According to Eyankware and Obasi, (2021) Eyankware, et al. (2016), soil sample that is saturated with mercury contamination may indicate that the poisonous element is absorbed by any plants or crops that grow there. On the one hand, this may limit the yields and growth potential of some crops and wild species. Result from Table 1, revealed that the concentration of Hg in soil ranges from 0.3 to 10 mg/kg with an average value of 5.15 mg/kg. It was observed that the concentrations of Hg in soil increases towards the southwest of the study area as shown in Fig. 6. Eyankware and Obasi, (2021) attributed high concentrations of Hg to indiscriminate waste disposal, geogenic and anthropogenic process. Findings from 6, showed that the concentration of Hg within the study is low except for locations Amatagwolo (KA/09), high concentration of Hg in soil could be attributed to anthropogenic activities like mining, the chlor-alkali industry, pesticide applications, solid waste incinerators, and the burning of fossil fuels, natural sources of mercury in soil include rock weathering, geothermal emissions, and volcanic eruptions (Eyankware et al., 2024).

Barium (Ba)

The majority of Ba in soil is either bound to soil constituents or found in rock-forming minerals like apatite, calcite, micas, and K-feldspars (Madejón, 2012). According to Eyankware, et al., (2024), the primary sources of barium discharged into the atmosphere by human activity are industrial boilers that burn coal and oil, metal production facilities, and barium mines. Copper smelters and oil drilling waste disposal facilities are the sources of barium discharged into the soil and water. Deduction from Table showed that the concentration of Ba in soil within the study area ranges from 0.001 to 0.005 mg/kg with an average value of 0.003 mg/kg. From Fig. 7, it was observed that high concentrations of Ba was increasing towards northwest, southwest, and southeast parts of the study area. The occurrence of Ba in soil can be attributed to mostly geogenic activities as suggested by Madejón (2012).

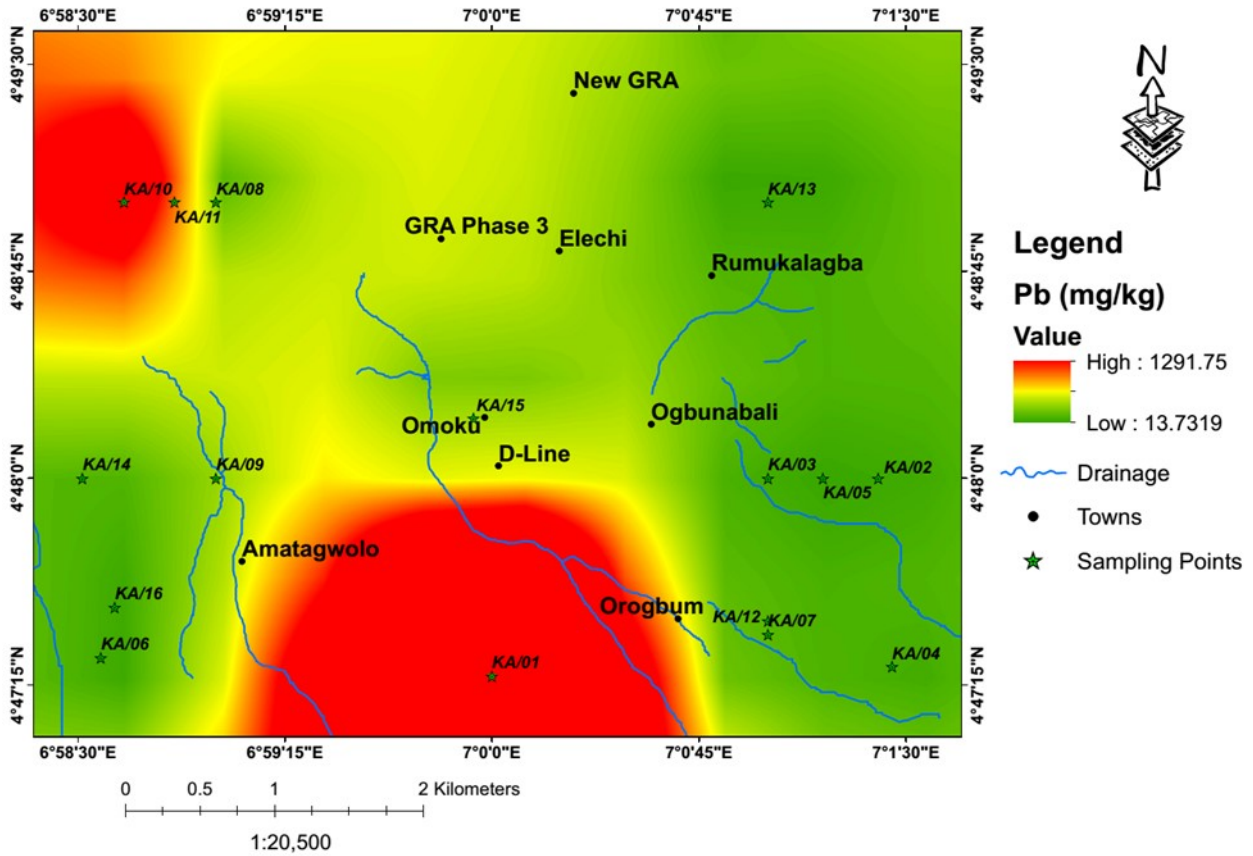


Fig 5: Spatial distribution of Pb within the study area

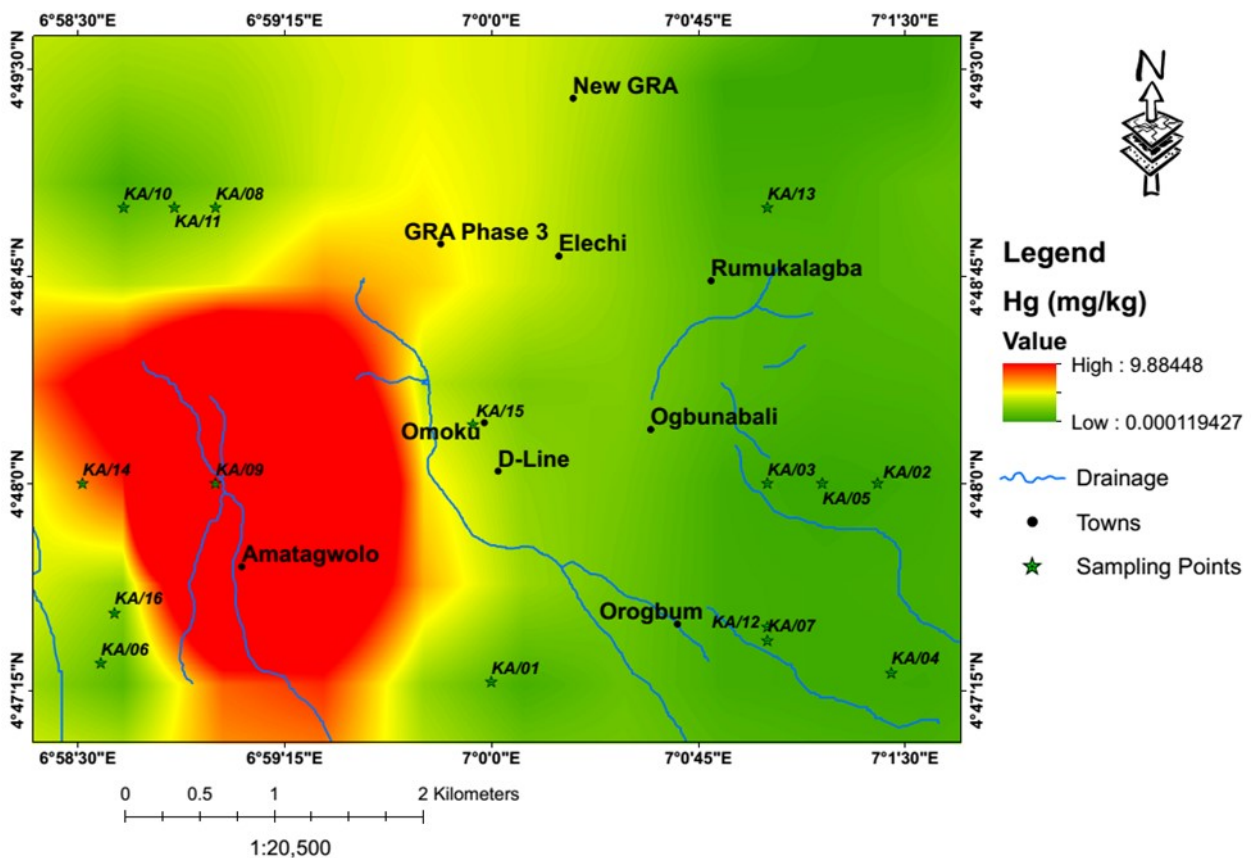


Fig 6: Spatial distribution of Hg within the study area.

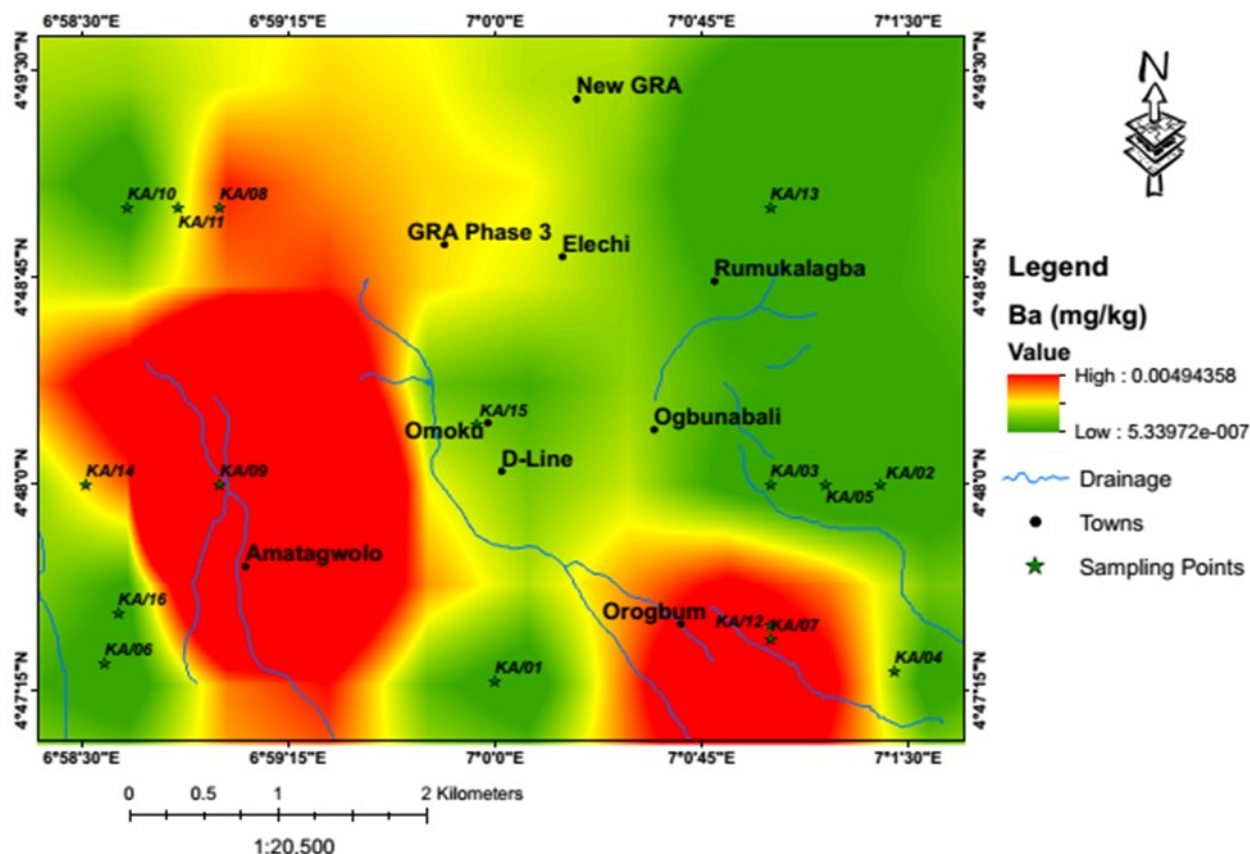


Fig 7: Spatial distribution of Ba within the study area

Vanadium (v)

Depending on the parent material of the soil, igneous rocks have higher vanadium contents than sedimentary rocks (Kabata-Pendias, 2011). Furthermore, as previously mentioned, the anthropogenic sources of vanadium determine its content in soils. Findings from Table 1, revealed that the concentration of V in soil ranges from >0.001 to >0.001 mg/kg with an average value of 0.001 mg/kg.

Nickel (Ni)

There are also several ways that Ni can be found in soils, such as inorganic crystalline minerals or precipitates, water-soluble, free-ion, or chelated metal complexes in soil solution, and adsorption of complex formation on organic cation surfaces or inorganic cation exchange surfaces (Igwe, et al., 2022). The concentration of Ni for this study ranges from 1.7 to 21.0 mg/kg with an average value of 31.63 mg/kg as shown in Table 1. It was observed that concentration of Ni within the study area were below permissible limit except for sample location KA/ KA/09 and KA/10 (see

Table 4). Fig. 8, showed that the concentration of Ni increases towards the northwest parts of the study area. According to Eyankware, et al., (2024), Ni is present in soils through a range of chemical reactions triggered by geogenic and anthropogenic causes.

Copper (Cu)

Cu is one of the few metals that can be found in nature as an uncombined mineral. On the other hand, if 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

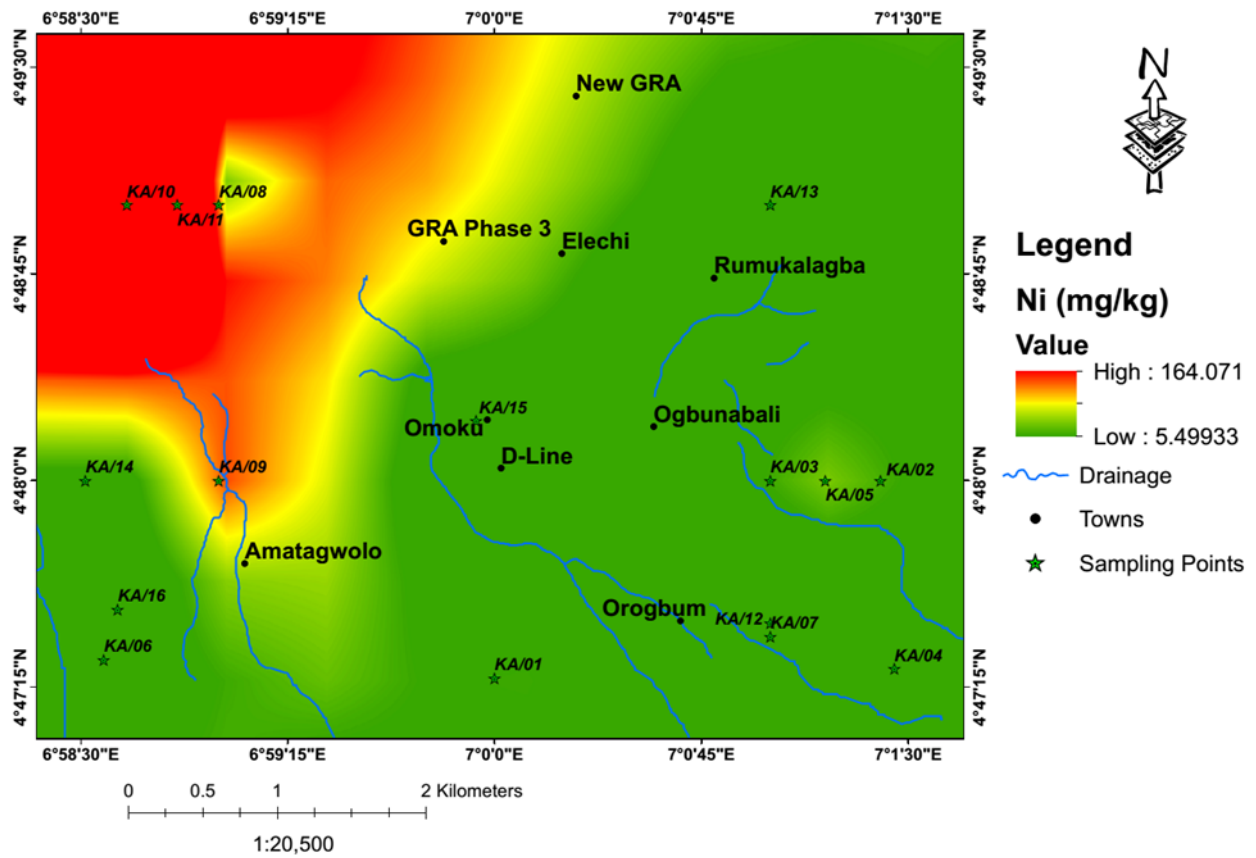


Fig 8: Spatial distribution of Ni within the study area

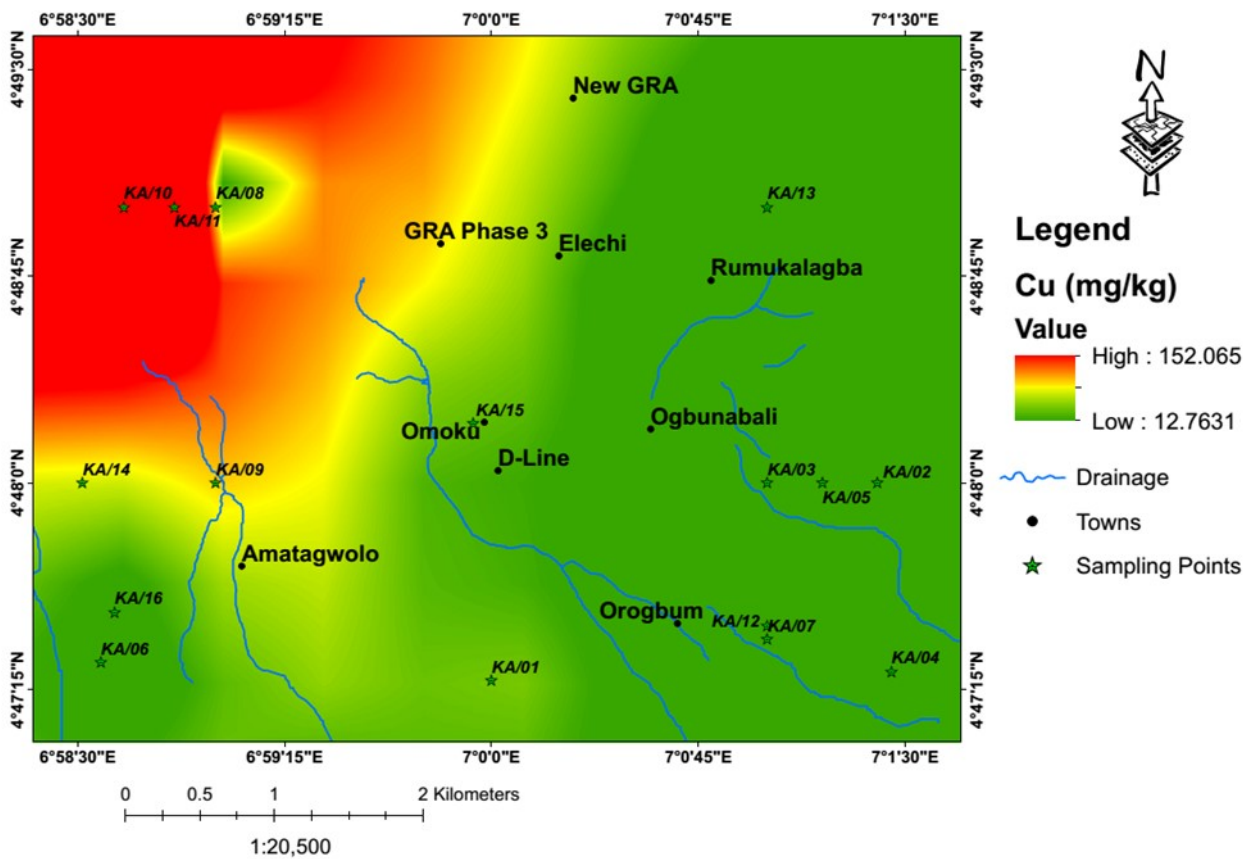


Fig 9: Spatial distribution of Cu within the study area.

or processing and be distributed over considerably longer distances, harming soil sediment quality (Eyankware et al., 2022a). As Deducted from Table 1 showed that the concentration of Cu in soil within the study area ranges from 10.9 to 1.90 mg/kg with an average value of 3.83 mg/kg. Findings from Table 4, showed that the concentration of Cu within the study area was below maximum permissible limit except for sample locations KA/09 and 10. Findings from Fig. 9, suggested that Cu in soil within the study area increases towards the northwest, and southwest parts of the study area. Elsewhere in Niger Delta region of Nigeria, Eyankware, et al., (2024), suggested that high concentration of Cu in soil can be attributed to geology and human activities.

Zinc (Zn)

Due to excess fertilizer application, industrial effluents, mining, smelting, and waste disposal, Zn contamination has been a common problem in agro-ecosystems in recent years (Eyankware, et al., 2024). The concentration of Ni for this study ranges from 29.9 to 720 mg/kg with an average value of 145.92 mg/kg as shown in Table 1. Furthermore, findings from Table 4 revealed that all sampling points were below maximum permissible limit except for sample location KA/07. The inappropriate disposal of wastes containing zinc from power utilities and metal manufacturing sectors can lead to high amounts of zinc in soil. The majority of zinc remains bonded to the solid particles in soil. Findings from Fig. 10, showed that the concentration of Zn increase towards the northwest, and selected parts of southwest parts of the study area. Studies conducted in Delta state revealed that high concentration of Zn in soil can be linked to mainly human activities.

Chromium (Cr)

Jankiewicz and Ptaszynski (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 individuals consume plants contaminated with heavy metals, it can cause damage to kidneys and livers (Harendra et al., 2017), thereby leading to serious health challenge. The concentration of

Zn for this study ranges from 4.4 to 380 with average value of 54.55 mg/kg

Table 4: Maximal permissible addition MPA of heavy metals and metalloids by the data of Dutch ecologists in mg/kg (Li et al. 2015).

Metal/metalloid	MPA
Beryllium (Be)	0.0061
Selenium (Se)	0.11
Thallium (Tl)	0.25
Antimony (Sb)	0.53
Cadmium (Cd)	0.76
Vanadium (V)	1.1
Mercury (Hg)	1.9
Nickel (Ni)	2.6
Copper (Cu)	3.5
Chromium (Cr)	3.8
Arsenic (As)	4.5
Barium (Ba)	9.0
Zinc (Zn)	16
Cobalt (Co)	24
Tin (Sn)	34
Lead (Pb)	55
Molybdenum (Mo)	253

Note: A dash stands for not determined

Conclusion

This study carried out assessment of soils impacted by oil spillages within Omoku in River State, southern part of Nigeria for heavy metals concentration, pollution indices including potential ecological risk (ERI). Geochemical analysis revealed concentration of heavy metals in soil Fe, As, Pb, Hg, Ba, V, Ni, Cu, Zn, and Cr with value ranges. Fe 60.4 to 8430, 60.4 to 8430, 0.001 to 0.846, 0.3 to 10, 0.001 to 0.005, <0.001 to <0.001, 1.7 to 21.0, 10.9 to 1.90, 29.9 to 720, and 4.4 to 380 mg/kg respectively. Heavy indexes use to investigate the concentration of heavy in soil include the following: Potential Ecological Risks Assessment, Index of Geoaccumulation (Igeo), Degree of Contamination (Cdeg), and Nemerow pollution (PNI). Heavy indexes use to investigate the concentration of heavy in soil include the following: Potential Ecological Risks Assessment, Index of Geoaccumulation (Igeo), Degree of Contamination (Cdeg), Nemerow pollution (PNI), All the evaluated samples have negative Igeo values, indicating no significant pollution for As, Ba, and V. While, Ni, Hg, Cu and Cr have negative. Cdeg of contamination may be classified based the scale ranging from <8 to >32: < 8, 8–16, 16–32 and > 32 indicates

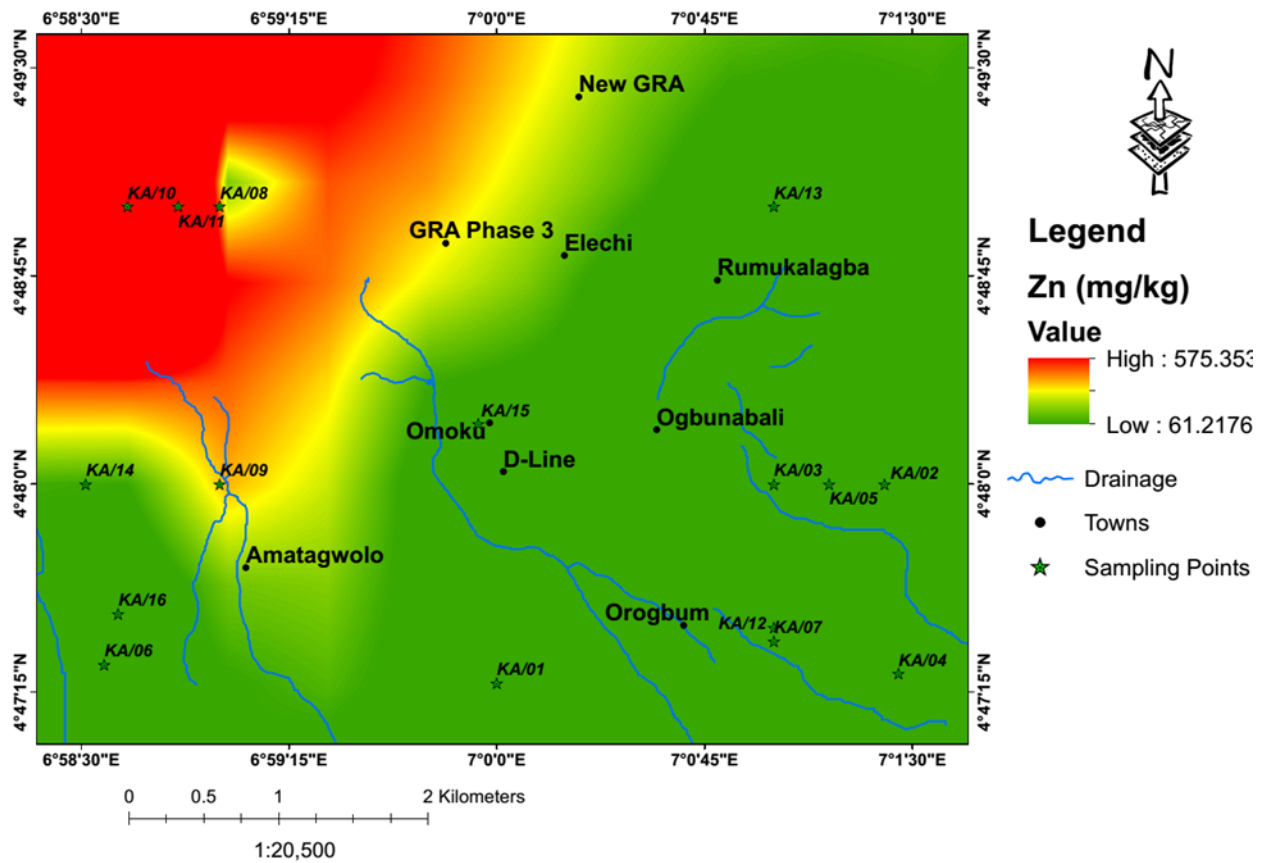


Fig 10: Spatial distribution of Zn within the study area.

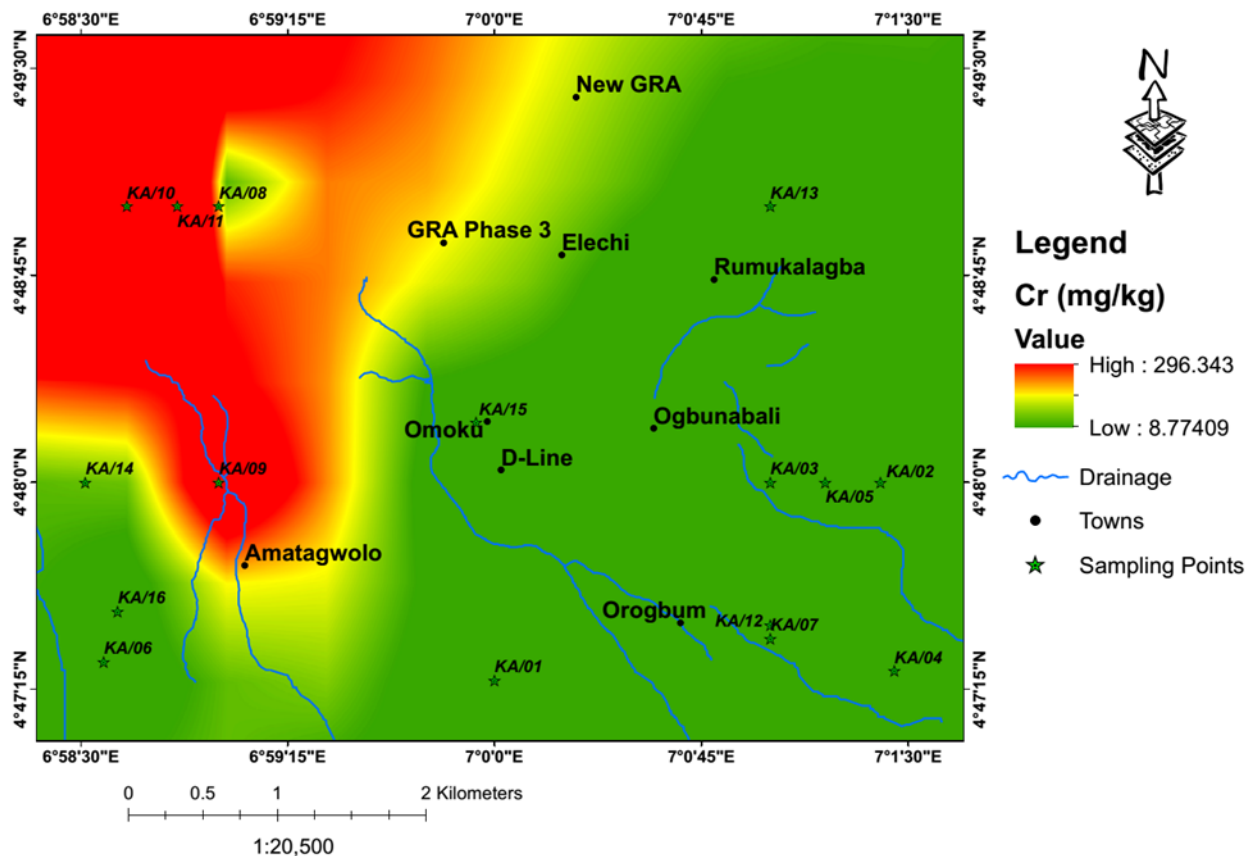


Fig 11: Spatial distribution of Cr within the study area

low degree, moderate, considerate and very high degree of contamination. NPI evaluations indicate that the seriously polluted. Deduction from spatial distribution of heavy metals within the study area suggested that 87 % heavy metal increases towards selected parts of northwest, southwest, and southeast parts of the research area. The existence of these heavy metals in soil may pose a threat to aquatic and human life, as well as contaminate groundwater, surface water, and the food chain. Because of the extreme danger that heavy metal fallout poses to human life, steps should be taken to stop it from building up in certain areas.

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