Spatial variability and pollution loads of selected heavy metals in cocoa plantation soils in Cross River State, Nigeria.

ABSTRACT

Understanding heavy metal concentrations and their spatial variability is crucial for improved soil health and increased crop productivity. This study assessed heavy metal concentrations and their pollution loads in soils of cocoa plantations in Ikom, Etung and Boki Local Government Areas of Cross River State. Sixty (60) composite soil samples were collected from the area and analyzed Cd, Cr, Pb and Al. The results obtained revealed that Cd was above the maximum permissible limit for soil. Lead had means of 0.011 mg/kg, 0.02 mg/kg and 0.010 mg/kg, Cd had means of 1.53 mg/kg, 1.45 mg/kg and 1.25 mg/kg while Cr was 0.05 mg/kg, 0.03 mg/kg and 0.02 mg/kg Ikom, Etung and Boki respectively. The contamination factor for Cr and Pb was low (CF < 1) while Cd was considerably contaminated (3≤ CF < 6). The results of PLI indicated an unpolluted condition (PLI<1). Apart from Cd, the values of Igeo for Cr, Pb and Al fell in class '0', indicating practically uncontaminated conditions in these areas. The soils of the area are safe for crop production but measures should be taken to reverse the trend of high concentration of Cd in the soils.

Keywords: Heavy metal, pollution load, maximum permissible limits, soil health

1.INTRODUCTION

Cocoa (Theobroma cacao L), a species native to humid tropics of central and south America has more than 700, 000 km^2 area of land worldwide dedicated to its cultivation (Aguirre-Ferero *et al*., 2020). The crop is cultivated in humid tropical countries of the world (Afolayan, 2020). Worldwide, Nigeria is the fourth largest producer of cocoa after Ivory Coast, Ghana and Indonesia (Owoyemi, 2023, Afolayan, 2020). In Nigeria, fourteen out of the thirty-six states produce cocoa with Cross River State having the largest expanse of land committed to cocoa production, only followed closely by Ondo State (Afolayan, 2020). However, cocoa production system relies heavily on pesticides use to control pests and diseases (Etaware, 2022; Aminu and Edun, 2019). Despite the importance of pesticides in agricultural crop production including cocoa (Arham *et al*., 2017; Bentley *et al*., 2004), studies have revealed that the use of pesticides enrich the environment or soil with heavy metals (Arham *et al*., 2017). This is because in pesticides formulation, heavy metals are used as impurities and some as active ingredients (Defarge *et al*., 2018). For instance, copper-based fungicide which is one of the most important components of pests and disease control program in cocoa production system is capable enriching the environment with copper (Adewoye and Amusa, 2021).

Heavy metals are elements in the periodic table with atomic number higher than 20 and densities greater than 6g/cm^3 (Sherene, 2010), moderately reactive, hard, dense, lustrous and are among the most harmful soil pollutants. The metals are carcinogenic in nature and adversely affect DNA, proteins, and lipids by producing free radicals that lead to severe health and environmental problems (Sadak, 2023)

Chromium is the 24th most abundant element in the earth crust belonging to the group of refractory metals which comprises all metals with a higher melting point than platinum (1,772 °C) (Lunk, 2015). Similarly, Chromium is the 24th most abundant element in the earth crust belonging to the group of refractory metals which comprises all metals with a higher melting point than platinum (1,772 °C) (Lunk, 2015). Cadmium is a soft, malleable, ductile, silvery-white divalent metal and occurs in a few minerals and in small quantities in other ores especially zinc ores, from which it is produced as a by-product. Lead is the fiftieth most abundant element on earth and is initially found at low concentration in the earth crust predominantly as sulfide (Diouf, 2016). It has an atomic number 82, atomic mass 207.2, density 11.4 g/cm3, melting point of 327.4 °C and boiling point of 1725°C. Lead is non-essential and very toxic heavy metal that has deleterious effects on biological system (Pattee and Pain, 2003).

However, contamination of agricultural soils by heavy metals as a result of pesticides use has recently generated much public concern (Yeboah *et al*., 2024) due to their hazardous effects on man and the environment. Excessive heavy metals in soil could lead to their accumulation in crops causing decline in crop quality (Ali *et al*., 2020) and negatively impacting human health when the crops are consumed (Arham *et al*., 2017). According to Rao *et al*. (2022), long term exposure through consumption of heavy metals enriched agricultural produce can result in several ailments including cancer, hypertension, kidney and liver disease. Apart from health effects of heavy metals on man, pollution of soil by heavy metals is capable of causing decline in soil fertility through its effects on soi nutrient indicators including micro organisms, pH, organic matter and nitrogen (Osinuga *et al*., 2023).

Nevertheless, the enormity of the effects heavy metal pollution is beginning to raise concern about the safety of crops and soils in Cross River State, particularly those of Ikom, Etung and Boki where pesticides are intensively used in cocoa production. Furthermore, the current rapid expansion of cocoa plantations in Cross River State caused by ongoing cocoa boom implies increase in the release of heavy metals into the soil environment from pesticides use.

Unfortunately, there is lack of public awareness on level of heavy metals in soils and little or nothing is known about their spatial distribution in these soils. Spatial variability of heavy metals unveils areas where such metals exist above and below maximum permissible limits which can guide in proper land use and environmental management. The knowledge of spatial variability of heavy metals is an important requirement for suitably monitoring and evaluating eco-environment quality in a primary agricultural production area (Yang *et al*., 2009). Implementing soil remediation techniques based on the result of spatial analysis can improve soil health and increase crop yield including cocoa, thereby enhancing food security and economic growth of nations. Studies by Afu *et al*. (2021) and Afu *et al*. (2020) in Cross River State on soils of different parent materials and elsewhere have showed that heavy metal concentration varied spatially. The aim of this study was therefore to evaluate heavy metal concentrations, their pollution loads and spatial variability in soils of cocoa plantations in Cross River State, Nigeria.

2.MATERIALS AND METHODS

2.1 The study location

The study area, Boki, Ikom and Etung Local Government Areas of CRS the highest cocoa producing areas in Nigeria, lies between latitudes $5^{0}00$-$6^{0}40$ N and longitudes $8^{0}50$-$9^{0}00$ E in the tropical rain forest belt of Nigeria. The area is characterized by two seasons; rainy and dry seasons with an annual rainfall range of 1600-3520 mm, relative humidity of 75-83 %, temperature of 27.1-28.6 ^{0}C (Olim *et al*., 2019). The geology of the study area is Mamfe embayment which is comprises of precambian basement complex and sedimentary rocks and basalt (Sholokwu and Egesi, 2018). The vegetation of the study area is comprised of tall trees, grasses and herbaceous plants. The major plant species found in the area include gmelina, oil palm, timber trees, grasses etc. The major land uses of the area include cocoa plantation, forest, banana/plantain plantation, fallowed land, oil palm plantation and pineapple plantation. Yam, maize, okro and cassava are also cultivated in the area. The study area and is bounded to the north by northern CRS, south by Akamkpa and Obubra Local Government Areas and to the east by the Republic of Cameroon.

2.2 Collection of soil samples

Sixty (60) composite soil samples, 20 samples each from Ikom, Etung and Boki Local Government Area were collected from thirty cocoa plantations in the study area for this study. In Boki, communities where soil samples were collected are Abu Emeh, Abu Police, Abu Ebam, Bashua and Orimekpang. In Ikom soil samples were collected from cocoa plantations in Adijinkpor, Otare and Akparabong while in Etung, samples were obtained from Abia, Bendeghe Ekiem, Ekimaya and Efraya. Soil samples were collected with the use of soil auger at the depth of 0-30 cm using stratified random sampling technique. In each sampling point or farm, 3 sub-samples were collected randomly using soil auger, hand mixed into a composite sample and placed in a well labeled polythene bag. All samples were transported to the laboratory for heavy metal analysis.

2.3 Laboratory analysis

In the laboratory, soil samples were air-dried, crushed and sieved with 2 mm mesh. The concentration of Cr, Cd, Pb, Zn and Cu in soil samples was extracted with DTPA solution (0.005*M* DTPA

+ 0.01 M $CaCl_2$ + 0.1*M* triethanolamine, pH 7.3 as outlined by Lindsay & Norvell (1978) and determined by atomic absorption spectrophotometer. Aluminum was determined as outlined in Udo *et al*. (2009).

2.4 Statistical analysis

Data distribution was described with classical statistics including mean, minimum, standard deviation and coefficient of variation. Significant treatment means were separated using Fishers Least Significant Difference (LSD) at 5 % level of probability. Pollution load indices were calculated using equations presented in Tables 1. The spatial interpolation of heavy metals and pollution indices was done using Inverse Distance Weighting (IDW). According to Burrough and McDonnell (1998), "IDW is based on the assumption that the value of an attribute in an unsampled area is that of the weighted average of the known data points within a local neighborhood surrounding the unsampled location". Estimated values will be interpolated based on the data from surrounding locations using the formula:

$$Z(xo) = \sum_{i-1}^{n} wiZ(xi) \qquad (1)$$

Where,

Z(x0) is the estimated value, *wi*is the weight assigned to the value at each location *Z (χi)*, *n* is the number of close neighboring sampled data points used for estimation.

The weights were estimated using:

$$wi = \frac{1/d_i^p}{\sum_{i=1}^{n} 1/d_i^p} \qquad (2)$$

Where,

di is the distance between the estimated point and the sample point, *p is* an exponent parameter.

Table 1. Metal pollution indices

Pollution index	Equation	Class/value	Soil risk grade	Reference
Contamination factor (Cf)	$C_f = \frac{C_{metal}}{C_{background}}$	CF < 1	low Cf	Hakanson (1980)
		1 ≤ CF < 3	Moderate Cf	
		3≤ CF < 6	Considerable Cf	
		CF ≥ 6	Very high Cf	
Geo-accumulation index (Igeo)	$I_{geo} = \log_2\left(\frac{C_n}{1.5*B_n}\right)$	Class0= Igeo≤0	Uncontaminated	Muller (1969)
		Class 1= 0 <Igeo< 1	Uncontaminated to moderately contaminated	
		Class2 = 1 <Igeo< 2	Moderately contaminated	
		Class 3 = 2 <Igeo< 3	Moderately to heavily contaminated	
		Class 4 = 3 <Igeo< 4	Heavily contaminated	

		Class 5 = 4 <Igeo< 5	Heavily to extremely contaminated	
		Class 6 = Igeo>5	Extremely contaminated	
Enrichment factor (EF)	$EF = \frac{(C_M/C_{Al})_{sample}}{(C_M/C_{Al})_{earth\ crust}}$	EF < 1	no enrichment	Giri *et al*. (2013)
		EF=1-3	minor enrichment	
		EF=3-5	moderate enrichment	
		EF=5-10	moderately severe enrichment	
		EF=10-25	severe enrichment	
		EF=25-50	very severe enrichment	
		EF>50	extremely severe enrichment	
Pollution loadindex (PLI)	$PLI = (CF_1 \text{ x } CF_2 \text{ x } CF_3 \text{ x} \ldots \text{x } CF_n)^{1/n}$	PLI<1	No metal pollution	Tomlinson *etal.* (1980)
		PLI = 1	Baseline levels of pollutants	
		PLI >1	Polluted condition	

C_{metal}:measured concentration of the examined metal (n) in the soil, $C_{background}$: concentration of the examined metal (n) in the reference environment, Bn:background value of metal in Ref. Env., 1.5: constant, $(C_M/C_{Al})_{sample}$: ratio of metal concentration (mg kg^{-1}) in relation to Al (mg kg^{-1}) in soil samples, $(C_M/C_{Al})_{earth\ crust}$: ratio of metal concentration (mg kg^{-1}) in relation to Al (mg kg^{-1}) in earth crust.

3. RESULTS AND DISCUSSION

3.1 Heavy metal concentrations

The means of heavy metal content of the soils are given in Table 2. From the table Al varied from 0.0 to 485.6 mg/kg, 0.0 to 539.6 and 0.0 to 625.93 having means of 53.96 mg/kg, 99.82 mg/kg and 202.35 mg/kg in Ikom, Etung and Boki soils respectively. The concentrations of Al in this study have variations when compared to the reports of Afu *et al*. (2020) and Afu *et al*. (2021). The Al values in this study are far below the background value of 47200 mg/kg (Turekian and Wedepohl, (1961).

The highest concentration of Pb was obtained in Etung. Lead had means of 0.011 mg/kg, 0.02 mg/kg and 0.010 mg/kg in Ikom, Etung and Boki. The values of Pb in this study are lower than those obtained by Arham *et al*. (2017) in a related study in East Kolaka, Indonesia. Contrary results in Ikom area of Nigeria have also been reported by Afu *et al.* (2021). Further results revealed that Cd was higher in Ikom and Etung than Boki soils. Cadmium varied from 0.18 to 2.62 mg/kg, 0.41 to 2.61 and 0.36 to 2.87 mg/kg with means of 1.53 mg/kg, 1.45 mg/kg and 1.25 mg/kg. Similarly, Cr was higher in Ikom and had means of 0.05 mg/kg, 0.03 mg/kg and 0.02 mg/kg Ikom, Etung and Boki accordingly. Higher values of heavy metals recorded in Ikom and Etung may be due longer duration of pesticides application since plantations in these areas were observed to be older.

Except for Cd which was above the maximum permissible limit (0.8 mg/kg), the levels of heavy metals in the soils were far below the maximum permissible limits 85 mg/kg (Pb) and 100 mg/kg (Cr) for soils (Denneman and Robberse, 1990). Similarly, Yeboah *et al*. (2024) in a related study in Ghana obtained heavy metal values that were all below maximum permissible limit in soil.

Table 2: Heavy metal concentrations (mg/kg)

	Al	Pb	Cd	Cr
Ikom				
Mean	53.96	0.011	1.53	0.05
Min	0.0	0.0	0.18	0.01
Max	485.6	0.02	2.62	0.34
SD	0.51	0.01	0.79	0.09
CV (%)	259.09	63.13	52.0	178.46
Etung				
Mean	99.82	0.02	1.45	0.03
Min	0.0	0.0	0.41	0.01
Max	539.6	0.04	2.61	0.05
Median	0.0	0.02	1.51	0.02
SD	0.63	0.01	0.75	0.01
CV (%)	171.99	57.63	51.33	33.06
Boki				
Mean	202.35	0.010	1.25	0.02
Min	0.0	0.0	0.36	0.01
Max	625.93	0.020	2.87	0.05
Median	0.68	0.010	0.61	0.03
SD	0.56	0.010	0.88	0.01
CV (%)	74.97	67.59	70.65	34.42
MPL	10-300000	2-200	0.01-0.7	1-1000
BV	47200	85	0.8	100

MPL=maximum permissible limits (Lindsay, 1978)
BV=background value (Turekian & Wedepohl,1961).

3.2 The spatial variation of heavy metals

The spatial variation of heavy metals Cr, Cd and Pb are presented in Fig. 1. In Boki, Cr were mostly low with values $\leq$ 0.047 mg/kg dominating the entire study area. However, Cd values were mostly between 0.92 mg/kg to 1.76 mg/kg with patches of values above 1.76 mg/kg found in Boki. The concentration of Pb were low, and values between 0.0099 mg/kg to 0.023 mg/kg dominates the study area with patches of values between 0.023 mg/kg to 0.032 mg/kg found in Efraya and Ekimaya axis in Etung. The spatial variation of Cr, Cd, and Pb in cocoa plantations is a significant environmental concern, particularly due to the impact of agricultural practices. Previous studies by Arham *et al.* (2017) and Bravo *et al.* (2021) indicated that heavy applications of agrochemicals, including pesticides in cocoa plantations release heavy metals into the soil.

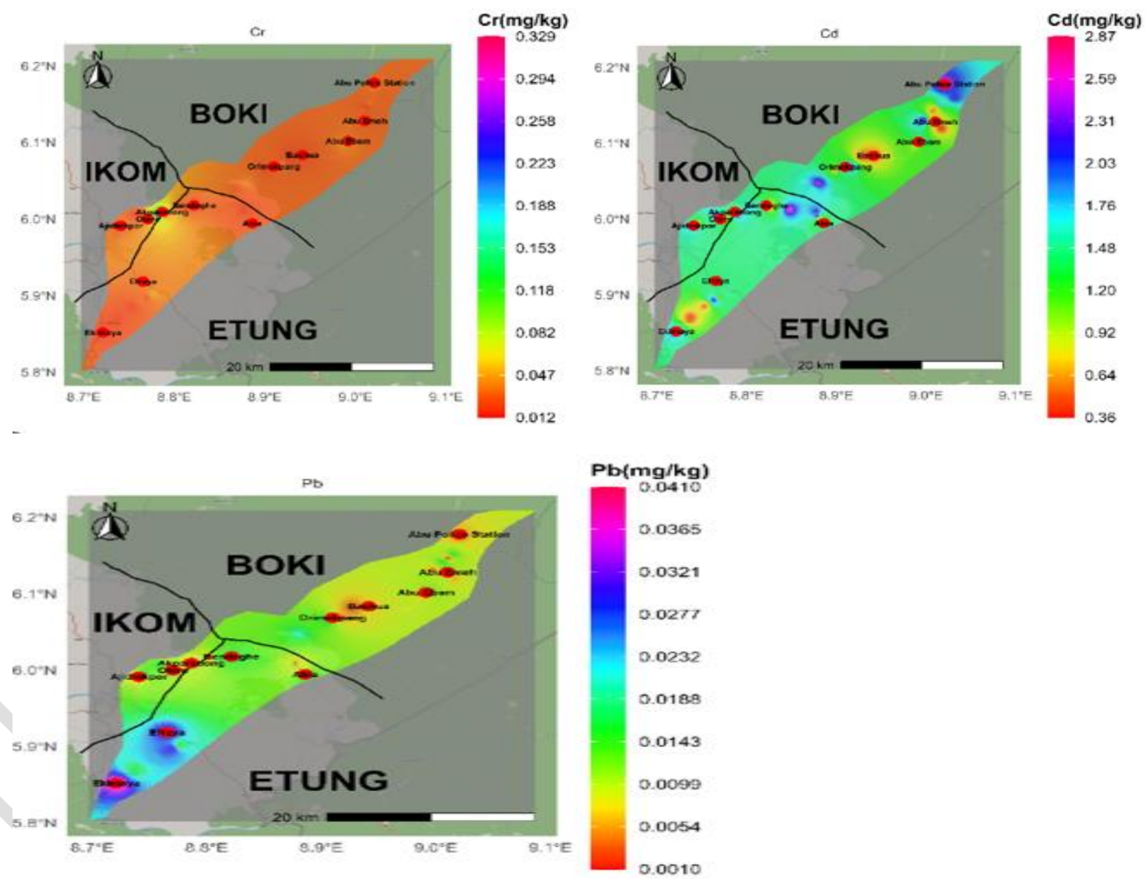

Fig. 1: Spatial distribution of heavy metals in cocoa plantations

3.3 Pollution loads

3.3.1 Contamination factor (Cf)

The result presented in Table 3 shows the contamination factors (Cf) for the studied heavy metals. The mean Cf values for Cr and Pb were all less than unity, whereas for Cd the mean values of Cf were 4.156, 5.074 and 4.84 in Boki, Ikom and Etung respectively. Similarly, for Al the mean values were 2.38, 0.45 and 0.93 in Boki, Ikom and Etung, respectively. These results indicate that the soils in Boki, Ikom and Etung are low in Pb Cr, and considerably contaminated with Cd. However, soil in Boki was moderately contaminated with Al. Soils contaminated by heavy metals can cause serious ecological risks and negatively impact human health due to various forms of interaction where highly toxic heavy metals can enter the food chain (Yaradua *et al.,* 2019).

3.3.2 Pollution load index (PLI)

These results of PLI were below 1, indicating an unpolluted condition for the assessed heavy metals (Table 3). The results of the present evaluation revealed that the soils in Boki, Ikom and Etung are unpolluted by heavy metals even though there is moderate contamination factor for Cd. The result of the present study is comparable with those of Andem *et al.* (2015), Afu *et al*. (2020) and Afu *et al*. (2021) who reported unpolluted condition in their separate studies in Nigeria.

3.3.3 Geo-accumulation index (Igeo)

The Igeo values of this study are presented in Table 4. The Igeo mean value were 1.072, -18.99, -13.32, -9.59, -7.08 and 0.707 for Cd, Cr, Pb and Al in Boki, Also, 1.48, -18.73, -14.10 and 0.054 were reported for Cd, Cr, Pb and Al respectively in Ikom. However, for plantations in Etung, Igeo had means of 1.45, -18.95, -13.12 and -0.042 for Cd, Cr, Pb and Al, respectively. The values of Igeo for all the heavy metals except Cd fell in class ‘0’, indicating practically uncontaminated conditions in these areas. However, Cd was moderately contaminated in Boki, Ikom and Etung. The values of Igeo of the present study are comparable with those reported in a number of previous studies (Afu *et al*., 2020; Afu *et al*., 2021; Barakat *et al.,* 2012; Andem *et al.,* 2015).

3.3.4 Enrichment Factor (EF)

The EF of the heavy metals are presented in Table 4. In Boki, Cd (EF =1.41) and Cr (EF =1.02) were enriched, and Pb (EF = 6.87) was moderately severe enriched, Similarly, in Ikom, Cr (EF =1.09) and Pb (EF = 1.09) were enriched, while Cd was not enriched. However, in Etung only Cd (EF =3.28) was moderately enriched while Cr and Pb were not enriched. However, the investigated soils had been enriched by the studied heavy metal (Giri *et al.*,2013). This enrichment may have been caused by the use of pesticides and measures should be taken to reduce or arrest this situation.

Table 3: Contamination factor and pollution load index of metals

	Cf-Cd	Cf-Cr	Cf-Pb	Cf-Al	PLI
Boki					
Min	1.2	0.00013	0.00005	0.00	0.00
Max	9.57	0.0005	0.0009	6.068	0.0664
Mean	4.156	0.00027	0.00044	2.383	0.036
Ikom					
Min	0.606	0.00013	0.00005	0.00	0.00
Max	8.733	0.00377	0.001	3.941	0.102
Mean	5.074	0.00057	0.00051	0.459	0.0094
Etung					
Min	1.366	0.00015	0.00005	0.00	0.00
Max	8.7	0.00052	0.0020	5.323	0.074
Mean	4.84	0.00028	0.00091	0.935	0.021

Cd = Cadmium, Cf = Contamination factor; *Cd = Degree of contamination;
PLI = pollution load index; Cr = Chromium, Pb = Lead, Zn = Zinc, Cu = Copper,
Al = Aluminium

Table 4: Geoaccumulation Index and enrichment factor

	geo-Cd	geo-Cr	geo -Pb	geo-Al	EF-Cd	EF-Cr	EF-Pb
Boki							
Min	-0.321	-19.949	-19.194	0.00	0.00	0.00	0.00
Max	2.673	-18.042	0.00	2.016	6.109	2.85	3.15
Mean	1.072	-18.99	-13.329	0.707	1.413	1.02	6.87
Ikom							
Min	-1.305	-19.949	-19.194	-1.325	0.00	0.000	0.00
Max	2.541	-15.125	0.00	1.393	12.587	1	1.16
Mean	1.481	-18.737	-14.102	0.054	0.743	1.09	1.09
Etung							
Min	-0.134	-19.727	-19.194	-3.082	0.00	0.00	0.00
Max	2.536	-17.979	0.00	1.827	45.753	1.60E-05	0.00011
Mean	1.451	-18.948	-13.116	-0.042	3.28	1.80E-06	1.59E-05

3.4 Spatial assessment of pollution loads

The spatial distribution of contamination factor in figure 2 shows that in Boki, the Cf for Al between 1.33 to 2.67 predominated whereas in both Ikom and Etung the dominant Cf for Al were mostly less than 0.67. The result further showed that the dominant Cf for Cd in Boki, Ikom and Etung soils were mostly those within the range of 3.07 to 5.85. However, patches of values above 5.85 were found in several places in Boki soils especially around Abu Police and southern part of Orimekpang. Across the study area, the Cf for Cr were mostly low and values less than 0.000052 were observed predominantly. Furthermore, spatial variation of EF shown in figure 3 indicated that EF for Cr that were less than 1.7E-06 predominated the entire Boki area. The result further showed that the dominant EF for Cd were less than 4.9 in the entire study area while EF of Pb were mostly less than 0.000025.

Similar maps presented in this study has been reported by Borkowski and Kwiatkowska-Malina (2020). Spatial variability maps help in understanding the sources and distribution patterns of heavy metals, facilitating adoption of environmental management strategies. The Igeo for Cr that were between -18.91 to -17.35 predominates the entire study area. The result further showed that the dominant Igeo values for Cd were between 1.11 to 2.28. However, in Boki values between -0.06 to 0.72 dominates and mostly in Abu Police and Bashua axis. Similarly, the Igeo for Pb that predominates were values between -14.9 to -10.6. Further results indicated that the Igeo for Al having the predominates values for the entire study area were between -0.21 to -1.44. The result presented in this reported is in line with that of Krami *et al*. (2013)

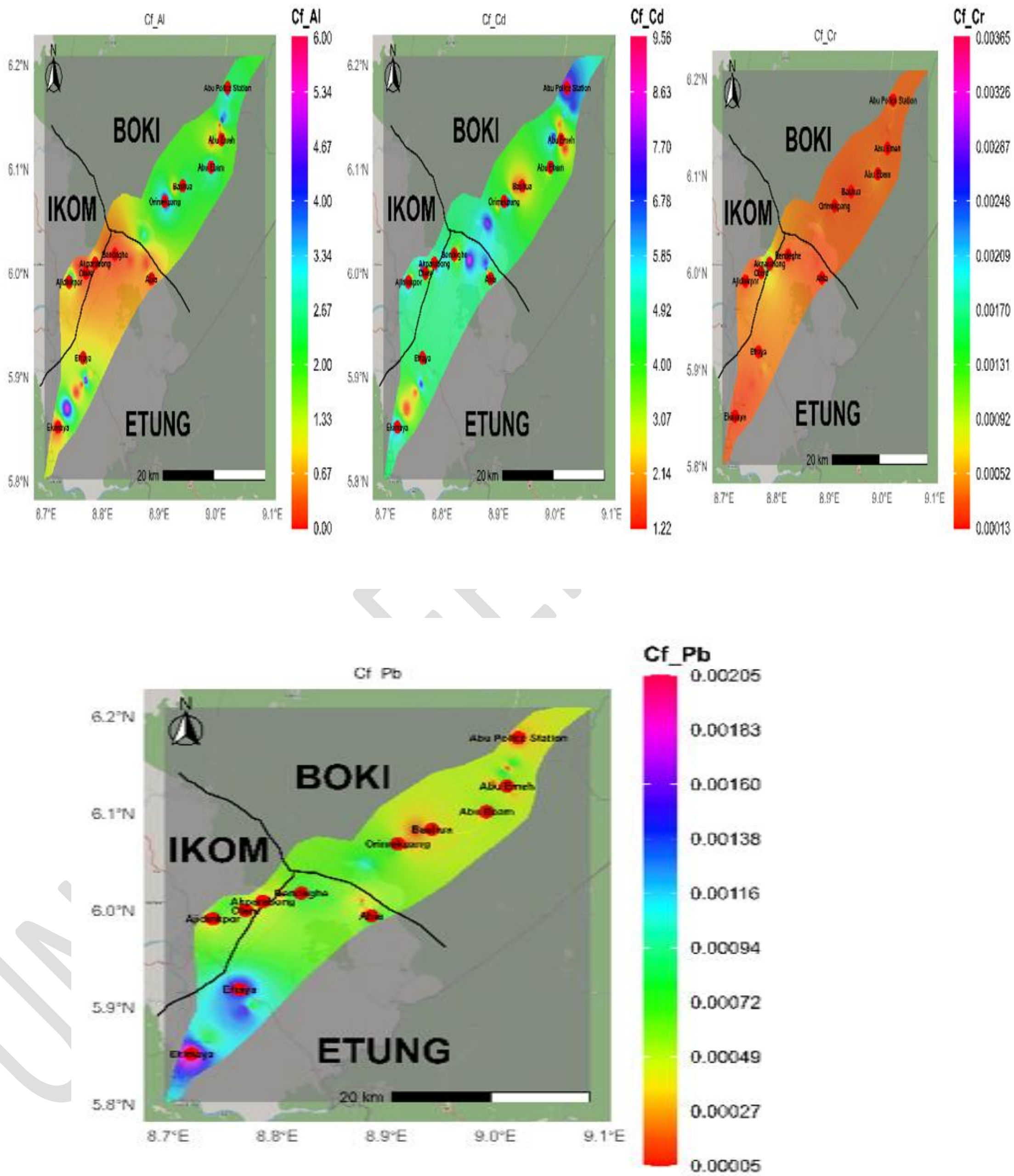

Fig. 2: Spatial distribution of contamination factor in cocoa plantations

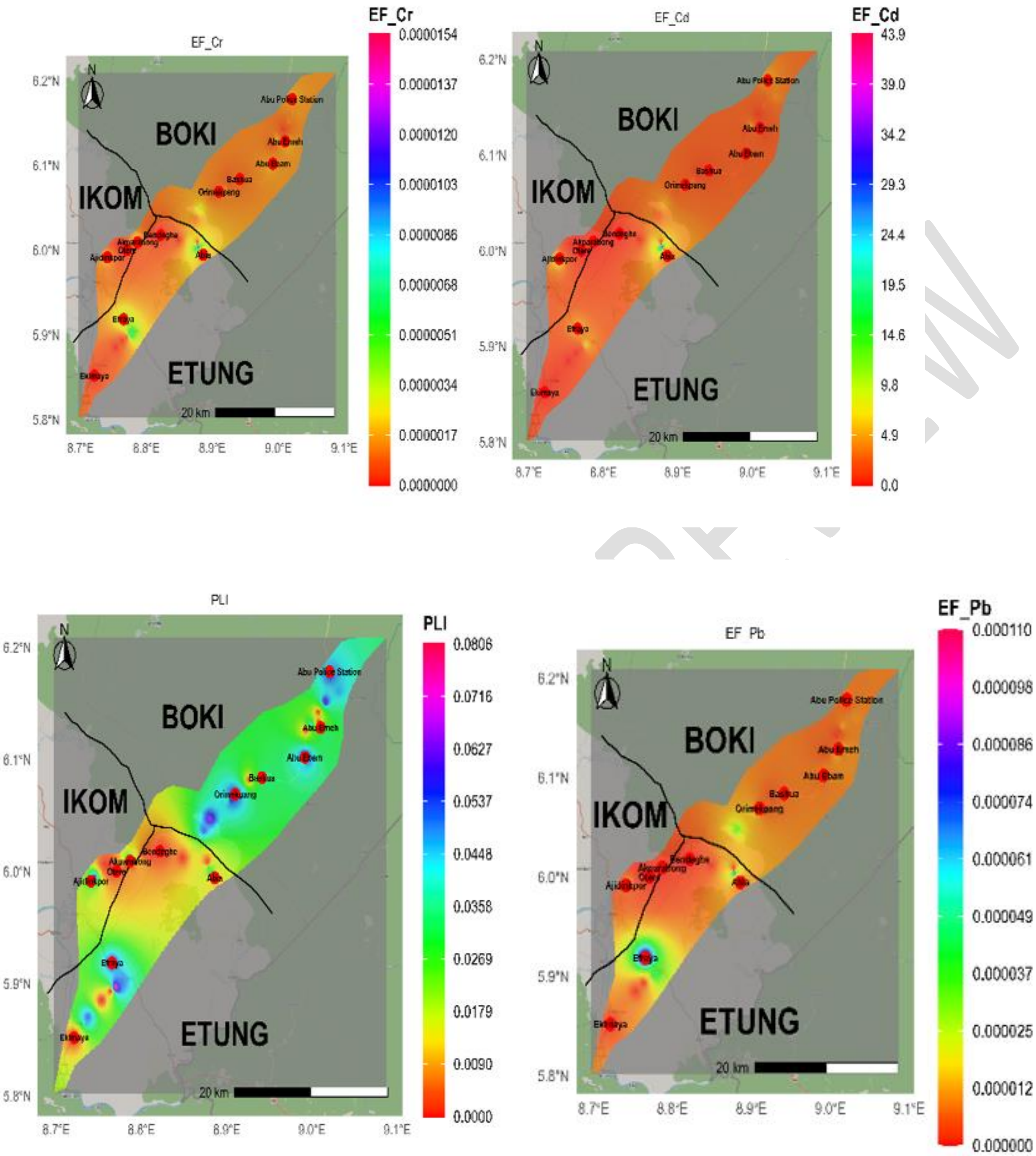

Fig. 3: Spatial distribution of enrichment factor and PLI in cocoa plantations

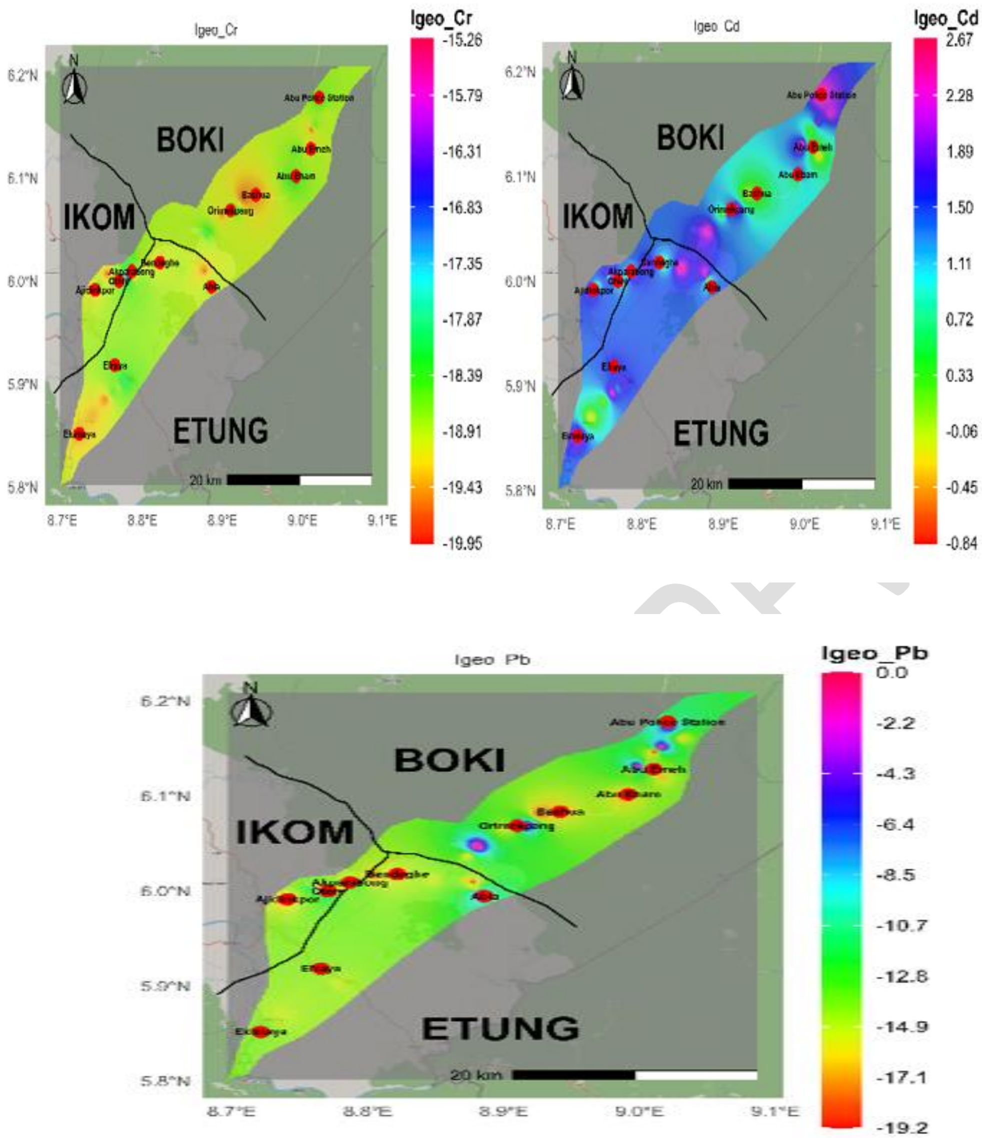

Fig. 4: Spatial distribution of geo-accumulation index in cocoa plantations

4. CONCLUSION

This study revealed that Al content of the study area was far below the background value of 47200 mg/kg. Lead, Cr and Cd concentrations were higher in Ikom and Etung than Boki soils. Except Cd, Cr and Pb were below maximum permissible limits in the soil. Th results of pollution load obtained for the study indicated that the soils in the study area are low in Pb and Cr and slightly higher in Cd. PLI were below 1 for all studied metals, indicating an unpolluted condition for the assessed heavy metals. The mean contamination factor values for Cr and Pb were all less than unity indicating low contamination, whereas the values of Cd indicated that it has considerable contamination. The values of Igeo for Cr and Pb fell in class '0', indicating practically uncontaminated conditions while Cd showed moderate contamination in these areas. Effort should therefore be made to reduce Cd levels in the study area to ensure safety of agricultural produce and maintain fertility of soils in the area.

DISCLAIMER (ARTIFICIAL INTELLIGENCE)

We, the authors hereby declare that NO generative AI technologies such as Large Language Models (ChatGPT, COPILOT, etc.) and text-to-image generators have been used during the writing or editing of this manuscript.

ETHICAL APROVAL

The authors hereby declare that standard procedures for analysis of heavy metals were strictly followed during the time of analysis in the Soil Science Laboratory of University of Calabar.

COMPETING INTEREST

The authors have declared that no competing interest exists about this study.

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