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ASSESSMENT OF POTENTIALLY TOXIC METALS AND PHYSICO-CHEMICAL PROPERTIES OF SOILS OF A SANDSTONE LANDSCAPE IN CROSS RIVER STATE, NIGERIA

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ABSTRACT

The presence of metals in concentrations that exceed safe thresholds have the capacity to endanger food production and human health security through bioaccumulation in animals and plants. The antagonistic effects of the potentially toxic metals (PTMs) may potentially cause a decline in soil fertility which eventually results in crop growth decline, impaired development and decreased productivity. This study seeks to evaluate the concentration of PTMs in soils of sandstone origin in a tropical rainforest in Cross River State, Nigeria. A profile pit was sunk in each of crest, middle slope and valley-bottom along a landscape in the Agoi Ibami-Mfamosing area. The landscape extended from the Agoi Ibami area to Mfamosing. Soil samples were collected and subjected to physico-chemical analyses and heavy metals extraction by aqua regia mixture of 3 parts of HCl and 1 part of HNO_3. The extract was analyzed using inductively coupled plasma optical electron spectroscopy (model iCAP 7000). The particle sizes were dominated by sand with amounts exceeding 600 g kg^{-1}, while bulk density was lower than 1.6 Mg m^{-3} and soil pH ranged from strongly acid to neutral (5.3-7.2) across all sampled locations. Amongst the potentially toxic metals studied, arsenic (As), boron (B), barium (Ba), beryllium (Be), cadmium (Cd), cobalt (Co), chromium (Cr), copper (Cu), nickel (Ni), lead (Pb), antimony (Sb), vanadium (V) and zinc (Zn) were reported in the study area, however, only Be (1.85-4.16 mg kg^{-1}), Cd (0.21-1.88 mg kg^{-1}) and Sb (1.87-4.48 mg kg^{-1}) exceeded the required threshold across the entire study area. Lead concentration was found to exceed the required threshold only in Agoi Ibami. Hence, Be, Cd, Sb and Pb are most likely to be a threat to the activities of micro and macro fauna and flora in the area. There is therefore the need to embark on a full-scale evaluation with larger sample size to ascertain the status of potentially toxic metals' concentration in the Cross River State tropical rainforest soils.

Key words: potentially toxic metals, sandstone, soil, tropical rainforest

INTRODUCTION

Soil is a dynamic non-renewable natural resource that is necessary for the survival of man. Soils contain natural levels of heavy metals. This is as a result of the lithology from which the soils are derived (De Temmerman *et al*., 2003). However, human activities like agricultural activities such as pesticides, fertilizers, insecticides and fungicides usage, mining, aerial deposition from industrial sites, construction sites, surface depositions at waste-sites as well as from automobiles have contributed in raising the natural levels of these metals (Kang *et al*., 2020; Zhao *et al*., 2022). The presence of potentially toxic metals (PTMs) that exceed safe thresholds may be a threat to food security as the metals become bio-accumulated in exposed crops and animals. For instance, Zandsalimi *et al.* (2011) found a positive correlation between arsenic levels in soils and plants. This accumulation of the PTMs in soils tends to cause a decrease in soil productivity as the PTMs interact with nutrients leading to a decline in crop growth, development and yield (Kabata-Pendias, 2011; Tyopine *et al.,* 2022).

Plants take up various metal complexes leading to the bio-accumulation of toxic metals in their tissues. When these crops are eventually consumed by man, it may result in health-related complications. Several international organizations (World Health Organization, Food and Agriculture Organization of the United Nations, etc.) collaborate to shield man away from excessive metals intake, especially Cd and Pb in plant food, for which threshold limits have been established (Kabata-Pendias and Mukherjee, 2007). Potentially toxic metals entering plants in

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active forms alter their metabolic processes and become bio-accumulated or stored in inactive forms in cells, tissues and membranes, leading to changes in the chemical makeup of organisms without causing physical injury (Jaishankar *et al*., 2014). Such nonvisible changes are even more dangerous to humans upon consumption.

Despite variability in toxicity levels, mercury, copper, nickel, lead, cobalt, cadmium, silver, beryllium and antimony have been identified as the most lethal metals in plants, animals and soils (Kabata-Pendias, 2011). Cadmium is eco-toxic and exhibit adverse effects on biological processes in plants, man and other animals, and causes detrimental effects on the ecosystem and quality of food (Kabata-Pendias, 2011). Potentially toxic metals, particularly Cd, Cu, Zn, and Ni occur in available forms and are bioavailable in tropical soils (Kabata-Pendias, 2011), whereas Ma (1983) reported harmful concentrations of Zn at 3500 mg kg^{-1} in environments where earthworms occur in large numbers compared to other soil faunal biomass.

The tropical rainforest areas of Cross River State is of rich biodiversity due to soil micro flora/fauna, the plants growing on the soil, and the animals that rely on the plants (Ediene *et al.,* 2016). Most of such plant and animal species are consumed by man several kilometers away without any consciousness of the organism's chemical makeup. It is, therefore, necessary to study the sandstone soils in Agoi Ibami-Mfamosing rainforest landscape to ascertain the concentration of PTMs. The objective of this study was to ascertain the natural concentration of potentially toxic metals in soils of sandstone origin in a tropical rainforest in Cross River State - Nigeria.

MATERIALS AND METHODS

Study Area

Agoi Ibami and Mfamosing are located at 05° 42′ 40″, 05° 44′ 20″ N and 08° 10′ 0″, 08° 11′0″ E, and 05° 3′ 30″, 05° 5′ 0″ N and 08° 30′ 0″, 08° 32′30″ E, respectively. Agoi Ibami and Mfamosing are located about 119 and 44.6 km away from Calabar, the capital city of Cross River State, respectively. Both locations are agrarian communities that are found in the interlocking Yakurr-Akamkpa area in the tropical rainforest of Cross River State. Farming is the major occupation of the inhabitants of the area with crops like cassava, oil palm, yam, plantain and banana commonly cultivated. However, mining, hunting and wood logging are some common activities in the area.

The lithology of Cross River State is best defined by a complex of igneous and metamorphic rocks as well as Sedimentary Basin without any clear boundary between both geologies (Figure 1) (Ekwueme, 1987). Sediment-fill of Cretaceous to Tertiary ages in Nigeria's Niger-Delta characterize the Sedimentary Basin (Fatoye and Gideon, 2013). Recent alluvial sediments dominate the coastal areas adjoining rivers and streams whereas, limestone and sandstone lithologies of Cretaceous and Tertiary ages intercalate with shale and siltstone, as well as fine-grained sandstone (Ofem *et al*., 2020). The study areas are geologically characterized by their unique limestone, sandstone, and alluvial lithologies.

The climate of Cross River State is humid tropical (Ofem *et al*., 2022). Rainfall amount ranges from minimum amounts of 1760 and 2109, to maximum of 2684 and 3771 mm per year in Agoi Ibami and Mfamosing, respectively (Sambo *et al.,* 2016). Similar temperature of 23 to 32 °C characterize both locations.

Field and Laboratory Procedures

The digital elevation model (DEM) of the study area was obtained at 30 m from USGS explorer. From the DEM, contour-topographic map of the study area was generated highlighting various high and low points using ArcGIS 10.8. A soil pit was dug in the crest, middle-slope and valley positions extending from Agoi Ibami to Mfamosing (Figure 2). Within each position, the profile pits were sunk by the free-soil survey method. The soil pits were excavated at length of 200 cm and breadth of 150 cm to a variable depth of *x* cm depending on the depth to water table and impenetrable layer. Three profiles were dug for the research: two in Agoi Ibami (AI1 and AI2) and one in Mfamosing (MF1). The field study lasted three months, from December 2018 to February 2019. Ten soil samples were collected from predetermined depths of 0-30, 30-60, 60-90, 90-120, 120-150, 150-180 and 180-200 cm, and processed for laboratory analyses. Vertically-drilled core cylinder samples were used for bulk density determination. The core samples were saturated and dried to constant weight in an oven at a temperature of 105 °C. Then, soil bulk density was calculated by dividing mass of dry soil by volume of soil in core (Obi and Obalum, 2016). Soil samples from three points within a depth range were bulked to form composite samples.

The samples were air-dried and the peds crushed, made to pass through 2-mm aperture sieve before laboratory analyses. Particle size analysis was by Bouyoucous hydrometer method. Soil pH-H_2O was determined in a soil: water ratio of 1:2.5 with a glass electrode pH meter. Organic carbon content was obtained using the procedures of Walkley–Black modified acid–dichromate, while basic cations in the soils' exchange complex were extracted with 1 *N* ammonium acetate at neutral pH. The Ca and Mg in the extract were ascertained by the Versenate EDTA titration method, and K and Na by the flame photometer method. Soil cation exchange capacity (CEC) was obtained by extraction using 1 *N* NH_4OAc at pH = 7.0. All laboratory analyses were carried out by the procedures in Soil Survey Staff (2014). Pseudo-total concentrations of arsenic (As), (boron) B, barium (Ba), beryllium (Be), cadmium (Cd), cobalt (Co), chromium (Cr), copper (Cu), nickel (Ni), antimony (Sb), vanadium (V) and zinc (Zn) were extracted from the soils with aqua regia mixture. The mixture is comprised of 3 parts of HCl and 1 part of HNO_3. The extract was analyzed using inductively coupled plasma optical electron spectroscopy (model iCAP 7000) and separated into three fractions and analyzed in triplicates and the average taken. The extraction and recording procedures are reported in Cools and De Vos (2016).

Statistical Analysis

Correlation analysis was performed in the STATISTICA 12 software environment to check the relationship between soil properties. Also, simple *t*-test was performed to check for significant ($p < 0.01$ or 0.05) difference between landscape positions.

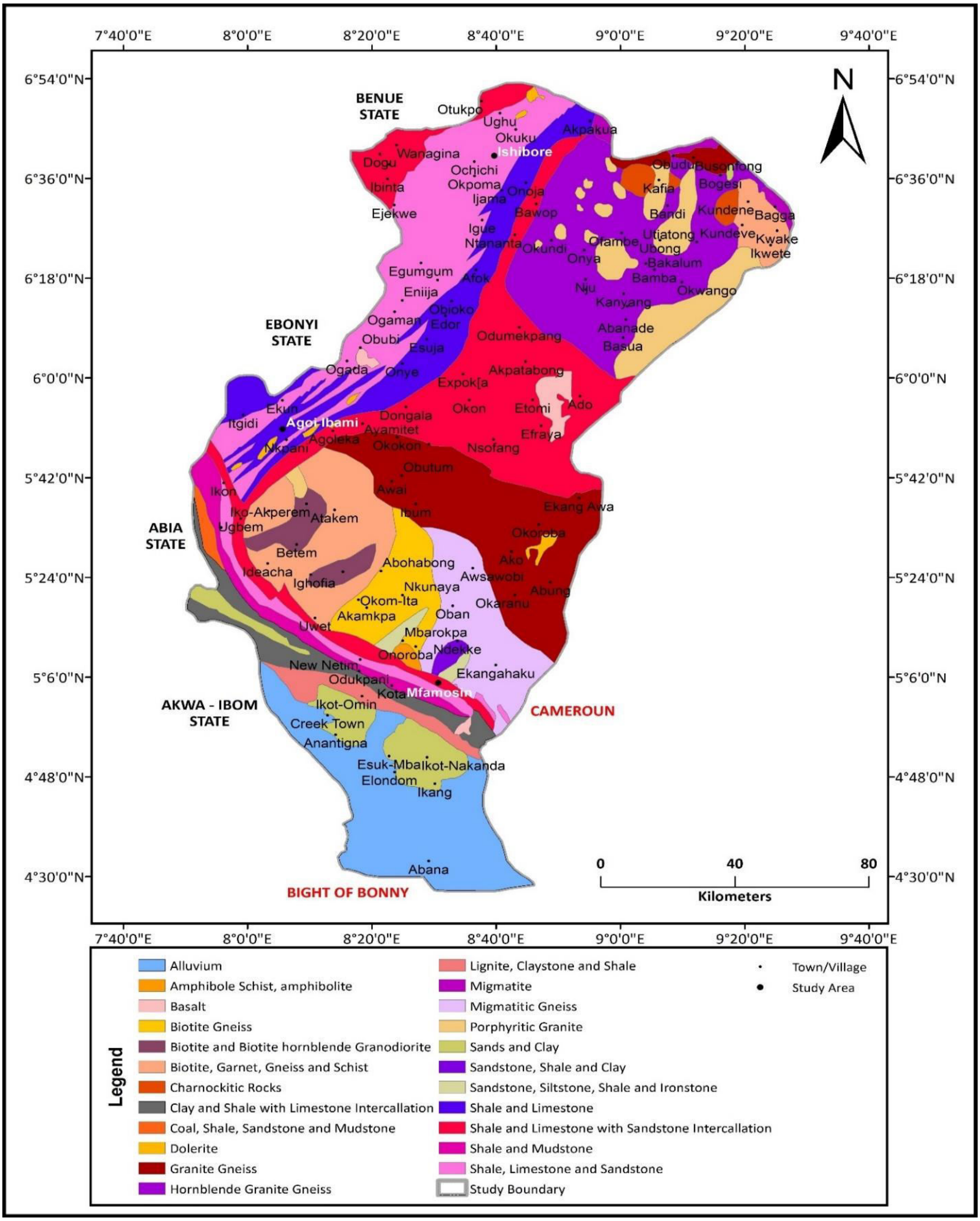

Figure 1: Geology map of Cross River State

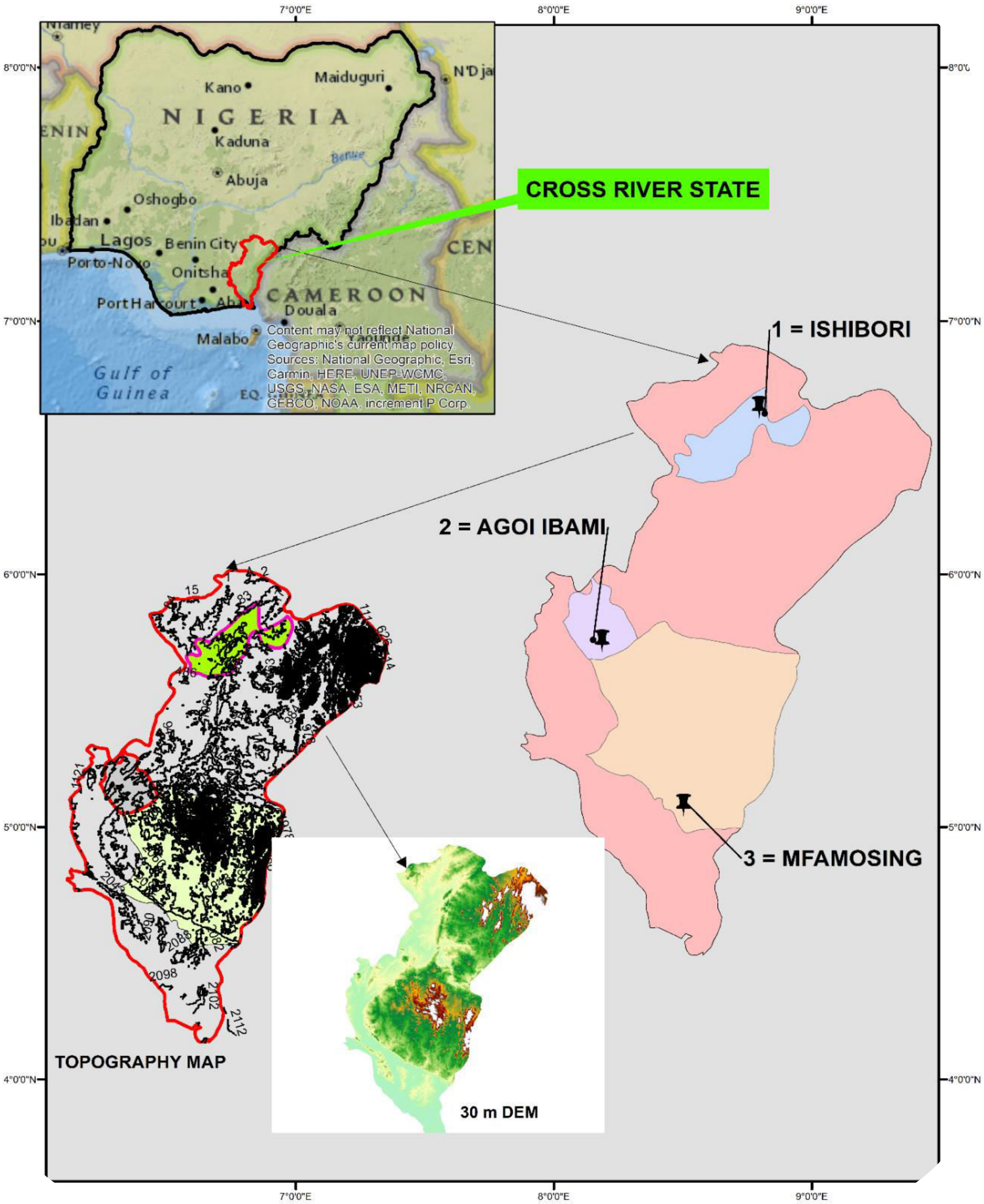

Figure 2: Topography and DEM maps of Cross River State indicating Agoi Ibami - Mfamosing

RESULTS AND DISCUSSION

Physical and Chemical Soil Properties

Physicochemical properties of the soils are shown in Table 1. The soils were characterized by sand-sized particles. Sand fraction exceeded 600 g kg^{-1} at all depths irrespective of landscape positions. However, clay amount increased with depth as also reported for coarse-textured soils of the derived savanna (Obalum *et al*., 2013a), whereas silt content varied in an irregular manner within the soil profile. High amount of sand in the soils reflects its sandstone lithology (Souza *et al.,* 2019). Such sand-dominated soils are defined by high porosity, infiltration rate, and leaching of basic cations, and when occurring in high-rainfall areas like the study location, generally are of low fertility status (Ofem *et al.,* 2021; Ifeanyi-Onyishi *et al.,* 2024). Clay and sand amounts varied significantly ($p < 0.05$) between the surface soils of the landscape positions such that highest clay content was in the middle slope and sand content in the crest (Table 1). This suggests greater ease of movement of clay particles compared to sand. Least sand in the valley bottom is due to the difficulty with which sand is carried down the slope by surficial erosion.

Sandstone derived soils are sandy, erodible, have low soil pH, and are marginal in terms of productivity (Bulktrade, 1989; Udoh, 2015; Ofem *et al*., 2020). Results that are similar to those in this study were reported by Laffan *et al.* (1998) in the soils derived from sandstone in New Zealand.

Bulk density was between 1.0 and 1.6 Mg m^{-3} and tended to increase with depth. Highest values at the surface were obtained in the middle slope and significantly varied from other landscape positions at $p < 0.05$ (Table 1). Bulk density values in the surface soils ranged from 1.1 to 1.4 Mg m^{-3} which is considered optimum for plant growth and root penetration (Donahue *et al.*, 1983; Esu, 2010).

Soil pH (H_2O) ranged from 5.3 to 7.2. These values are within the strongly acid to neutral range on the scale of Holland *et al*. (1989). Such soil pH is optimum for microbial activities and the availability of most soil nutrients. Low pH (< 5.5 pH units) in the studied soils is as a result of low soil base status (Souza *et al.,* 2019) emanating from leaching. Such values indicate that high concentrations of exchangeable Al^{3+} and H^+ are present in the soils to influence plant growth (Esu, 2010). Soil organic carbon content was generally below 15 g kg^{-1} with values ranging from 0.69 to 13.73 g kg^{-1} in the soils and decreased steadily with soil depth (Table 1). The values were rated low to medium on the scale of Holland *et al.* (1989). The decreasing values with soil depth indicate the dominance of organic matter accumulation over mineralization in the tropical rainforest area. Thus, low soil organic carbon in the tropics is often attributed to organic matter mineralization, loss to leaching, and bush burning. The values obtained in this study are within the range of 0.80-15.4 g kg^{-1} obtained by Ofem *et al*. (2020) and Bulktrade (1989) on similar soils in the Bekwarra area.

The exchange complex of the soils was mainly occupied by exchangeable Ca such that Ca > Mg > K > Na with ranges of 0.8-6.0, 0.4-2.2, 0.0-0.11 and 0.0-0.06 cmol(+) kg^{-1}, respectively. Exchangeable Ca was higher in the valley than the crest and middle slope positions, however, the values did not vary significantly. The concentrations of Ca and Mg in the exchange complex were rated medium, whereas K and Na were rated low on the scale of Holland *et al.* (1989). The soil exchangeable bases, particularly Ca and Mg are weakly held in the soil exchange complex (Ofem *et al*., 2021). Such weak attachments predispose the cations to easy leaching especially as the soils are porous and sandy. Soils that are leached of K^+, especially those with coarse soil textures may not be very suitable for crop production in the tropics (Ofem *et al*., 2016). In this current study, significant variation in exchangeable Na and K in the surface soils was observed. The highest values were obtained in the valley bottom position (Table 1). A study by Ofem *et al.* (2020) reported 4.0-7.6 and 0.8-1.8 cmol(+) kg^{-1} for the concentration of Ca and Mg in the exchange complex of surface sandstone derived soils of Bekwarra area.

Cation exchange capacity was higher (though not significantly) in the valley bottom (19.2-19.6 cmol(+) kg^{-1}) than the crest (12.0-19.6 cmol(+) kg^{-1}) and middle slope (4.4-15.2 cmol(+) kg^{-1}) positions with values in the crest and middle slope positions increasing regularly in a similar fashion as the clay amount with $r = 0.39$ at $p < 0.05$, compared to $r = -0.13$ with organic carbon (Table 2). Comparatively higher values were also obtained in the subsurface soils. Based on the rating scale of Holland *et al.* (1989), the crest and valley bottom soils are medium, while the middle slope soil is low. Values of CEC below 8.8 cmol(+) kg^{-1} were reported in an earlier study by Souza *et al*. (2019) in Brazil, while Ofem *et al.* (2020) reported a range of 14-50 cmol(+) kg^{-1} for similar sandstone-derived soils. Udoh (2015) reported lower values of CEC for similar soils in the Niger Delta of Nigeria. The relatively higher CEC values in subsurface soils like the clay distribution with depth suggests that the soils are of low structure stability and points at clay and not organic matter as a likely factor responsible for the soils exchange capacity (Obalum *et al*., 2013b; Ofem *et al*., 2020).

Table 1: Selected physical and chemical properties of the soils

Soil depth (cm)	Clay	Silt	Sand	BD	pH	SOC	Na	K	Mg	Ca	CEC
		g kg^{-1}		(Mg m^{-3})		g kg^{-1}			cmol(+) kg^{-1}		
Agoi Ibami: Crest: Sandstone (N05°43.435′, E008°09.029 ′, 93 m)											
AI1 0-30	100	60	840	1.19	7.2	8.92	0.05	0.09	1.0	3.9	12.0
AI1 30-60	140	80	780	1.46	6.4	3.43	0.02	0.05	1.2	2.0	17.6
AI1 120-150	260	70	670	1.59	5.3	2.1	0.02	0.05	0.5	1.3	18.6
AI1 180-200	290	70	640	1.53	5.4	2.4	0.02	0.05	0.8	0.8	19.6
Agoi Ibami: Middle slope: Sandstone (N05°44.386′, E008°10.660 ′, 80 m)											
AI2 0-30	160	120	720	1.35	6.7	7.55	0.04	0.07	1.4	1.6	4.4
AI2 30-60	160	100	740	1.59	5.7	4.12	0.02	0.06	0.8	1.6	5.2
AI2 60-90	180	100	700	1.59	5.7	4.12	0.02	0.06	0.8	1.6	5.2
AI2 90-120	220	140	640	1.49	6.5	3.43	0.02	0.05	2.2	5.6	15.2
Mfamosing: Valley bottom: Alluvium (N05°04.714′, E008°30.541 ′, 58 m)											
MF1 0-30	140	180	680	1.29	6.6	13.73	0.06	0.11	0.6	6.0	19.2
MF1 60-90	200	130	770	1.39	5.6	0.69	0.0	0.0	0.40	5.6	19.6
t-ratio ($p = 0.05$)	0.017*	NS	0.004*	0.001**	0.001**	NS	0.013*	0.016*	0.049*	NS	NS

SOC - soil organic carbon, BD - bulk density, CEC - cation exchange capacity;
*significant at $p < 0.05$, **significant at $p < 0.01$, NS - not significant

Table 2: Concentrations of potentially toxic metals in the studied soils

Soil depth	As	B	Ba	Be	Cd	Co	Cr	Cu	Ni	Pb	Sb	V	Zn
(cm)	mg kg^{-1}												
Agoi Ibami: Crest: Sandstone (N05º43.435′, E008º09.029 ′, 93 m)													
AI1 0-30	2.03	2.11	243.54	1.98	0.21	0.62	5.34	16.23	1.93	15.03	1.87	7.48	9.87
AI1 30-60	1.85	1.85	274.75	1.85	0.44	0.50	6.09	14.51	1.72	13.98	2.25	11.16	12.68
AI1 120-150	1.66	1.85	1076.79	1.85	0.56	0.50	6.74	9.76	1.25	11.27	2.25	14.63	11.67
AI1 180-200	1.35	1.85	180.45	1.85	1.42	0.50	8.38	3.87	2.35	36.04	3.54	21.02	13.36
Agoi Ibami: Middle slope: Sandstone (N05º44.386′, E008º10.660 ′, 80 m)													
AI2 0-30	1.85	1.85	122.02	1.85	0.21	0.50	0.86	5.12	0.98	4.97	2.25	1.43	7.93
AI2 30-60	1.85	1.85	84.96	1.85	1.88	0.50	3.94	7.12	5.24	15.93	4.48	7.48	22.35
AI2 60-90	1.85	1.85	270.98	1.85	1.21	0.50	1.63	5.87	3.47	11.50	2.25	4.80	19.51
AI2 90-120	1.85	1.85	296.53	4.16	1.51	9.22	2.41	16.14	14.14	23.14	2.25	6.21	25.39
Mfamosing: Valley bottom: Alluvium (N05º04.714′, E008º30.541 ′, 58 m)													
MF1 0-30	1.85	1.85	32.98	1.85	0.73	0.50	5.67	3.44	4.81	12.72	3.64	7.93	18.25
MF1 60-90	1.85	1.85	47.87	1.85	0.72	0.50	6.58	8.22	5.60	14.31	2.25	7.85	25.35
t-ratio (p = 0.05)	0.001**	0.002*	NS	0.005*	NS	0.005*	NS	NS	NS	NS	0.041*	NS	NS
World soil average[1]	6.83	42	460	1.34	0.41	11.3	59.5	38.9	29	27	0.67	129	70
Threshold value[2]	5	NA	NA	NA	1.0	20	100	100	50	60	2	100	200
Lower guide value[2]	50e	NA	NA	NA	10e	100e	200e	150e	100e	200e	10t	150e	250e
Higher guide value[2]	100e	NA	NA	NA	20e	250e	300e	200e	150e	750e	50e	250e	400e

Source: Ministry of the Environment, Finland (2007) [2], Kabata-Pendias (2011) [1]. e: ecological risks, t: health risks
*significant at $p < 0.05$; **significant at $p < 0.01$, NS - not significant

Concentrations of Potentially Toxic Metals

Metals concentrations in the soils are presented in Table 3. Arsenic had concentration ranging from 1.35 from 2.03 mg kg^{-1}, boron concentration ranged from 1.85 to 2.11 mg kg^{-1}, while barium ranged from 32.98 to 1076.79 mg kg^{-1} (Table 3). The contents of As and B were less than the respective world soil averages of 6.83 and 42.0 mg kg^{-1} (Kabata-Pendias, 2011). However, values of Ba (1076.79 mg kg^{-1}) exceeded the world soil average of 460 mg kg^{-1} in AI1 (120-150 cm). Areas with low anthropogenic activities such as the tropical rainforest areas adopted for the current study but having raised concentrations of Ba require an evaluation to examine the mobility and bioavailability of Ba (Biondi *et al*., 2011). Nriagu *et al*. (2007) opined that high toxicity of As is a threat to human health and global ecosystems. The average of As in the earth's crust is 1.8 mg kg^{-1}, and in untampered soil bodies falls below 10 mg kg^{-1} (Mench *et al*., 2009). Arsenic often gets accumulated since it has low mobility in soils (Mench *et al.,* 2009; Beesley and Marmiroli, 2011). In agreement with these results, Njoku *et al.* (2021) reported that As concentration in southeastern Nigeria suggests extremely polluted conditions.

Cobalt, chromium, copper, nickel and lead had concentrations values with ranges of 0.50-9.22, 1.63-8.38, 3.44-16.23, 1.25-14.44 and 4.97-36.04 mg kg^{-1} compared to their respective world soil averages of 11.3, 59.5, 38.9, 29.0 and 27.0 mg kg^{-1}, respectively (Table 3). Amongst these metals, Cr recorded the highest mean value whereas Co recorded the lowest mean values. This negates the report of Tyopine *et al.* (2022) in Ikwo soils that Sb > B > As. However, Pb contents in AI1 (180-200 cm) exceeded 27.0 mg kg^{-1} representing the world soil average. The transfer potential of cobalt from soil to fruits, seeds, leaves, roots and other edible parts of crops is slow (Luo *et al*., 2010). The metal has been reported to play important roles in human health. However, in excess concentrations, Co can result in damages to the lungs and heart (Agency for Toxic Substances and Diseases Registry, 2004). Positive correlation of Co with Mg^{2+} (Table 2) indicates increasing values of Co when Mg^{2+} increases in soils. Prolonged exposure to raised doses of Cr may cause detrimental effects to the liver and kidney. Soils with such raised concentrations may rarely be remediated *in-situ* as the process can be quite complicated (Palmer and Wittbrod, 1991; Pagilla and Canter, 1999). It would be especially important to control a further buildup in order to regulate raised concentrations of Cr in the soil.

The values of Ni, Pb and Zn in this study were comparatively higher with ranges of 0.98-14.14, 4.97-36.04 and 7.93-25.39 mg kg^{-1}, respectively, while Cu and Cr were comparatively lower than those reported by Santos and Alleoni (2013) with ranges of 3.44-16.23 and 0.86-8.38 mg kg^{-1}, respectively. Njoku *et al*. (2021) reported polluted concentration of Ni in southeastern Nigeria, while Santos and Alleoni (2013) obtained the concentrations of 2.1 mg kg^{-1} (Ni), 9.0 mg kg^{-1} (Pb), 3.0 mg kg^{-1} (Zn), 20.6 mg kg^{-1} (Cu) and 44.8 mg kg^{-1} (Cr). According to Fishet (2014), raised contents of Cu in soils is mainly due to the activities of man. For example, mining and agricultural use of chemicals farmlands most often introduce these PTMs to soil bodies. Raised levels of Ni adversely affect the man by degrading the immune and reproductive systems (Agency for Toxic Substances and Diseases Registry, 2005). The mobility of Ni and its potential for bioavailability is among the least compared to other PTMs (Ma and Rao, 1997), hence its low concentration in the studied soils. Though Pb occurred in low concentration in the soils except in AI1 (180-200 cm). It is important to note that even at low exposure levels, Pb can affect the central nervous system especially in children, and cause high blood pressure, kidney disease and cancer (International Agency for Research on Cancer, 2006; Agency for Toxic Substances and Diseases Registry, 2007).

Vanadium (1.43-21.02 mg kg^{-1}) and zinc (7.93-25.39 mg kg^{-1}) had concentrations below world soil averages of 129 and 70 mg kg^{-1}, respectively. The relatively low values of V and Zn indicates that the metals have low potentials for adverse soil health effects. Furthermore, positive correlation of vanadium with clay and CEC (Table 2) indicates the likelihood for increasing vanadium when the soil inorganic surface area is improved. PTMs in soils that are minimally influenced by man are usually below toxic concentration levels and do not pose threats to man, and other components of the ecosystem (Paye *et al*., 2010; Lu *et al*., 2012). However, the impact of agriculture on the PTMs content is not completely ruled out especially as adjoining areas have been put to agriculture. As essential as Zn is to plants and humans, it may be toxic to organisms in excess amounts (Swartjes, 2011). Zinc deficiency in soils is due to high soil pH (Alloway, 2008), whereas excess of it may be due to geologic and anthropogenic sources (Tóth *et al*., 2016).

Beryllium and cadmium had concentrations ranges of 1.85-1.98 and 0.2-1.88 mg kg^{-1} exceeding the world soil averages of 1.34 and 0.41 mg kg^{-1}, respectively. In a similar way, antimony (Sb) ranged from 1.87-4.48 mg kg^{-1} exceeding 0.67 mg kg^{-1} recommended as the global soil average. Antimony had raised concentrations with values that exceed threshold level of 2.0 mg kg^{-1} in the soils of Agoi Ibami and Mfamosing. The level of Cd in the soils of Agoi Ibami exceeds the threshold concentration of 1.0 mg kg^{-1} set by Kabata-Pendias (2011), but was below the lower guideline concentration of 10 mg kg^{-1} set by Ministry of the Environment, Finland (2007). The PTMs like Cd, Cr, and Pb pose a threat to human health by bio-accumulation in edible plant parts which are later consumed by man and animals (Proshad *et al*., 2021). Heavy metals contamination in soils is transferred to plants and they become bio-accumulated in the human body via consumption of contaminated food and water (Yi *et al.,* 2017). Also, the PTMs in soils are most often leached into estuarine and coastal environments by streams and sediments transportation. This results in raised levels in the surrounding marine ecosystem (Förstner *et al*., 2004). There is therefore the likelihood for a buildup of these metals in marine organisms. Arsenic and cadmium have been reported to be moderately to strongly polluted in some wetland soils (Bai *et al*., 2012). Also, Cadmium is naturally present in most soils in the tropics therefore, it is not out of place to have Cd values exceed tolerable levels in the tropical rainforest soils (Ofem *et al*., 2023). Besides the study by Ofem *et al*. (2023), Duru *et al*. (2021) reported higher concentrations of As, Zn, Cr, Ni, Cu and Cd in some reclaimed soils of Southeastern Nigeria. Similar concentration levels have been reported in the tidal soils of the Yellow River Estuary. In the soils, Cr, Cu, and Ni originated mainly from the adjoining parent rocks and Pb possibly from tidal seawater and oil field pollution (Bai *et al.,* 2011). Beryllium correlated with Mg^{2+} ($r > 0.80$) whereas chromium correlated with CEC ($r = 0.82$), indicating increasing Be and Cr when Mg^{2+} and CEC increase, respectively.

Relationship between the mobile fraction of Sb in soils and its concentration in the leaves of spinach has been established by Hammel *et al.* (2000). This indicates that high concentration of Sb in soil can result in its accumulation in plants. Persistent bio-accumulation of Sb could be dangerous to end-consumers of such plant materials. Boron, beryllium and cobalt significantly varied across the surface soils of the crest, middle slope and valley bottom with the highest values occurring in the crest, whereas the highest value of Sb occurred in the valley bottom.

CONCLUSION AND RECOMMENDATION

Some properties and potentially toxic metals in the soils of a tropical rainforest area in Cross River State were studied. The soils were found to be dominated by sand with amounts exceeding 600 g kg^{-1} and ranging from 640-840 g kg^{-1}, while bulk density was below 1.6 Mg m^{-3} and soil pH ranged from acidic to neutral (5.3-7.2). The potentially toxic metals studied were As, B, Ba, Be, Cd, Co, Cr, Cu, Ni, Pb, Sb, V and Zn. Of the studied metals, only Be (1.85-4.16 mg kg^{-1}), Cd (0.21-1.88 mg kg^{-1}) and Sb (1.87-4.48 mg kg^{-1}) exceeded their world soil averages. Pb exceeded the world soil average only in Agoi Ibami. Hence, Be, Cd, Sb and to some extent Pb are most likely to be a threat to the activities of micro and macro fauna and flora in the area. There is, therefore, the need to embark on a full-scale evaluation of the soils with larger sample size for the status of PTMs in the Cross River State tropical rainforest area.

REFERENCES

Alloway B.J. (2008). Zinc in soils and crop nutrition. International Fertilizer Industry Association, and International Zinc Association

Agency for Toxic Substances and Disease Registry (2004). Toxicological rofile for cobalt. United States Department of Health and Human Services, P. 486

Agency for Toxic Substances and Disease Registry (2005). Toxicological profile for nickel. United States Department of Health and Human Services, P. 351

Agency for Toxic Substances and Disease Registry (2007). Toxicological profile for lead. United States Department of Health and Human Services, P. 582

Bai J.H., Huang L.B., Yan D.H., Wang Q.G., Gao H.F., Xiao R. and Huang C. (2011). Contamination characteristics of heavy metals in wetland soils along a tidal ditch of the Yellow River Estuary, China. *Stoch. Env. Res. Risk. A.,* **25**, 671-676

Bai J.H., Xiao R., Zhang K.J. and Gao H.F. (2012). Arsenic and heavy metal pollution in wetland soils from tidal freshwater and salt marshes before and after the flow-sediment regulation regime in the Yellow River Delta, *China. J. Hydrol.,* **450-451,** 244-253

Beesley L. and Marmiroli M. (2011). The immobilization and retention of soluble arsenic, cadmium and zinc by biochar. *Environ. Pollut*., **159,** 474-480

Biondi C.M., Nascimento C.W.A. and Fabrício Neta A.B. (2011). Teores naturais de bário em solos de referência do estado de Pernambuco. *Rev. Bras. Cienc. Solo*., **35,** 18-26. https://doi.org/10.1590/S0100-06832011000500036

Bulktrade and Investment Company Limited (1989). Soil and land use survey of Cross River State, main Report, Ministry of Agriculture and Natural Resources, Cross River State Nigeria

Cools N. and De Vos B. (2016). Part X: Sampling and analysis of soil. In: UNECE ICP Forests Programme Coordinating Centre (ed.), *Manual on Methods and Criteria for Harmonized Sampling, Assessment, Monitoring and Analysis of the Effects of Air Pollution on Forests.* Thünen Institute of Forest Ecosystems, Eberswalde, Germany, pp. 29. Annex. Available at https://www.icp-forests.org/pdf/manual/2016/ICP_Manual_2016_01_part10.pdf

De Temmerman L., Vanongeval L., Boon W. and Hoenig G. (2003). Heavy metal content of arable soils in northern Belgium. *Water Air Soil Pollut*., **148,** 61-76. https://doi.org/10.1023/A:1025498629671

Donahue R.L., Miller R.W. and Shickluna J.C. (1983). *An Introduction to Soils and Plant Growth* (5th edn.). Prentice Hall Inc. Englewood Cliffs, New Jersey, pp. 667

Duru C.E., Enyoh C.B., Enedo M.C., *et al.* (2021). Assessment of heavy metals in soils from reclaimed section of Nekede mechanic village, Owerri, southeastern Nigeria. Chemistry Africa. https://doi.org/10.1007/s42250-020-00216-6

Ediene V.F., Ofem K.I., Unuigbe B.O. and Enyiegoro K.P. (2016). Assessment of the physicochemical and microbial properties of rhizosphere soils under mono-plantations and rain forest in South Eastern Nigeria. *Int. J. Life. Sci. Scienti. Res*., **2 (5),** 531-540

Ekwueme B.N. (1987). Structural orientations and Pre-cambrian deformational episodes of Uwet Area, Oban Massif, SE Nigeria. *Precambrian Res.*, **34 (3-4),** 269-289

Esu I.E. (2010). *Soil Characterization, Classification and Survey* (p. 232). Hinneman Educational Book Publishers PLC, Nigeria

Fatoye F.B. and Gideon Y.B. (2013). Geology and occurrences of limestone and marble in Nigeria. *J. Natural Sci. Res.*, **3 (11),** 60-65

Fishet F.M. (2014). Pesticide toxicity profile: Copper-based pesticides (p. 5). University of Florida

Förstner U., Heise S., Schwartz R., Westrich B. and Ahlf W. (2004). Historical contaminated sediments and soils at the river basin scale. Examples from the Elbe River catchment area. *J. Soils. Sediments,* **4,** 247-260

Hammel W., Debus R. and Steubing L. (2000). Mobility of antimony in soil and its availability to plants. *Chemosphere,* **41 (11),** 1791-1798

Holland M.D.G., Barton A.D. and Morph S.T. (1989). Land Evaluation for Agricultural Recommendation of Cross River National Park. Oban Division. Overseas Development Resources Institute in Collaboration with WWF for the Federal Republic of Nigeria and the Cross River State Government, 7, 34-76

Ifeanyi-Onyishi I.F., Ezeaku V.I., Umeugokwe C.P., Ezeaku P.I. and Obalum S.E. (2024). Distribution of soil fertility indices in aggregate size fractions under different land-use types for coarse-textured soils of the derived savannah. *J. Degraded Mining Lands Manage.* **12 (1)**, 6695-6704. http://doi.org/10.15243/jdmlm.2024.121.6695

International Agency for Research on Cancer (2006). Inorganic and organic lead compounds. IARC Monographs on the Evaluation of Carcinogenic Risks to Human vol. 87, p. 519

Jaishankar M., Tseten T., Anbalagan N., Mathew B.B. and Beeregowda K.N. (2014). *Interdiscip. Toxicol*., **7 (2),** 60-72. https://doi.org/10.2478/intox-2014-0009

Kabata-Pendias A. (2011). *Trace Elements in Soils and Plants* (p. 548). 4th edn. CRC, Boca Raton

Kabata-Pendias A. and Mukherjee A.B. (2007). *Trace Elements from Soil to Human* (p. 550). Springer, Berlin

Kang Z., Wang S., Qin J., Wu R. and Li H. (2020). Pollution characteristics and ecological risk assessment of heavy metals in paddy fields of Fujian province. *China. Sci. Reports,* **10,** 12244. https://doi.org/10.1038/s41598-020-69165-x

Laffan et al. (1998). Some properties of soils on Sandstone, Granite and Dolorite in relation to dry and wet Eucalypt forest types in Northern Tasmania. *TasForest*, **10**, 49-58

Lu Z., Cai M., Wang J., Yang H. and He J. (2012). Baseline values for metals in soils on Fildes Peninsula, King George Island, Antarctica: the extent of anthropogenic pollution. *Environ. Monit. Assess.*, **184,** 13-21. https://doi.org/10.1007/s10661-011-2476-x

Luo D., Zheng H., Chen Y., Wang G. and Ding F. (2010). Transfer characteristics of cobalt from soil to crops in the suburban areas of Fujian Province, Southeast China. *J. Environ. Manag.* **91 (11)**, 2248-2253.

Ma W. (1983). Biomonitoring of soil pollution: ecotoxicological studies of the effect of soil-borne heavy metals on lumbricid earthworms, Annual Report 1982, Research Institute Nature Management, Arnhem, 83

Ma L.Q. and Rao G.N. (1997). Chemical fractionation of cadmium, copper, nickel, and zinc in contaminated soils. *J. Environ. Qual*. **26 (1),** 259-264

Mench M., Schwitzguebel J.P., Schroeder P., Bert V., Gawronski S. and Gupta S. (2009). Assessment of successful experiments and limitations of phytotechnologies: contaminant uptake, detoxification, and sequestration, and consequences to food safety. *Environ. Sci. Pollut. Res.,* **16,** 876-900

Ministry of the Environment, Finland (2007). Government Decree on the Assessment of Soil Contamination and Remediation Needs (214/2007, Mar. 1, 2007)

Nriagu J.O., Bhattacharya P., Mukherjee A.B., Bundschuh J., Zevenhoven R. and Loeppert R.H. (2007). Arsenic in soil and groundwater: an overview. *Trace Metals Other Contamin. Environ.*, **9,** 3-60

Njoku I.J., Nwaokafor B. and Okeke N.K. (2021). Assessment of the contamination of rice husk ash of Izzi CP, Ikwo CP and Izzi R8 rice species of Southeastern Nigeria. *Environ. Challenges*, **5,** 100232

Obalum S.E., Oppong J., Igwe C.A., Watanabe Y. and Obi M.E. (2013). Spatial variability of uncultivated soils in derived savanna. *Int. Agrophys.,* **27 (1)**, 57-67. https://dx.doi.org/10.2478/v10247-012-0068-9

Obalum S.E., Watanabe Y., Igwe C.A., Obi M.E. and Wakatsuki T. (2013). Improving on the prediction of cation exchange capacity for highly weathered and structurally contrasting tropical soils from their fine-earth fractions. *Commun. Soil Sci. Plant Anal.*, **44 (12)**, 1831-1848. https://doi.org/10.1080/00103624.2013.790401

Obi M.E. and Obalum S.E. (2016). *Laboratory Manual for Soil Physics*. Department of Soil Science, University of Nigeria, Nsukka – Nigeria. 45 pp.

Ofem K.I., Abua S.O., Umeugokwe C.P., Ezeaku V.I. and Akpan-Idiok A.U. (2020). Characterization and suitability evaluation of soils over sandstone for cashew (*Anacardium occidentale* L) production in a Nigerian southern guinea savanna. *Int. J. Sci. Res. Publ.*, **10 (7),** 353-368

Ofem K.I, Akpan-Idiok A.U., Afu S.M. and Esu I.E. (2016). Land suitability evaluation of residual and colluvio-alluvial soils for oil palm cultivation in Biase, Cross River State, Nigeria. *Afr. J. Agric. Sci. Technol.,* **4 (4),** 683-691

Ofem K.I., Asadu C.L.A., Ezeaku P.I., Eyong M.O., Umeugokwe C.P. and Awaogu C.E. (2021). Dynamics of soil porosity as influenced by some soil properties in a tropical humid environment. *J. Environ. Sci. Technol*., **14,** 58-67

Ofem K.I., Kefas P.K., Abam P.O., Ediene V.F., Kingsley J. and Mark P. (2023). Soil health Implications of some d-block metals in selected agricultural soils in Southeast Nigeria. *Environ. Monit. Assess.*, **196 (38)** https://doi.org/10.1007/s10661-023-12225-2

Ofem K.I., Kefas P.K. and Garjila Y.A. (2022). Land suitability evaluation for oil palm production in Cross River State, Nigeria. *Agro-Science*, **21 (3),** 85-93. https://dx.doi.org/10.4314/as.v21i3.10

Pagilla K. and Canter L. (1999). Laboratory studies on remediation of chromium-contaminated soils. *J. Environ. Eng.,* **125 (3),** 243-248

Palmer C.D. and Wittbrod P.R. (1991). Processes affecting the remediation of chromium contaminated sites. *Environ. Health Perspect.,* **92,** 25-40

Paye H.S., Mello J.W.V., Abrahão W.A.P., *et al*. (2010). Valores de referência de qualidade para metais pesados em solos no estado do Espírito Santo. *Rev Bras Cienc Solo*, **34,** 2041-51. https://doi.org/10.1590/S0100-06832010000600028

Proshad,R., Islam M.S., Kormoker T., Sayeed A., Khadka S. and Idris A.M. (2021). Potential toxic metals (PTMs) contamination in agricultural soils and foodstuffs with associated source identification and model uncertainty. *Sci. Total Environ.,* **789**, 147962, https://doi.org/10.1016/j.scitotenv.2021.147962

Tóth G., Hermann T., Da Silva M.R. and Montanarella L. (2016). Heavy metals in agricultural soils of the European Union with implications for food safety. *Environ. Int.,* **88**, 29909

Sambo E.E., Ufoegbune G.C., Eruola A.O. and Ojekunle O.Z. (2016). Pattern of climate change in Cross River Basin of Nigeria: Implication to agricul-ture and food security. *Climate Variability and Change: Impact, Science, Innovation and Policy*, Nigerian Meteorological Society (NMETS), Federal College of Education Osiele, Abeokuta. 21-24 Nov., 2016

Santos S.N. and Alleoni L.R F. (2013). Reference values for heavy metals in soils of the Brazilian agricultural frontier in Southwestern Amazonia. *Environ. Monit. Assess*., **185,** 5737-48. https://doi.org/10.1007/s10661-012-2980-7

Soil Survey Staff (2014). Kellogg Soil Survey Laboratory Methods Manual. In: Burt R. and Soil Survey Staff (eds.). *Soil Survey Investigations Report No. 42, Version 5.0* (p. 1001). U.S Department of Agriculture, Natural Resources Conservation Service

Souza D.F., Barbosa R.S., da Bezerra Silva Y.J., de Soares Moura M.C., de Porto Oliveira R. and Martins V. (2019). Genesis of sandstone- derived soils in the Cerrado of the Piauí State Brazil. *Revista Ambiente and Água*. https://doi.org/10.4136/1980- 993X

Swartjes F.A. (2011). Introduction to contaminated site management (2011) In: Swatrjes (ed.), *Dealing with Contaminated Sites* (Chap. 1, pp. 3-81). Springer Science Business Media B.V.

Tyopine A.A, Obalum S.E, Igwe C.A. and Okoye C.O.B. (2022). Spatial distribution and relative enrichment of some upper group trace elements in rhizosphere of highly anthropized and rapidly developing tropical environment. *Int. J. Environ. Qual.,* **49,** 19-33

Udoh B.T. (2015). Suitability of soils derived from sandstone and beach sands for cashew (*Anacardium occidentalis* and Coconut (*Cocos nucifera*) cultivation in the Niger Delta area, Nigeria. *Sky J. Soils Environ. Manage*, **4 (2),** 22-33

Yi Y., Tang C., Yi T., Yang Z. and Zhang S. (2017). Health risk assessment of heavy metals in fish and accumulation patterns in food web in the upper Yangtze River, China. *Ecotox. Environ. Safety*, **145**, 295-302

Zandsalimi S., Karimi N. and Kohandel A. (2011). Arsenic in soil, vegetation and water of a contaminated region. *Int. J. Environ. Sci. Tech*., **8 (2),** 331-338

Zhao H., Wu Y., Lan X., Yang Y., Wu X. and Du L. (2022). Comprehensive assessment of harmful heavy metals in contaminated soil in order to score pollution level. *Sci. Reports*, **12,** 35-52, https://doi.org/10.1038/s41598-022-07602-9