



Profile distribution and soil health implication of some oxides in agrarian soils overlying geologic formations in Southeast Nigeria

K. I. Ofem¹ · C. L. A. Asadu² · P. I. Ezeaku² · Kingsley John³ · Kateřina Vejvodová³ · Václav Tejnecký³ · Karel Němeček³ · Ondřej Drábek³ · Vít Penížek³

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Abstract

This study monitored the concentration and distribution of the oxides of Cr, Ni, Cu, Zn and As in soils overlain by different lithological materials in southeast Nigeria. A 30 × 30 m spatial resolution of digital elevation model guided the selected eight soil profile pits dug for the study. A total of $n = 27$ soil samples were collected from the eight soil profile pits. Samples were air dried, and milled into 3–4 μm powder and analyzed using X-ray fluorescence. The result revealed that the oxides were irregularly distributed vertically, with the least heavy metal oxides obtained in the Ap horizons. Nevertheless, Cr₂O₃ was the most dominant and potentially toxic alongside NiO in Ishibori. Also, As₂O₃ was potentially toxic in most of the studied soils, with those in Ishibori as the most prone. Using multiple linear regression, the prediction was within the acceptable range ($R^2 > 0.50$) except for As. For the prediction function of Cr, fine and coarse sand were negatively correlated with Cr, while CEC was positively correlated with Cu and Zn.

Keywords X-ray fluorescence · Soil quality · Heavy metals · Main transition series

Introduction

Soil health is the capacity of a specific kind of soil to function as a living system within a natural or influenced ecosystem and land-use boundaries to sustain plant and animal productivity, enhance water or air quality, and support human health habitation. Such soils maintain a diverse community of soil organisms that help regulate soil functions such as clean air, water, bountiful crops and forests, productive grazing areas and beautiful landscapes, and food security. Healthy soils must ensure co-existence between soil organisms and crops for healthy and optimum production. The terms soil health and soil quality are functionally

synonymous and often interchangeably used within scientific communities. However, scientists prefer soil quality, while farmers prefer soil health (Harris and Bezdicek 1994). The use of soil health by scientists is on the rise as it implies a connection with soil biology.

Oxides of Cr, Ni, Cu, Zn and As are collectively called first main transition series. They are oxides of potentially toxic metals (Tóth et al. 2016). However, Cu, Ni and Zn are beneficial and essential for plant growth and development (Loftleidir 2005). Ions of these elements are regarded as micronutrients, especially when their concentrations are found within acceptable or threshold values for tolerance by crops and harmless to animals. Consequently, concentrations exceeding acceptable limits in the environment cause toxicity. This explains the guideline value. The content of heavy metals in the parent rocks translates to its natural content in the soils overlying them. However, heavy metals content in the surface soils is jointly influenced by soil-forming processes and pollution (McGrath 1995). Previous studies (Opaluwa et al. 2012; Oluyemi et al. 2008) had focused on bioaccumulation as the resultant impact of low amounts of metals in soils. Such metals originate mainly from their mobile components in dumpsites, quarries, oil-polluted

✉ K. I. Ofem
ofem8303@unical.edu.ng

¹ Department of Soil Science, University of Calabar, Calabar PMB 1115, Cross River State, Nigeria

² Department of Soil Science, University of Nigeria, Nsukka PMB 420001, Enugu State, Nigeria

³ Department of Soil Science and Soil Protection, Faculty of Agrobiological, Food, and Natural Resources, Czech University of Life Sciences, Kamycka 129, 16500 Prague, Czech Republic

areas or from parent materials to farmlands through leaching, runoffs and eventual uptake by crops.

Heavy metals occur naturally in the ecosystem and vary in concentration with location (Opaluwa et al. 2012), especially when influenced by anthropogenic sources or natural processes (Vare 2006; Singh et al. 2011). Such influence may negatively impact the environment through the food chain, underground sea-page, and biodegradability. An important natural source of contamination is geologic bed-rock or substratum (Tchounwou et al. 2012).

Elements of the first main transition series are of important plant nutritional significance. Chromium, Cu and As (Duruibe et al. 2007; Shaheen et al. 2016), and Ni and Zn are of particular concern because of known detrimental health effects on humans through food consumption. For instance, a low concentration of Ni can stimulate growth in higher plants (Welch 1981), while a high concentration may result in Zn and Fe deficiency (Anderson et al. 1973).

Soil is a vital resource for sustaining a quality environment and food supply. Its fitness for agricultural purposes must be held in high esteem, especially when blanket and blind fertilizer application is practiced in agricultural areas. Unreported investigations on oxides of heavy metals in soils derived from diverse lithology in the study area complicate identifying potential problems resulting from agricultural practices. As crucial as heavy metals and their oxides are to the environment, there have not been many available studies on the concentration and contribution of metal oxides in the soil of Sub-Saharan Africa under different lithological materials.

The present research aims to evaluate the concentration, vertical distribution and potential risk of oxides of Cr, Ni, Cu, Zn, and As in farmlands by simple comparison with standard limits. The study also investigated the relationship between metals oxides and soil properties *via* a multivariate statistical method.

Materials and methods

Location, geology, and climate of the study area

The research was conducted in Cross River State (5°32' & 4°27' N, 7°50' & 9°28' E), Southeast Nigeria. The selected study sites were Ishibori (06°39'17" N, 08°47'51" E), Agoi Ibami (05°43'27" N, 08°10'37.2" E), and Mfamosing (05°04'41.8" N; 08°27'49.8" E). The Sedimentary lithology of Cretaceous and Tertiary ages in the area is associated with shale, siltstone, and fine-grained sandstone (Ofem et al. 2020). They are common in the Ikom depression (Mamfe Rift) and Calabar flank.

Tropical humid climate with distinct wet and dry seasons characterize the study areas. The Ishibori area is moist

sub-humid and characterized by southern guinea savannah. At the same time, Agoi Ibami and Mfamosing are mainly moist, humid to per humid and are found in the tropical rainforest. Rainfall varies between 1251.4 and 3347.8 mm/annum in Ishibori, while a range of 1760.3–3770.8 mm/annum is typical of Agoi Ibami and Mfamosing. The temperature of 22.96–33.75 °C characterizes Ishibori, while 22.56–31.95 °C was reported for Agoi Ibami and Mfamosing (Sambo et al. 2016a). Mean relative humidity in Ishibori was reported as 72.14 %, with a mean evaporation rate of 2.24 mm/day and a range of 1.8–2.8 mm/day. In Agoi Ibami, a mean value of 81.71 % was reported for relative humidity, while the evaporation rate had a mean of 3.61 mm/day with a range of 2.9–5.0 mm/day. In Mfamosing, 7.92–80.75 % and 84.99 % were obtained as range and mean, respectively, for relative humidity, while the evaporation rate had a range of 0.9–3.0 mm/day (Sambo et al. 2016b).

Field and laboratory procedures

Google satellite imagery, geology maps and digital elevation models (DEMs) (at 30 m × 30 m spatial resolution) of Ishibori, Agoi Ibami and Mfamosing in Southeast Nigeria were obtained. DEMs were obtained from United States Geological Survey Explorer SRTM 1 (Shuttle Radar Topography Mission). The elevation ranges of the study areas were delineated from high to low, and one soil profile pit was sited along each slope range. Soils over shale-limestone-sandstone formation (SLS), limestone-sandstone formation (LS) and alluvium (ALV) were studied across locations. Consequently, IH1P1, AI1P1 and MF2P1 (SLS), AI2P2 and MF1P1 (LS), and IH2P2, AI3P1 and MF3P2 (ALV) were randomly sited and dug to represent the eight (8) soil units (Fig. 1). A total of 27 composite soil samples were used for the study.

Composite soil samples were obtained from pedogenic horizons (bottom to top) and processed for the determination of bulk density (undisturbed core method), particle size distribution (Bouyoucos hydrometer), soil pH (H₂O), organic carbon (Walkley–Black modified acid–dichromate) and cation exchange capacity by neutral NH₄OAc using the standard procedures (Soil Survey Staff 2014). An automatic mill was used to pulverize and homogenize air-dry soil samples into a fine powder (3–4 μm). The powder samples were analyzed with the 2019 version of XRF Delta Premium Spectrometer (Tejnecky et al. 2015). The oxides were converted to their elemental forms using a standard conversion excel sheet. This was done for easy rating of the oxides.

Modeling approach

Multiple linear regression (MLR) was performed in the StatView environment to model the prediction of heavy

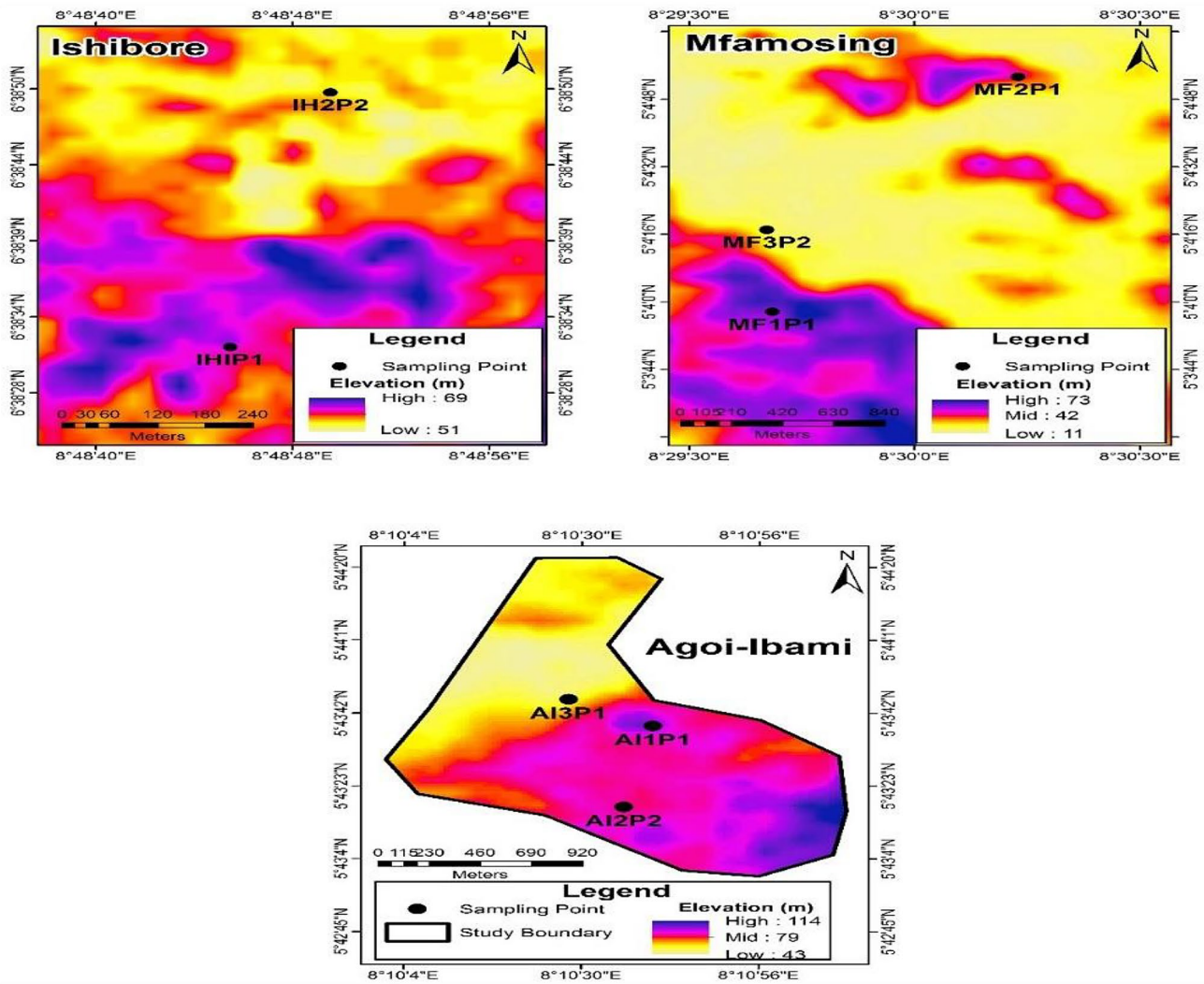


Fig. 1 Digital elevation model of the study areas indicating sampling points

metals using mineral particle sizes, organic carbon and CEC. The MLR model is expressed thus:

$$\text{metal(mg/kg)} = \beta_0 + \beta_{x_1} + \beta_{x_2} + \dots + \beta_k x_k + \epsilon_j, \quad (1)$$

where metal is the response variable, represented by Cr, Ni, Cu, Zn or As. x_1, x_2, \dots, x_k are predictor variables; coarse sand (CS), fine sand (FS), silt, clay, organic carbon (OC) and CEC. ϵ is the residual term of the model and β_0 is regression intercept, while β_x represent regression coefficients.

Test for significance

$$H_0: \beta_1 = \beta_k = 0; H_a: \beta_j \neq 0; \text{ for at least one } j.$$

$$F_{\text{value}} (\text{calculated}) > F_{\text{stat}}; \text{ reject null hypothesis.}$$

Model adequacy

Root mean square error (RMSE), and coefficient of determination (R^2) were used to evaluate the performance of the models. A lower value of RMSE is preferred, while values of R^2 closer to 1 are preferred such that; $R^2 \geq 0.75$ is the best and $R^2 \geq 0.50 - 0.75$ is acceptable prediction (Li et al. 2016).

Statistical analysis

Statistical analyses and model computations were performed using StatView version 5.0.1.

Results

General soil characteristics

The general soil characteristics are presented in Table 1. The soil particle size distribution is dominated by the sand fraction (fine sand dominated the total sand fraction). Soil bulk density was less than 1.6 g/cm³ and presented soils which will encourage root proliferation, air and water movement and without hard-pans. Soil pH ranged between 5.1 and 7.2 in the entire soils with the highest mean value of 6.2 occurring in IH1P1, AI2P2, and MF3P2. Soil pH values

indicated strongly acid and neutral reactions. Low soil pH values (4.5–5.5) indicate the presence of significant amounts of exchangeable Al³⁺, which becomes insoluble when silica is soluble and leachable at higher pH. Organic C was rated low (< 10 g/kg) to very high (> 20.0 g/kg) in the entire soils. Organic C in soils over alluvium was quite high compared to the corresponding soils in the uplands of similar locations. This indicates the dominance of accumulation over the decomposition of organic matter in poorly drained soils. Cation exchange capacity (NH₄OAc) varied with soil depth and lithology and varied from means of 7.7 in AI2P2 and 44.5 cmol/kg in MF2P1. The values were low (< 12 cmol/

Table 1 General properties of the soils

Statistic	Sand	Silt %	Clay	BD g/cm ³	pH	OC g/kg	CEC cmol/kg
IH1P1; Shale-limestone-sandstone formation; (N06°38.53', E008°48.75', 64 m); land use: Oil palm							
Mean	63.5	11	25.5	1.55	6.2	5.29	30.6
CV	6.5	10.5	17.4	6.5	8.2	39	19
Range	60–68	10–12	20–30	1.45–1.66	5.5–6.7	2.75–7.55	23.6–35.6
IH2P2; Alluvium; (N06°38.836', E008°48.824', 51 m); Land use: Rice cultivation							
Mean	69	12.3	18.7	0.97	5.6	55.75	36.5
CV	5.2	12.4	16.4	30.8	8	52.7	54.3
Range	66–73	11–14	16–22	0.71–1.30	5.2–6.1	28.21–86.64	15.2–54.4
AI1P1; Shale-limestone-sandstone formation; (N05°43.435', E008°09.029', 93 m); Land use: Oil palm and Cassava							
Mean	74.5	6.5	19	1.44	6.1	4.12	16.7
CV	10.6	15.4	43.4	12.2	14.8	79.6	19.6
Range	68–84	6–8	10–26	1.19–1.59	5.3–7.2	1.72–8.92	12–19.6
AI2P2; Limestone-sandstone formation; (N05°44.386', E008°10.660', 80 m); Land use: Oil palm and Gmelina							
Mean	71.5	11.5	17	1.47	6.2	4.21	7.7
CV	16.7	20.4	6.8	7.4	8.6	58.2	65.5
Range	64–76	10–14	14–22	1.35–1.59	5.7–6.7	1.72–7.55	4.4–15.2
AI3P1; Alluvium; (N05°43.725', E008°10.214', 54 m); Land use: Bamboo							
Mean	80	7	13	1.25	5.3	12.47	8.4
CV	3.5	60.6	10.9	30.5	1.3	–	40.4
Range	78–82	4–10	12–14	0.98–1.52	5.2–5.3	2.78–22.16	6–10.8
MF1P1; Limestone-sandstone formation; (N05°04.714', E008°30.541', 58 m). Land use: Oil palm and plantain							
Mean	70	14.7	15.3	1.37	6.1	5.49	20.9
CV	2.5	19.7	7.5	5.3	8.2	–	12.2
Range	68–71	13–18	14–16	1.29–1.43	5.6–6.6	0.69–13.73	19.2–23.8
MF2P1; Shale-limestone-sandstone formation; (N05°04.828', E008°30.389', 44 m); Land use: Oil palm							
Mean	78	7.5	14.5	1.26	5.4	14.67	44.5
CV	3	25.5	6.9	19.2	3.9	–	46.3
Range	76–80	6–10	14–16	0.9–1.41	5.1–5.6	1.37–46.34	16.8–62.8
MF3P2; Alluvium; (N05°04.274', E008°29.695', 23 m); Land use: Maize							
Mean	78.3	9.7	12	0.97	6.2	11.37	16.5
CV	5.2	33.3	16.7	39.7	1.9	–	61.3
Range	74–82	6–12	10–14	0.53–1.22	6.1–6.3	6.82–19.39	11.2–25.6

N/B: *BD* bulk density, *OC* organic carbon

kg), moderate (12–25 cmol/kg) or high (> 25 cmol/kg). High CEC indicates the high capacity of the soils to retain cations.

Concentration and distribution of the metals

Oxides of the metals obtained by XRF as well as their metal equivalents are presented in Table 2. The distribution of the oxides in soil profiles is presented in Fig. 2 and indicates irregular distribution with soil depth. However, NiO in IH1P1 and IH2P2 showed a regular decrease with soil depth. The results showed that the minimum mean concentration of

Cr₂O₃ was 33.2 in AI3P1 and maximum value of 176.4 mg/kg was obtained in the Ap horizon of IH1P1 (Fig. 2). Mean of 11.0 was recorded in MF3P2 and 86.0 mg/kg in IH2P2, while NiO recorded means of 11.0 and 86.0 mg/kg in MF3P2 and IH2P2, respectively. The concentration of CuO was lowest in AI3P3 with an average value of 9.3 and highest in the Ap horizon of IH2P2 with an average concentration of 35.4 mg/kg. ZnO concentration ranged from mean of 17.0 in AI3P1 to 99.0 mg/kg in MF2P1. Amongst the oxides, As₂O₃ recorded the least values with means of 4.7 in MF3P2 and 10.6 mg/kg in IH1P1. The oxides in the studied soils

Table 2 Soil oxides and their metals for the entire soils

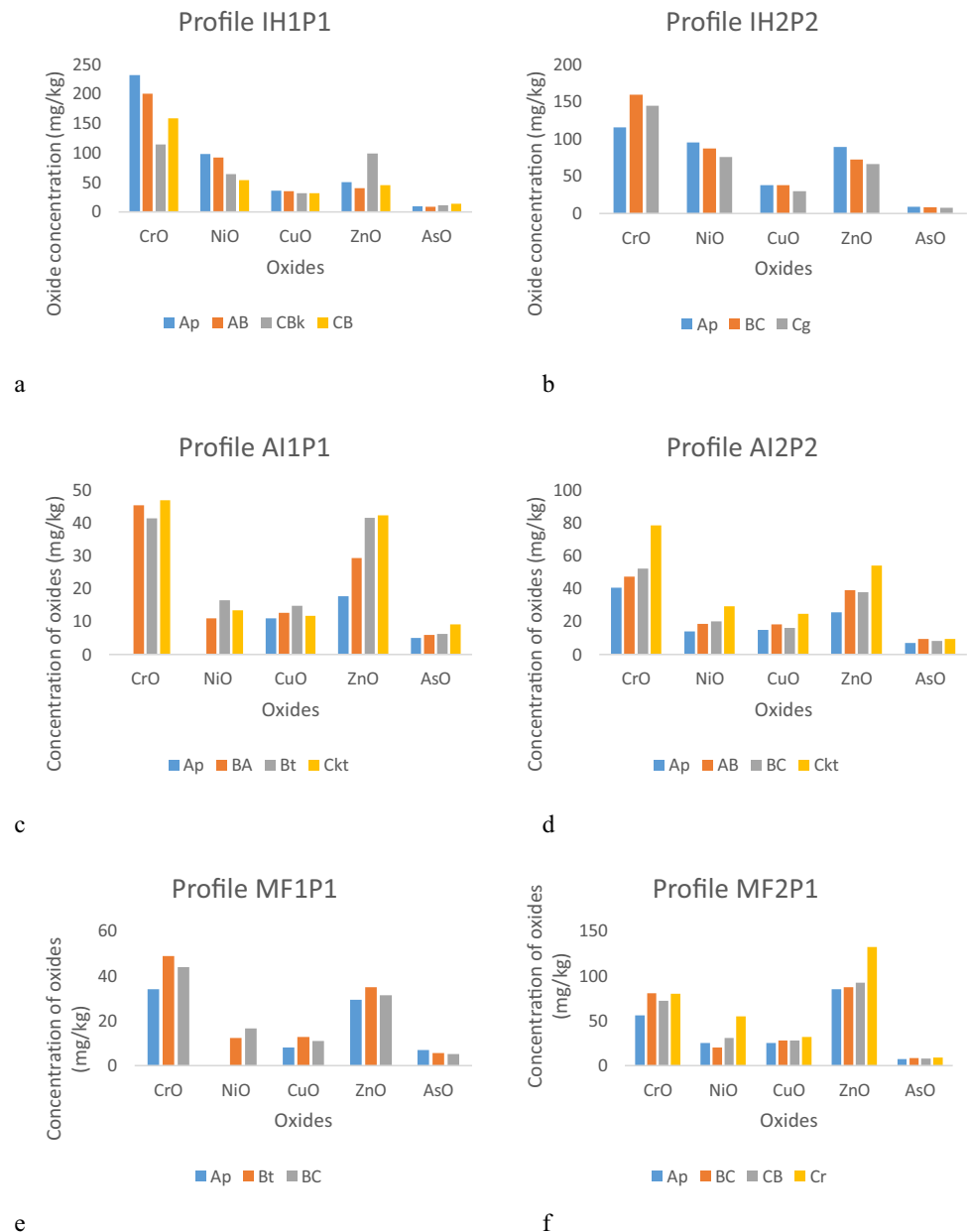
Statistic	Cr ₂ O ₃ mg/kg	Cr	NiO	Ni	CuO	Cu	ZnO	Zn	As ₂ O ₃	As
IH1P1; Shale-limestone-sandstone formation; (N06°38.53', E008°48.75', 64 m); land use: Oil palm										
Mean	176.4	120.7 ^{bc}	77.4	60.9 ^{ba}	33.6	26.8 ^{ac}	58.9	47.3 ^a	10.6	8.0 ^{bc}
CV	29	29	28.1	28	6.8	6.9	45.9	45.9	20.2	20.2
Range	114.5–232	78.3–158.7	53.9–98.7	42.4–77.6	31.5–36	25.2–28.8	40.7–99	32.7–79.5	8.7–13.5	6.6–10.2
IH2P2; Alluvium; (N06°38.836', E008°48.824', 51 m); Land use: Rice cultivation										
Mean	140.1	95.9 ^{ac}	86	67.6 ^{bc}	35.4	28.3 ^{ac}	76.1	60.3 ^a	8.4	6.4 ^{bc}
CV	15.8	15.8	11.4	11.4	13.3	13.2	15.6	17.3	6.1	5.6
Range	116–159.7	79.4–109.3	75.7–95.3	59.5–74.9	30–38.3	24–30.6	66.3–89.3	50.9–71.5	9–Aug	6.1–6.8
AI1P1; Shale-limestone-sandstone formation; (N05°43.435', E008°09.029', 93 m); Land use: Oil palm and Cassava										
Mean	44.5	30.4 ^a	13.6	10.7 ^a	12.6	10.1 ^a	32.7	26.3 ^a	6.6	5 ^{ba}
CV	6.3	6.3	19.9	20.2	13.2	12.9	35.6	35.6	26.6	26.7
Range	30–46.8	20.5–32	10–16.4	7.8–12.9	11–14.8	8.8–11.8	17.7–42.3	14.2–34	5–9.1	3.8–6.9
AI2P2; limestone formation; (N05°44.386', E008°10.660', 80 m); Land use: Oil palm and Gmelina										
Mean	54.7	37.4 ^a	20.5	16.1 ^a	18.5	14.7 ^{ac}	39.1	31.4 ^a	8.5	6.4 ^{ba}
CV	30.1	30.1	31.3	31.2	23.6	22.3	29.7	29.6	12.9	12.6
Range	40.7–78.3	27.9–53.6	14–29.3	23–Nov	15–24.7	12–19.3	25.7–54	20.7–43.4	7–9.3	5.3–7
AI3P1; Alluvium; (N05°43.725', E008°10.214', 54 m); Land use: Bamboo										
Mean	33.2	22.7 ^a	16.4	12.8	9.3	7.4 ^a	17	13.6 ^a	4.9	3.7 ^a
CV	4.9	5			0.8	10.4	10.4	15.3	16	17.7
Range	32–34.3	21.9–23.5	14.2–18.5	11.1–14.4	9.2–9.3		15.7–18.2	12.6–14.6	4.3–5.4	3.3–4.1
MF1P1; Shale-limestone with sandstone intercalation; (N05°04.714', E008°30.541', 58 m). Land use: Oil palm and plantain										
Mean	42.2	28.9 ^a	14.4	11.4 ^a	10.5	8.4 ^a	31.9	25.6 ^a	6	4.5 ^a
CV	17.8	20.6	20.6	22.7	22.5	9.1	9	16	15.6	16
Range	34–48.7	23.3–33.3	11.4–16.5	9.0–13	8–12.7	6.4–10.2	29.3–35	23.5–28.1	5.2–7	3.9–5.3
MF2P1; Shale-limestone-sandstone formation; (N05°04.828', E008°30.389', 44 m); Land use: Oil palm										
Mean	72.1	49.3 ^{ac}	32.8	25.8 ^{ac}	28.2	22.6 ^{ac}	99	79.6 ^{aa}	8	6.1 ^{ba}
CV	16	46.8	47	9.8	9.9	22.3	22.3	8.7	8.2	
Range	55.7–80.3	38.1–54.9	20.3–55	16–43.2	25–31.8	20–25.4	85–131.8	68.3–105.9	7.3–8.8	5.5–6.7
MF3P2; Alluvium; (N05°04.274', E008°29.695', 23 m); Land use: Maize										
Mean	38.3	26.2 ^a	11	8.6 ^a	13.9	11.1 ^a	30.6	24.6 ^a	4.7	3.7 ^a
CV	48.2	–	–	–	5.4	5.2	54.7	54.6	12.4	16.7
Range	38–38.5	26–26.3	9.2–13.1	7.2–10.3	13–14.3	10.4–11.4	11.3–40.3	9.1–32.4	5–Apr	3–4.2

N/B: ^aLess than threshold value

^bAbove threshold but less than guideline value; Cr=100, Ni=50, Cu=100, Zn=200, As=5 mg/kg (threshold values); Cr=200, Ni=100, Cu=150, Zn=250, As=50 mg/kg (guideline values); Source: (MEF 2007).

2. ^cGreater than world-wide data average; Cr=42, Ni=18, Cu=14, Zn=62, As=4.7 mg/kg; Source: (Kabata-Pendias and Pendias 1999).

Fig. 2 Distribution of oxides in some profile pits in the study area



indicate irregular trends with soil depth without clear and consistent deposition at any particular depth.

Prediction of the metals via a linear regression (MLR)

The multiple linear regression functions describing the relationships between the Cr, Ni, Cu Zn and As with soil properties are presented in Table 3. The result revealed that r^2 for Cr equation was 0.65 (Eq. 2) and could explain Cr variation in the study area, with coarse sand and fine sand being represented as the most important variables in the prediction. Ni model produced $r^2 = 0.66$ with organic carbon being the only important variable. Furthermore,

the r^2 values for Cu, Zn and As are 0.61, 0.50 and 0.46, respectively with decreasing preference for acceptance. All the models produced acceptable functions except for As which yielded r^2 value of less than 0.5. Such values are unacceptable for prediction (Li et al. 2016).

Table 3 Multiple linear regression functions of soil properties and metals

Response variable	Predicted variables	Eqn	R ²	RMS Residual(€)
Cr	1048.6—10.6CS*—11.4FS*—8.1Silt—6.7Clay+0.38OC+0.22CEC	2	0.65	25.8
Ni	453—4.6CS—5.1FS—3.6Silt—2.3Clay+0.58OC*+0.026CEC	3	0.66	15.9
Cu	83.1—0.81CS—0.88FS—0.66Silt—0.2Clay+0.12OC+0.19CEC*	4	0.61	5.8
Zn	—546.8+5.6CS+5.7FS+4.9Silt+6.1Clay+0.07OC+0.92CEC*	5	0.50	19.3
As	—4.91+0.087CS+0.05FS+0.17Silt+0.23Clay+0.003OC+0.008CEC	6	0.46	1.38

CS coarse sand, FS fine sand, OC organic carbon, CEC cation exchange capacity

*Significant predictors

Discussion

Concentration and potential risk of the metals

Chromium oxide

Values of Cr oxide in IH1P1, MF2P1 (SLS) and IH2P2 (ALV) exceeded the world-wide average of 42 mg/kg (Kabata-Pendias and Pendias 1999), as well as the threshold limit of 100 mg/kg. The values were within the guideline value of < 200 mg/kg (MEF 2007) in IH1P1 (SLS) and IH2P2 (ALV). The values in the affected soils also exceeded acceptable limit of 100 mg/kg (Stępniewska et al. 2001). Soils overlying SLS may have impacted the adjoining low elevation soils of ALV (IH2P2) with Cr₂O₃ via leaching and surface runoff as shales have been identified as hosts to Cr (Frank et al. 2020). The distribution of Cr₂O₃ is quite erratic in the soil profiles as it varied between horizons and lithology and may be attributed to the sedimentary lithology. Cr₂O₃ concentration classifies the soils as potential ecological threats. Such elevated concentrations may be toxic to plants, especially if it emanates from industrial wastes or spills (Avudainayagam et al. 2003). Rates exceeding 3000 mg/kg have resulted in toxicity and yield reduction (Naidu et al. 2000) and inhibit the activities of soil microbes (Megharaj et al. 1999) thereby facilitating the accumulation of organic matter.

Nickel oxide

The concentration of NiO in the soils was less than 50 mg/kg recommended as threshold value (MEF 2007). However, in IH1P1 (SLS) and IH2P2 (ALV) where concentrations were between the threshold and guideline values, NiO may be a potential threat to the soil system. By the world-wide average (WWA) of 18 mg/kg (Kabata-Pendias and Pendias 1999), values of NiO in IH1P1, IH2P2 and MF2P1 were in excess and may be a threat to the ecosystem. However, AI1P1 (SLS) and AI2P2 (LS) in the Yakurr area may require

Ni fertilizers, especially if N-fixing crops are advocated. In the soils over ALV, the below threshold levels may induce essential biochemical and physiological reactions in plants (Nagajyoti et al. 2010). The findings of this study are in agreement with earlier studies that reported concentrations of less than 86–100 mg/kg (McGrath 1995). Ni concentration in the soils may be traced to the parent material, especially its low content in the alluvial soils (Cempel and Nikel 2006) or the use of phosphate fertilizers in the agrarian area. The direct relationship between NiO, and organic C and CEC in the Ni function indicates its increasing concentration with an increase in these parameters. Similar findings have earlier been reported (Suavé et al. 2000; Tye et al. 2004). NiO varied irregularly between soil horizons in the sedimentary lithologies and negates the uniform distribution of Ni (Cempel and Nikel 2006).

Copper oxide

CuO concentration in the studied soils was below the threshold value of 100 mg/kg (MEF 2007). However, values in IH1P1, MF2P2 (SLS), AI2P2 (LS) and IH2P2 (ALV) exceeded the world-wide average of 14 mg/kg (Kabata-Pendias and Pendias, 1999) and may be a threat to the environment. Low levels of Cu²⁺ may enhance photosynthesis (Mahmood and Islam, 2006), though the critical values for the toxicity of Cu vary from one crop to another. For instance, 25 mg/kg is pegged for cabbage leaf (Hara et al. 1976), while 17–21 mg/kg has been reported for lettuce leaf (Davis and Beckett, 1978). In any case, the studied soils were within acceptable range for lettuce and cabbage production, however, values in MF2P1, IH1P1 (SLS) and IH2P2 (ALV) were above the range. Consequently, Cu toxicity is a potential threat to IH1P1. Its positive correlation with organic C and CEC and the studied oxides imply interdependence. High organic matter favours high CEC and heavy metal sorption in soils (Kabata-Pendias 2007), while excess Cu in soils is toxic to plants and humans, and affect photosynthesis, pigment synthesis, protein metabolism, membrane

integrity (Yang et al. 1995) and decreases shoot fresh weight (Yang et al. 2002). Copper oxide seems regular with higher concentrations in the B horizons.

Zinc oxide

ZnO concentration in the studied soils is within acceptable threshold limits of < 200 mg/kg (MEF 2007) and less than the WWA of 62 mg/kg (Kabata-Pendias and Pendias, 1999) except in MF2P1. Natural background concentration of total Zn in soils is 10–300 mg/kg (WHO 2001), while in the Netherlands, the critical limits of Zn in soils is 720 mg/kg (NMHPPE, 1991). Values obtained in this study were either within or less than the above limits, and the soils are said to be safe in terms of Zn contamination. Furthermore, a direct positive correlation between Zn and CEC as shown in the Zn function (Eq. 5) insinuates its adsorption and bonding to the soil exchange complex when the surface area of the soils is enhanced. Soils high in organic matter have higher adsorptive capacity and bonding for Zn (Chukwuma et al. 2010). Similarly, Zn availability in soils is affected by organic matter, CEC, and clay (Okafor and Opuene 2007; Nabulo et al. 2008). The somewhat low total Zn in the soils may have been due to its interaction with organic ligands. Zinc oxide also seems to be more concentrated in the transition B and C horizons but partly irregularly distributed with soil depth.

Arsenic oxide

The concentration of As_2O_3 was in excess of the threshold value of 5 mg/kg, but less than the guideline value of 50 mg/kg (MEF, 2007), and above the WWA of 4.7 mg/kg (Kabata-Pendias and Pendias 1999) in IH1P1, IH2P2, AI1P1, AI2P2 and MF2P2. Such values are most likely to pose a threat to the ecology. However, in AI3P1, MF1P1 and MF3P2 values were less than the threshold value and tolerable for crop production. These values are within soil natural levels of 1–40 mg/kg (Zandsalimi et al. 2011). The levels may be increased by the use of pesticides and fertilizer application (Nagajyoti et al. 2010). Natural background concentration of As_2O_3 in agricultural soils was also stated as 5 mg/kg (Mandal and Suzuki, 2002), while the EU recommended a maximum of 20 mg/kg (Leonard, 1991). Values of As_2O_3 in all the studied soils were equal to or above the limits, an indication that aeolian addition, pesticide or fertilizer application may have increased its concentration in the soils. The values are less than 10 mg/kg reported in Finland (Makela-Kurtto et al. 2007) and 3.2 mg/kg in Sweden (Eriksson et al. 1997). In the present study, As_2O_3 has a direct positive relationship with clay, and a poor correlation with organic matter. Values below threshold limits are likely to induce essential biochemical and physiological reactions in plants.

Relationship between metals oxides and soil properties via a MLR

Increasing toxicity of Zn as a result of the addition of Cu is described as the most consistent effect on plant growth (Luo and Rimmer 1995). The amount of Zn and Cu adsorbed depends on organic matter, clay minerals, metal oxides, and hydroxides (Ross 1994). Increasing soil CEC by raising soil organic matter and the surface area of clay minerals, invariably increases Zn and Cu concentration. The R^2 values of Cu and Zn indicate that the models explain 0.61 and 0.50 of the variability, respectively.

Important correlations did not exist between arsenic and any of the predictor variables and contradicted previous studies (Martín et al. 2011; Romero-Freire et al. 2014). According to these authors, the solubility and toxicity of As is controlled by soil properties. The low adjusted R^2 value indicates that any additional input variables are not likely to add value to the model. This negates the earlier presentation of high adjusted R^2 (> 0.50) for Cr, Ni, and Cu, indicating that additional input variables will add value to the model.

The p - values of the ANOVA tables suggests a good fit model for predicting Cr, Ni, Zn and Cu compared to the mean value. Similarly, MLR models predicting Cr, Ni, Zn and Cu had R^2 values within 0.50 and 0.75 and are within the acceptable limits described by Li et al. (2016).

Conclusion

The oxides were irregularly distributed spatially and vertically with soil depth. The Ap horizons have the least value of all the oxides except in soils influenced by shale-limestone-sandstone (SLS) lithology, which had a reverse or irregular trend. Nevertheless, Cr_2O_3 was the predominant and potentially toxic oxide alongside NiO in soils underlain by SLS. Furthermore, the arsenic oxide was potentially toxic in most of the studied soils, with soils over SLS emerging as the most prone. This has placed the soils on the watch list for Cr_2O_3 , NiO and As_2O_3 toxicity. The prediction functions were all important except that of As_2O_3 . For the prediction function of Cr, fine and coarse sand were negatively correlated with Cr, while CEC was positively correlated with Cu and Zn. Similarly, organic carbon was positively correlated with Ni.

Highlights of the study

- Arsenic oxide was potentially toxic, while NiO and Cr_2O_3 were a threat in the soils influenced by shale-limestone-sandstone formation in Ishibori.
- Positive and significant relationship was obtained from the Cu and Zn functions against CEC, while fine and

coarse sand correlated negatively with Cr. Organic C correlated positively with only Ni ($p < 0.05$).

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Declarations

Conflicts of interests There are no competing interests.

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