Multivariate Modeling of some Metals Concentrations in Agrarian Soils: Distribution and Soil Fertility Implications in the Tropics

Running title Multivariate modeling of metals in tropical soils

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Abstract

Predicting metals concentration in agricultural soils is a *sine qua non* in establishing environmental policies and evaluating the soils' agricultural potentials in an area. The relevance of metals to ecological health, agriculture and pollution has sprung a lot of related studies. This study was set-up to determine the concentration and profile distribution of aqua regia (AR) extractable Fe, Al, Mn, Mg and K in agricultural soils, and to predict AR extracted elements *via* Al_2O_3 (Alx), K_2O (Kx), physical and chemical properties for soil fertility interpretations. One soil pit was randomly sited in each slope transition obtained *via* digital elevation models (DEM), resulting in 27 composite soil samples. Soil samples meant for AR and X-ray florescence were analyzed in triplicate. The soils were dominated by AR extractable Fe with mean concentrations showing the trend; Fea> Ala> Mga> Mna≈Ka and ranges of 639.09-125719.46, 1252.63-14895.13, 67.61-2408.36, 4.51-2162.91 and 161.84-1356.23 mg/kg, respectively. The distribution of AR metals in the entire soils was quite similar, however, higher values of soluble Fe occurred in the 0-37 cm depth of IH1P1. Multiple linear regression functions were within acceptable and best prediction criteria (R^2 = 0.55–0.77). The best performing models were Ka and Mna, with lower errors. The models selected Kx, Mg and CEC which contributed 89.9, 79.9 and 73.4 %, respectively to the 44.2 % contribution of PC1 to data variation. The dominance of Kx and Alx with ranges of 2381.0-50401.0 and 57766.67-119433.35 mg/kg, respectively over Ka and Ala is due to limitations associated with AR extraction of elements in silicate minerals, hence the necessity for extracting soil mineral elements by more than one method.

1. Introduction

Estimating the concentration of metals in soils is a necessity when assessing their ecotoxicity, agricultural potential, and setting up environmental policies. Most metals are toxic in raised concentrations (Ofem *et al*. 2021), non-biodegradable, and accumulate in the environment over time, but also serve as essential plant nutrients. They are present in industrial effluents and emissions, domestic and commercial wastes as well as in pesticides, fungicides and manure (Ukpong *et al*. 2013; Denic *et al*. 2019).

Agricultural, industrial and mining activities have overwhelmed lithologic and pedogenic sources of heavy metals and introduced Fe, Al and Mn into the environment causing contamination and pedological anomaly (Tume *et al*. 2011). However, some authors (Negrel *et al*. 2018, Scheib *et al*. 2012, Negrel *et al*. 2015 and Ladenberger *et al*. 2015) are of the opinion that lithology is the major source of geochemical anomalies and is related to elemental distribution and concentration. The concentration of these metals in soils controls their phyto-availability and may be transferred to man or animals upon consumption.

The concentration of Al, Fe, Mn, Mg and K in soils is linked to soil and mineral weathering and influence soil fertility. For instance, Al plays an essential role in weathering processes and K is one of the tracers of silicate mineral weathering of felsic and mafic lithologies (Horstman, 1957; Takeda *et al*. 2004). Potassium plays a crucial role in weathering and clay formation (Tanaka and Watanabe, 2015) with orthoclase feldspars, micas and illite as its primary source. These minerals are susceptible to weathering and release nutrients that are either used by plants or leached away. Low K in soils indicates that more advanced weathering occurred and that mica may have been transformed into clay phases (Negrel *et al*. 2018). The oxides of Al (gibbsite, Boehmite, diaspore) and aluminosilicates are more resistant to weathering, tend to accumulate in tropical soils and are insoluble to aqua regia (AR) digestion. The total amount of Mn in the soil is derived from the parent substrate and sometimes added *via* fertilizer (Bogdanovic *et al*. 1997). Similarly, Voyslavov *et al*. (2018) attributed variation of Fe and Mn extracted by AR to the geogenic and anthropogenic origin.

AR is an acid mixture of 3:1 HCl : HNO_3 (Nieuwemhuiz *et al*. 1991; Ofem *et al*. 2020) that hardly attacks feldspar minerals and has little or no effect on most resistant accessory and silicate minerals (Negrel *et al*. 2018, Thestorf and Makki, 2020). This has led to low recovery (Croffie *et al*. 2020) and underestimation of minerals that are resistant and closely linked with silicate minerals containing Al and K (Scancar *et al*. 2000; Taraskevicius *et al*. 2003). Notwithstanding, HF : H_3BO_3 has demonstrated to dissolve silica matrices (Nadkarni, 1984). AR is adequate for digesting total recoverable heavy metals in soils and for estimating the maximum element availability to plants (Vercoutere *et al*. 1995). Consequently, AR provides relatively lower concentration values than other multi-acid extraction

procedures and X-ray fluorescence (XRF) (Davidson *et al*. 1994; Madrid *et al*. 2007). Residual elements that are not released by AR digestion, are silicate bound and important for estimating the elements' mobility and behaviour (Niskavaara *et al*. 1997).

Physical and chemical properties control the concentration of metals in soils, while other metals either antagonize or patronize their concentration. Small changes in grain sizes, soil organic matter and chemical properties affect baseline concentration of metals (Horckmans *et al*. 2005; Salminen and Gregorauskiene, 2000). Soil colloids and pH regulate Fe and Mn chemistry in soils (Sungur *et al*. 2014). When the concentrations of metals exceed acceptable limits in the environment, they result in toxicity (Ofem *et al*. 2021). These metals are increased in soils that are high in clay, silt and CEC (Sidhu and Sharma, 2010; Tume *et al*. 2011), and become toxic in highly acid soils.

Most regression models that predict soil metal concentration consist of pH, organic matter, total metal content and total trace elements (Ivezic, 2011). Models in the current study will serve low-income farmers in agrarian communities to predict the concentration of metals *via* physicochemical properties and their implication on soil fertility. Also, the total elemental concentrations of Al_2O_3 and K_2O have been incorporated into the models to aid the understanding of soil fertility. This way, their inter-relationships can be used to imply weathering and soil fertility based on the hypothesis that; high concentrations of Al_2O_3 indicate highly weathered soils with low fertility, while high K_2O suggest young soils with high fertility. Metals obtained by AR and XRF are likely to vary in their inter-relationships with physical and chemical properties, as well as the influence of soil weathering and fertility status on their concentration.

This study was set-up to determine the concentration and profile distribution of AR extractable Fe, Al, Mn, Mg and K in agricultural soils. It also predicted the AR extracted elements *via* Al_2O_3 and K_2O, as well as physical and chemical properties, and employed the resultant interactions in soil fertility interpretations.

2. Materials and methods

### 2.1. Location and land use, geology, and climate of the study area

Ishibori (679.1 Ha) (06°39'17" N, 08°47'51" E), Agoi Ibami (279.74 Ha) (05°43'27"N, 08°10'37.2" E) and Mfamosing (2201.65 Ha) (05°04'41.8"N, 08° 27'49.8"E) are three major agrarian communities in Cross River State (CRS), Nigeria. Ishibori is found in Ogoja and located 196 km away from Calabar, the CRS capital city and depicted by southern guinea savannah and cultivated to oil palm, teak and paddy rice. Agoi Ibami is a community in Yakurr and located about 119 km away from Calabar, found in the tropical rainforest and cultivated to oil palm, cassava and plantain. Mfamosing is a major town in

Akamkpa and the oil palm hub of southern CRS, found in the tropical rainforest and located 44.6 km away from Calabar.

The CRS's geology is readily described by the Basement Complexes and Sedimentary Basins (Ekwueme, 1987). The Sedimentary Basins are composed of sediment fill of Cretaceous to Tertiary ages in the Niger Delta region (Fatoye and Gideon, 2013), with recent alluvium dominating the low lying coastal areas. Sandstone abound in most of the Sedimentary Basins, while limestone of Cretaceous and Tertiary ages is often intercalated with shale, siltstone, and fine-grained sandstone (Ofem *et al*. 2020). The areas marked for the study in Ishibori, Agoi Ibami and Mfamosing have dominant sedimentary lithologies of limestone, sandstone-limestone and alluvium (Fig. 1).

Fig. 1

The Geology map of Cross River State, Nigeria
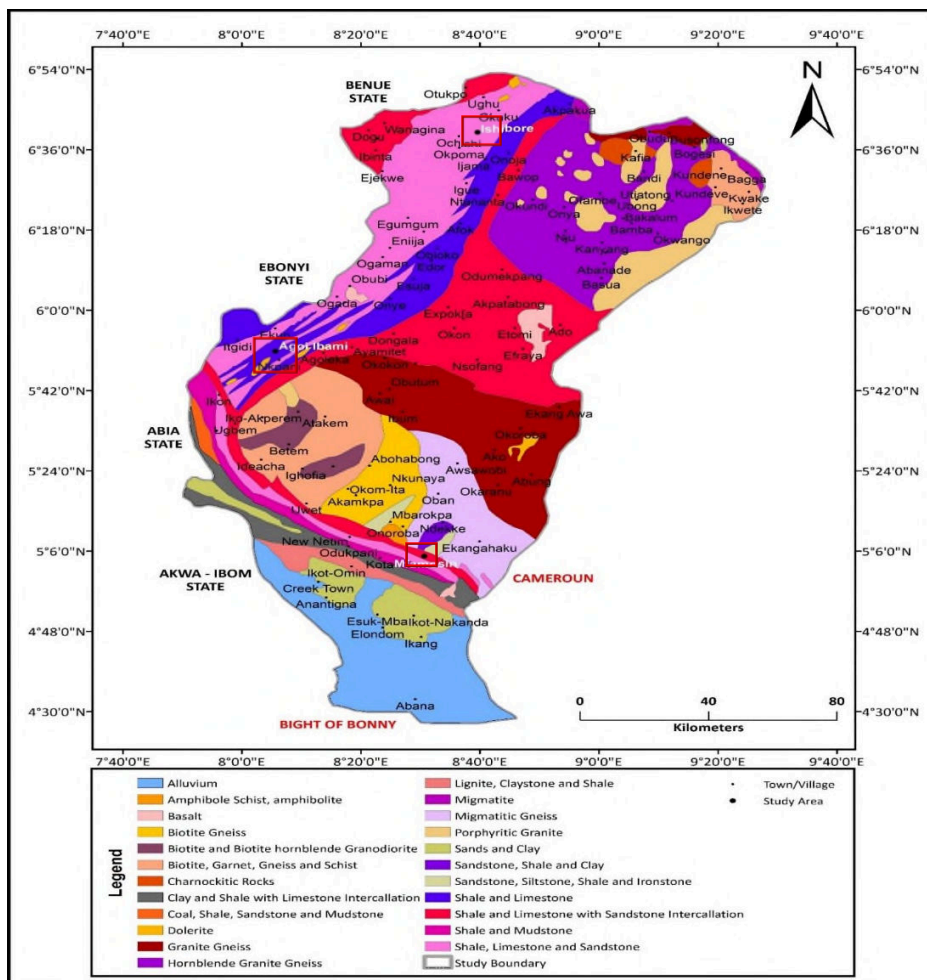
The CRS's climate is described as humid tropical, and extends from the southern guinea savannah in Ishibori to the tropical rainforests of Agoi Ibami and Mfamosing. Rainfall fluctuates from 1251-3348 mm/year in Ishibori to 1760–2684 mm/year and 2109–3771 mm/year in Agoi Ibami and Mfamosing,

respectively (Sambo *et al*. 2016). Temperature is 23-34 °C in Ishibori, while Agoi Ibami and Mfamosing have similar climate and vegetation with slight temperature variation (23-32 °C) (Sambo *et al*. 2016).

2.2. Field and laboratory procedures

The Digital elevation models (DEMs) of the locations were acquired from USGS Explorer SRTM 1 arc-second Global at a resolution of 30 m. The DEMs were used to generate slope maps in ArcGIS (ESRI, US) environment, while the elevation ranges created in the slope maps were used to delineate slope transitions (Ofem *et al*. 2020) and presented as Fig. 2. Each transition represented a soil mapping unit (MU). One soil profile was randomly sited in each MU and dug at 2m by 1.5m by X m. Where X m represents variable depth to the water table or consolidated bedrock. Eight soil pits were therefore used for the study; two in Ishibori (IH1P1, IH2P2), three in Agoi Ibami (AI1P1, AI2P2, AI3P1) and three in Mfamosing (MF1P1, MF2P1 and MF3P2). The field study was carried out between December 2018 and Fig. 2

Digital elevation models of Ogoja (Ishibori), Yakurr (Agoi Ibami) and Akamkpa (Mfamosing)
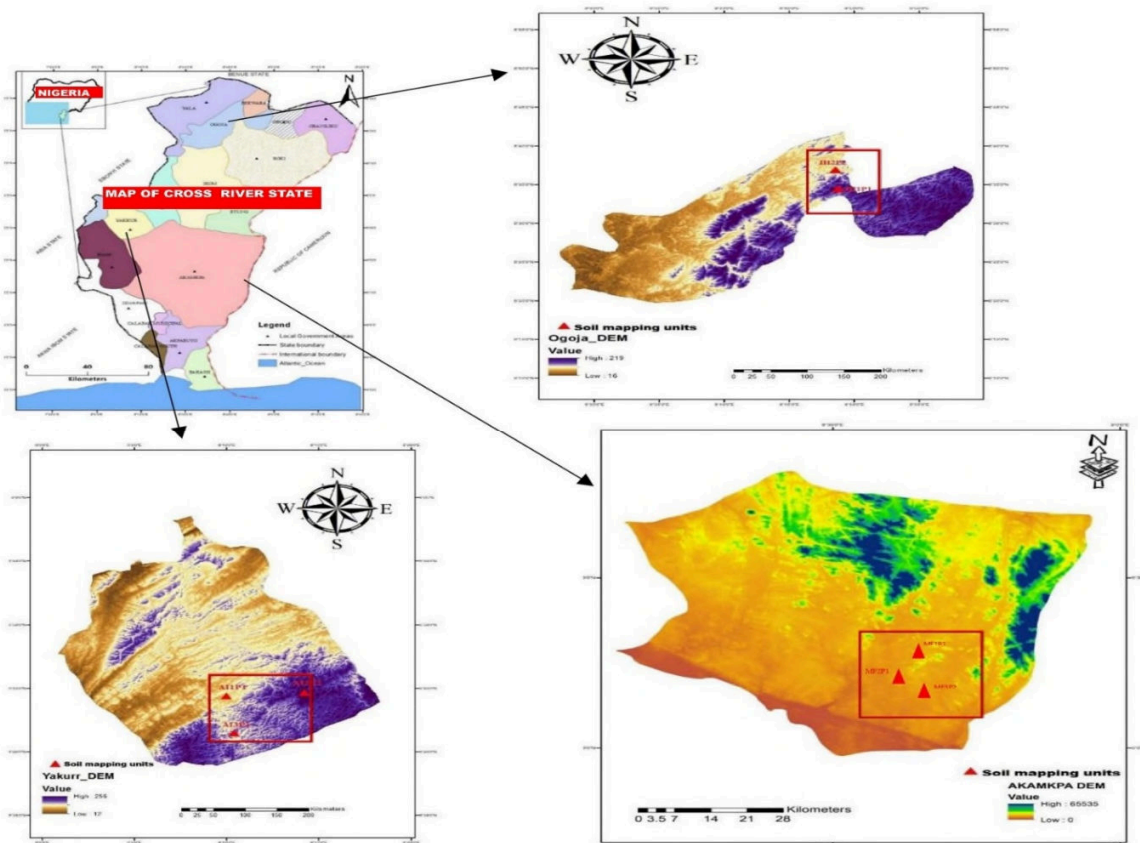
February 2019. A total of n=27 soil samples were obtained from pedogenic horizons and used for the study.

Undisturbed core soil samples were vertically collected from soil horizons and saturated with water for 24 hours and used to determine soil bulk density and moisture content (SMC). Bulk density was obtained by the undisturbed core method (Eqn. 1), while SMC was determined by dividing the mass of water at saturation by oven-dry (at 105 °C) mass of soil (Obi, 2000).

$$\rho d = \frac{m}{V} \qquad \text{(Equation 1)}$$

Where, ρd = bulk density (g/cm^3).

m = mass of oven-dry soil

V = volume of soil in the core cylinder

Composite soil samples from pedogenic horizons were air-dried under laboratory conditions until constant weight, ground and sieved with a 2 mm sieve. Less than 2 mm fraction was used to determine particle size distribution by Bouyoucos hydrometer and soil pH (CaCl$_2$) in soil: 1M solution ratio of 1:2.5 using glass electrode pH meter. Soil organic carbon was ascertained by the Walkley-Black modified acid-dichromate method. Exchangeable bases were extracted with 1 N NH$_4$OAc (neutral pH) solution. Exchangeable Ca and Mg were obtained by Versenate EDTA titration procedure, while K was determined with a flame photometer. Cation exchange capacity (CEC) was determined in 1 M NH$_4$OAc at pH 7.0. The above laboratory procedures are as outlined in Soil Survey Staff (2014) and analyzed in the Department of Soil Science, University of Nigeria, Nsukka.

Soil samples meant for analysis by AR digestion and XRF were further pulverized into a fine powder (3-4 µm) and homogenized with an auto-mill. Pseudo-total concentrations of Al (DL= 0.0386 mg/L), Fe (DL= 0.0184 mg/L), Mn (DL= 0.0001 mg/L), Mg (DL= 0.0029 mg/L) and K (DL= 0.0934 mg/L) were extracted with AR mixture of 3 : 1 of HCl : HNO$_3$ and analyzed using ICP-OES (model iCAP 7000) by the procedures of Cools and De Vos (2016). Where DL = Detection limit. Soil samples were also analyzed for total elemental oxides of Al$_2$O$_3$ and K$_2$O using XRF Delta Premium Spectrometer 2019 by the procedures of Tejnecky *et al*. (2015). Soil samples were analyzed for AR extractable and XRF metals in triplicate and the average obtained. Laboratory analysis was done in the Department of Soil Science and Soil Protection, Czech University of Life Sciences, Czech Republic from April to September, 2019.

2.3. Correlation

Simple correlation analysis was performed at 0.05, 0.01 and 0.001 levels of significance using StatView version 5.0.1.

2.4. Modeling approach

Multiple linear regression (MLR) was performed in the StatView software environment to model the prediction of AR metals using the best correlated physical and chemical properties as well as total

elemental oxides obtained by XRF. The MLR model used to predict AR extracted metals *via* selected soil properties is expressed as:

$$AR\ metal\ (mg/kg) = \beta_0 + \beta_{x1} + \beta_{x2} + \ldots \beta_k xk + \epsilon_j \qquad \text{(Equation 2)}$$

where AR is the response variable indicated by the AR extracted metal (Al, Mn, Mg, K or Fe). x_1, x_2 … x_k are predictor variables Alx, Kx (Al and K obtained by XRF), organic carbon (OC), Mg, CEC and soil moisture content (SMC). ϵ = residual terms of the model and βo represents regression constant or intercept, while β1 and β2 represent regression coefficients.

2.5.   Test for significance

Ho : β1 = βk = 0

Ha : βj ≠ 0; for at least one j.

F_{value} (calculated) > F_{stat}; reject null hypothesis

2.6.   Model adequacy

The selected soil properties were subjected to modeling. 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).

2.7.   Principal components analysis (PCA)

The PCA enabled the grouping of the soil properties based on location. The principal factors that account for the grouping enabled the extraction of principal factors accounting for the data's sources of variation.

2.8.   Statistical analysis

Correlation and principal component analyses were done using STATISTICA version 13.3. Other statistical analyses and the model computation were performed using StatView version 5.0.1.

3.   Results and discussion

3.1.   Concentration and distribution of AR metals

Concentration and distribution of AR extracted metals as well as soil physical and chemical properties are presented in Table 1 and Fig. 3, respectively. The soils were dominated by AR extractable Fe, with mean values showing a trend such that; Fea>Ala>Mga>Mna≈Ka. The ascendance of Fea over other metals is typical of most highly weathered tropical soils, while low Ka is credited to the leaching of the metal released from weathered clay minerals. Aqua regia extracted Fe in the current study exceeded an average of 12000 mg/kg for medium loamy soils (Kabata-Pendias and Pendias, 1999). Such high values, may be threatening to underground water pollution.

Table 1: Summary statistics of the soil properties (n = 27)

Soil properties	Mean	Std. Dev	Std. Error	Min.	Max.	Coef. Var
Fe_a (mg/kg)	29133.38	32144.7	6186.25	639.06	125719.46	1.10
K_a (mg/kg)	507.30	328.67	63.25	161.84	1356.23	0.65
Mg_a (mg/kg)	817.99	732.02	140.88	67.61	2408.36	0.90
Mn_a (mg/kg)	508.25	544.61	104.81	4.51	2162.91	1.07
Al_a (mg/kg)	8072.24	4259.79	819.8	1252.63	14895.13	0.53
Al_x (mg/kg)	82003.91	15552.44	2993.07	57766.67	119433.35	0.19
K_x (mg/kg)	22398.82	14539.37	2798.10	2381.0	50401.0	0.65
Clay (%)	17.33	5.44	1.05	10.00	28.0	0.31
Silt (%)	10.0	3.26	0.63	4.00	18.0	0.33
F. sand(%)	46.89	10.54	2.03	26.00	70.0	0.23
C. sand(%)	25.41	10.86	2.09	4.00	50.0	0.43
BD(g/m3)	1.31	0.28	0.05	0.53	1.66	0.22
SMC(%)	45.54	26.44	5.09	26.7	150.8	0.58
pH	4.97	0.71	0.14	4.20	6.5	0.14
OC(g/kg)	13.18	19.68	3.79	0.69	86.64	1.49
K(cmol/kg)	0.079	0.055	0.01	0.00	0.29	0.69
Mg(cmol/kg)	1.69	1.40	0.27	0.20	4.8	0.83
Ca(cmol/kg)	3.88	2.27	0.44	0.60	8.2	0.59
CEC(cmol/kg)	23.57	16.06	3.09	4.40	62.8	0.68

N (number of samples), 'a' (aqua regia extracted), 'x' (Determined by XRF), f. sand (fine sand), C. sand (Coarse sand), BD (bulk density), SMC (soil moisture content), OC (organic carbon)

Several reports have been made of soils of the tropics as being dominated by Fe and Al (Ofem *et al*. 2020, Ofem *et al*. 2021), while K most often appears leached. Low K in tropical soils is attributed to advanced weathering and mica transformation into clay mineral phases (Negrel *et al*. 2018). The mean value of Mna was higher than the world's average of 488 mg/kg (Kabata-Pendias, 2011) and below the median of 535 mg/kg reported for Brazilian soils (Licht, 2005) and may not be a threat to environmental pollution. Total elemental oxide content of Al and K obtained by XRF indicate complete dominance over corresponding elements digested by AR. Oxides of K and Al are mainly bound in silicate soil minerals. Since the AR digestion procedure does not extract silicate bound K and Al, while XRF penetrates deeply into the silicates, comparatively higher values are recorded. A similar finding has been reported by Negrel *et al*. (2018), and Thestorf and Makki (2020), that AR hardly attacks feldspars with little effects on silicate minerals, hence low recovery of the extracted metals (Croffie *et al*. 2020) and underestimation of resistant silicate minerals containing minerals with Al and K (Scancar *et al*. 2000; Taraskevicious *et al*. 2003). Similarly, lower values were obtained for exchangeable K (cmol/kg x 390= mg/kg) when compared to Ka and Kx. This demonstrates the necessity for the extraction of a nutrient using different techniques, and as a guide for fertilizer formulation and use as the availability of exchangeable K may not have been well dictated due to the complexity of the forms of K.

The distribution of AR extracted metals in the studied soil profiles is presented in Fig. 3 using cell
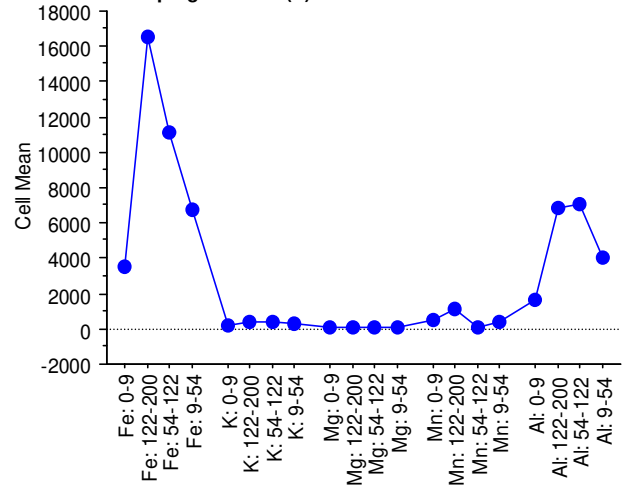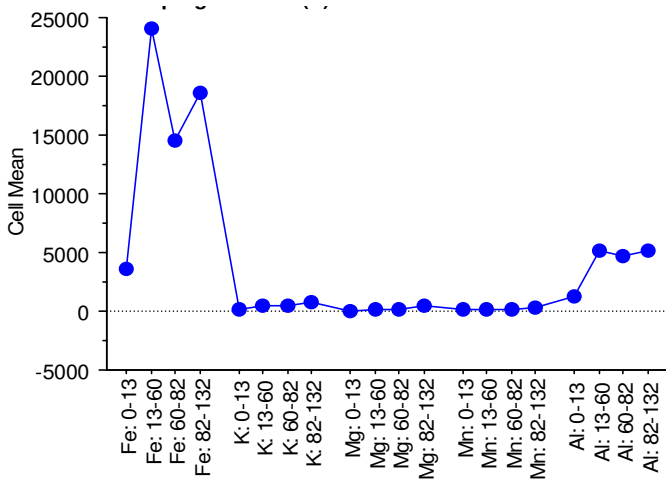
Fig. 3

Cell line chart indicating the distribution of AR extracted metals in soil profiles (units = same as in Table 1)
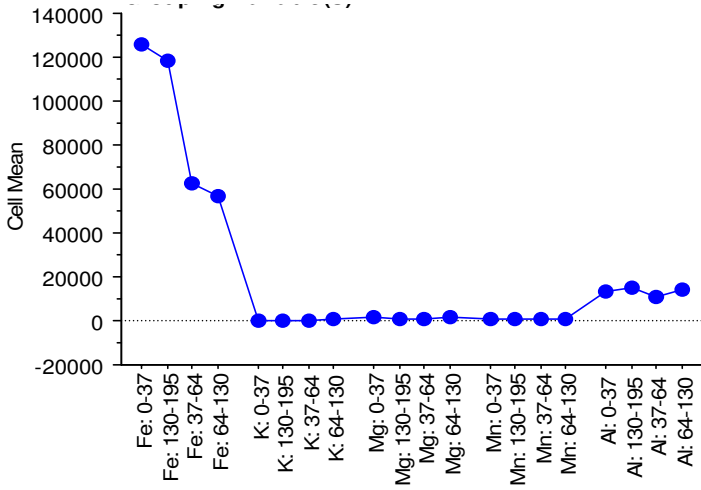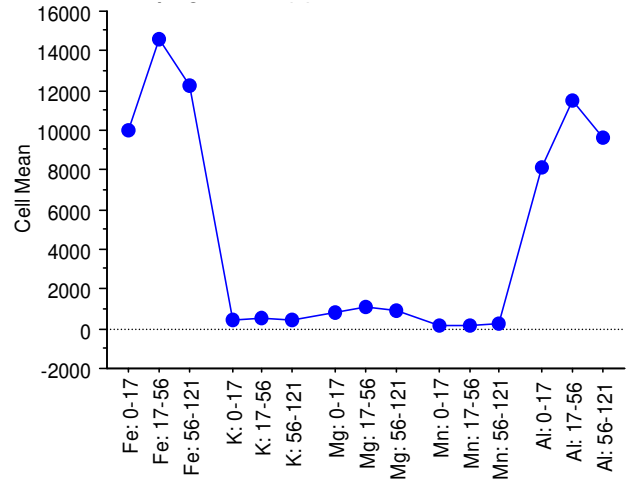

IH1P1 (a)

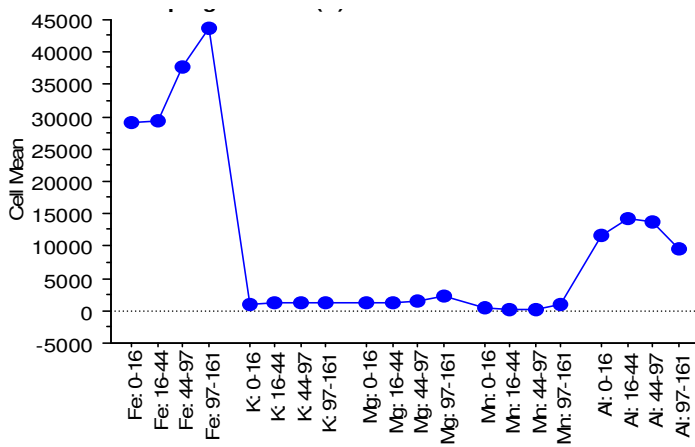AI1P1 (b)

AI2P2 (c)

MF1P1 (d)

MF2P1 (e)

line charts and appear quite similar for the various soils. The similarity reflects and is attributed to the sedimentary lithology of the studied soils. Most anomalies in elemental distribution and concentration are related to the lithology of underlying bedrock (Scheib *et al*. 2012; Ladenberger *et al*. 2015). In the studied soils, the value of Fea was only highest in the 0-37 cm depth (Ap horizon) of IH1P1, while in other soil profiles, higher values were obtained in the endopedons (subsurface horizons). Lower rainfall amount in the southern guinea savannah (IH1P1) has slowed the release or weathering intensity of Fe-containing minerals in the epipedons, hence its dominance in the 0-37 cm depth of IH1P1. Also, the higher Fea in the 0-37 cm depth of IH1P1 (Fig. 3a) may be attributed to rising water table during wet season under anaerobic condition. This process may have brought soluble Fe from subsurface layers to the soil surface (Sahrawat, 2003), hence the relatively higher values. Comparatively lower values of Fea in the epipedons (Ap horizon) of AI1P1 (0-9 cm), AI2P2 (0-13 cm), MF1P1 (0-17 cm) and MF2P1 (0-16 cm) and higher values in the endopedons indicates similarity in the rate of weathering and processes of soil formation in similar vegetation zones (tropical rainforest). Consequently, the obvious dominance of Fea and Ala over other metals (Fig. 3, Table 1), particularly in the subsoil depths aligns with clay distribution. Fe and Al may have migrated with clay to subsoil layers or had dominated the subsoil layers due to clay transformation. The unbalanced distribution of Fe and Al with K, Mg and Mn, is an interesting phenomenon in agricultural soils. This may result in the competition for cation uptake (Fageria, 2001; Marschner, 2012; Chen and Ma, 2012). The variation may also be linked to differences in land use and management practices. AR extracted K, Mg and Mn appeared similarly distributed (Fig. 3), and occupied the base of the cell mean axis. Ka and Mga were both uncorrelated (Table 2) with SMC and aligns with the report of Kopittke and Menzies (2007) who opined that soil chemical and physical properties do not influence the ratio of Mg and K. However, Gransee and Fuhrs (2013), reported that the combined application of K and Mg increased soil water content. The cell line charts representing the various soils appeared quite similar, indicating a similarity in the distribution of AR metals due to the soils' sedimentary origin.

Particle size distribution was dominated by the fine sand fraction with values ranging from 26 to 70 %, while mean bulk density was less than 1.6 Mg/m^3 (Table 1) and will permit plant root penetration and proliferation. Sand dominated soils have low surface areas with low capacity to adsorb exchangeable bases in the soil exchange complex, high hydraulic conductivity and are more prone to leaching.

On the other hand, soil pH (CaCl$_2$) values indicate that the soils were slightly acid (4.2-6.5). Soil pH values approaching neutral range are attributed to some of the soil's limestone origin and do not indicate the presence of significant amounts of Al^{3+} and H$^+$ to affect plant growth. According to Tan (1998), alumina becomes insoluble, while silica becomes more soluble at pH range of 5-9, and results in the

leaching of more soluble silica and the formation of kaolinite and gibbsite (Ollier, 1975). Mean value of organic carbon was 13.18 g/kg with a maximum value of 86.6 g/kg in the poorly drained soils. Soil organic matter tends to accumulate in poorly drained soils as a result of the inactive nature of aerobic decomposing microbes in soils with deficient oxygen supply. Increased acidity decreases CEC and induces K^+ leaching and deficiency (Slattery et al. 1999). Exchangeable bases of K, Mg and Ca appeared leached as values were relatively low (Table 1), with a similar inverse relationship between Kx and Mg (Table 3). Seasonal leaching of Mg from soils is affected by soil acidity, moisture, and CEC (Gransee and Fuhrs, 2013) as well as the dominance of sand and advanced weathering in the tropics.

3.2. Prediction of AR extractable metals *via* a Linear Regression (MLR)

An R^2 value of 0.55 obtained for Fea in this study is within the acceptable prediction value on the scale of Li et al. (2016), and indicate a moderately strong relationship between the MLR model and Fea when regressed with XRF and physicochemical properties. Furthermore, Kx predictor was the only statistically significant variable with the response variable (Fea). The negative regression coefficient (Table 2) shows an inverse relationship between Fea and Kx. Highly weathered soils encourage the accumulation of immobile and stable Fe, while K is lost from the soil exchange complex. Loss of K, especially in the tropics depicts low soil fertility. Low K is an index for advanced weathering and that micaceous minerals may have been transformed into clay phases (Negrel et al. 2018). The proportion of kaolinite and its participation in K reserve is slowly released through weathering (Nachtigall and Raij, 2005). Previous studies by Akpan-Idiok and Ogbaji (2013), Ofem and Esu (2015) and Kingsley et al. (2020) identified quartz, kaolinite, illite, muscovite and mixed layer structure of kaolinite and montmorillonite as dominant clay minerals in the tropical rainforest and southern guinea savannah areas of Cross River State. Adequate K in soil is required for high quality and profitable yield. Consequently, the time and method of K application as well as other mineral nutrients are important factors to consider.

Table 2: Multiple linear regression

Response variable	Predicted model	R^2	Adjusted R^2(%)	RMS Residual($\in$)
Fea	52525.6 + 0.25Alx - *1.5Kx - 181.8OC + 5671.7Mg - 241.8CEC - 247.3SMC	0.55	42	24547
Ka	-262.7 - 0.004Alx + *0.017Kx - *9.2OC + *161.8Mg + *20.6CEC + 2.5SMC	0.64	53	225.5
Mga	588.2 - 0.002Alx - 0.012Kx - 2.9OC + *280.6Mg + *14.3CEC - 2.1SMC	0.77	69	404.7
Mna	647.8 + 0.008Alx - *0.022Kx + *13.7OC + *157.1Mg - *18.6CEC - *6.4SMC	0.74	67	314.2
Ala	5712 + 0.046Alx - *0.155Kx - 54OC + 266Mg + *125.3CEC - 13.4SMC	0.77	70	2339.8

'a' (aqua regia extracted), 'x' (determined by XRF), SMC (soil moisture content), OC (organic carbon), CEC (cation exchange capacity)

The MRL model describing the relationship between Ka and XRF oxides as well as selected physicochemical properties is presented in Table 2. An R^2 value of 0.64 places the model within the acceptable prediction range on the scale of Li et al. (2016). It designates a fairly strong relationship

between the MLR model and Ka when regressed with XRF and soil physicochemical properties. The p-value of the ANOVA table was less than the significance level of 5 % and suggests a good fit model for the prediction of Ka compared to the mean value. The predictor variables; Kx, OC, Mg and CEC were statistically significant with Ka. This indicates that the data supplied by these predictors provide enough evidence that there is a non-zero correlation and are worthwhile additions to the model. However, Alx and SMC presented insufficient evidence to conclude that correlation exists. Since the soils were primarily made up of fine sand, the high CEC of the soils was due to organic matter and was responsible for retaining Kx and Mg.

The coefficients of the significant predictors indicate that increasing Ka in the soils is a possible guarantee for a rise in Kx, Mg and CEC. Soils with high CEC are known to have the ability to exchange cations in their exchange sites, they are more fertile and support a wider range of crops. On the other hand, a negative predictor coefficient on OC indicates an inverse relationship with Ka and will increase with a rise in Kx. Strongly weathered tropical soils have a reserve of K in a structural and non-exchangeable form (Benites *et al.* 2010) with a high amount of kaolinite in the clay fraction which accounts for over 50 % of total K in soils (Schaefer *et al.* 2008). Earlier studies of the clay fraction of soils in the flood plains, schistose and Basement Complex soils of Cross River State identified quartz, kaolinite and mixed layer structure of kaolinite and montmorillonite as common minerals in the soils, as well as illite (Akpan-Idiok and Ogbaji, 2013, Ofem and Esu, 2015, Kingsley et al. 2020). Kaolinite and its contribution to K reserves in soils advances with increased weathering. More micaceous minerals contribute to total K in younger soils (Melo *et al.* 2002). When the soils become acidic, the cations of Mg and K are replaced with H^+, Al^{3+} and Mn^{2+}, which may reduce the soils' CEC. This illustrates the Ka model and its relationship with Mg, Kx, OC and CEC.

The MLR model of Mga versus predictor variables is presented in Table 2. The regression summary presents an R^2 value of 0.77 and places the model within the best range on the scale of Li *et al.* (2016). This indicates a strong relationship between MRL model and Mga when regressed against Alx, Kx, OC, Mg, CEC and SMC. The ANOVA p-value was less than the alpha value ($p < 0.05$) and indicated a good fit model for the prediction of Mga. The dependent variable (Mga) was statistically significant with NH_4OAc extracted Mg and CEC, and indicated that the data provided by these independent variables were enough evidence to reject the null hypothesis that there is a non-zero correlation. Furthermore, the significant predictors had positive coefficients suggesting a direct relationship with the response variable. Increasing Mg and CEC will result in a rise in the value of Mga. The more OC in the soil, the lower the availability of Mn. Though not significant with Mna, soil pH correlated negatively with Mna.

When soil pH decreases further, Mn (II) toxicity may result (Pendias and Pendias, 1992), nevertheless, Mn (III) and (IV) may predominate at higher pH values which are not available (Rengel, 2000).

The regression summary of Mna model presents an R^2 value of 0.74 within the best range on the scale of Li *et al*. (2016) and indicates strong relationship between the MLR model and Mna. The *p*-value of the ANOVA table specifies that the model is a good fit for the prediction of Mna. Interactions with individual independent variables indicate significant statistical regression of Mna with all the predictor variables ($p < 0.05$) except Alx. This suggests that the predictor variables' data provided enough evidence to reject the null hypothesis that there is a non-zero correlation. The positive coefficients of OC and Mg indicates a direct relationship with the response variable, while Kx, CEC and SMC were inversely related to the response variable.

R^2 value of 0.77 was obtained from the relationship between response variable Ala and predictors. It places the model within the best range on the scale of Li *et al*. (2016), suggesting very strong relationship between the model, predictors and response variables. The ANOVA's *p*-value indicates that the model for Ala's prediction was a good fit model. Furthermore, majority of the individual predictor variables were not significantly regressed with Ala, except Kx and CEC which provided enough evidence to reject the null hypothesis that there is correlation between them and the response variable, and a worthwhile addition to the model. Consequently, negative coefficient for Kx indicates a rise in Kx when Ala decreases, while CEC and Ala are directly related.

Cation exchange capacity and total elemental oxide of K (Kx) are significantly related with all the response variables except Fea and Mga, respectively. Similarly, AR digested Mn was statistically significant with all the predictors except Alx which was unrelated to any response variables.

3.3.   Interaction between AR extractable Fe, K, Mg, Mn and Al, and soil properties

The correlation matrix between Fea, Ka, Mga, Mna and Ala, and soil properties is presented in Table 3. A rise in the values of Mga, Ala ($p<0.001$), Mna, Mg and clay ($p<0.01$) is most likely to increase the values of Fea, while elemental oxide of K ($p<0.001$), pH and fine sand ($p<0.05$) indicates an inverse relationship with Fea. These interractions emphasize the relevance of particle size in soil fertility evaluation as an increase in fine sand will result in a decrease in Fea, while an increase in clay brings about an increase in Fea. Fine-grained clays are results of the chemical weathering of rock minerals and provide the surface area for increased adsorption of nutrients (Fea), while the small surface areas of sand reduces nutrient adsorption and increases soil hydraulic conductivity.

Like the MLR prediction models for Fea, inverse relationship between Fea and Kx affirms increasing Fe content and loss of K in highly weathered tropical soils. High Fea loss may have co-existed with Mg as ferromagnessian minerals, hence the positive correlation. Aqua regia extracted K (Ka) significantly

correlated positively with Mga ($p<0.001$), Ala ($p<0.01$) and Mg ($p<0.05$) indicating a possible rise in value when Mga, Ala and Mg are increased. This outcome affirms earlier presentation in the MLR model of Ka against the predicted variable Mg, which indicated a positive coefficient.

Table 3: Correlation between AR extracted metals and other soil properties

	Fea	Ka	Mga	Mna	Ala	Alx	Kx	Clay	Silt	F.Sand	pH	OC	Mg
Ka	0.01												
Mga	0.60***	0.60***											
Mna	0.55**	0.03	0.61***										
Ala	0.71***	0.50**	0.79***	0.39*									
Alx	0.00	0.003	-0.01	0.00	0.12								
Kx	-0.64***	-0.21	-0.73***	-0.57**	-0.72***	0.24							
Clay	0.56**	0.04	0.27	0.37*	0.43*	0.66***	-0.10						
Silt	0.18	-0.11	0.19	0.14	0.24	-0.14	-0.11	0.04					
F.Sand	-0.51**	-0.27	-0.39*	-0.43*	-0.51**	-0.29	0.37*	-0.38*	0.12				
C.Sand	0.19	0.36*	0.22	0.19	0.26	0.00	-0.25	-0.11	-0.42*	-0.83***			
pH	-0.40*	-0.35	-0.44*	-0.29	-0.51**	-0.44*	0.32	NA	NA	NA			
OC	0.12	0.017	0.37*	0.47*	0.15	-0.23	-0.43*	NA	NA	NA	0.01		
Mg	0.57**	0.41*	0.78***	0.75***	0.50**	0.00	-0.63***	NA	NA	NA	-0.27	0.45*	
Ca	0.19	0.00	0.44*	0.30	0.38*	0.01	-0.43*	NA	NA	NA	0.26	0.53**	0.38*

'a' (aqua regia extracted), 'x' (Determined by XRF), F. sand (fine sand), C. sand (Coarse sand), SMC (soil moisture content), OC (organic carbon), NA (not available)

Aqua regia extracted Mg correlated positively with all other metals extracted by AR as well as Mg ($p<0.001$) and Ca ($p<0.05$), and indicated high probability for an increase when Mg and AR extracted metals are increased. However, Kx ($p<0.001$), pH and fine sand ($p<0.05$) may decrease the value of Mga when increased in the soil. The relationship is affirmed by the MLR model for Mga which recorded a positive coefficient for Mg, indicating a possible rise in Mga should Mg increase, and *vice versa*.

Manganese (Mna) correlated positively with Fea ($p<0.01$), Mga ($p<0.001$) and Ala ($p<0.05$), but negatively with Kx ($p<0.001$) indicating a rise in the AR extracted metals and fall in Kx with increasing Mna. Mna may have co-precipated with Fea, hence the positive correlation between the two metals. In the opinion of Kabata-Pendias (2011), Mn and Fe are closely related in geochemical processes and increases in concentration with increasing acidity. Such increase in the mobility of Mn will result in more phyto-availability and losses of Mn from terrestrial catchments (Watmough *et al*. 2007). Similarly, Mna correlated positively with OC, clay ($p<0.05$) and Mg ($p<0.001$) indicating a direct relationship and negatively with fine sand ($p<0.05$). This suggests the high surface area for adsorbtion provided by clay and organic matter, compared to fine and coarse sand. These interactions are corroborated by the MLR model describing Mna.

Like other AR extracted metals, Ala correlated positively with Mna ($p<0.05$), Mga, Fea ($p<0.001$), and Ka ($p<0.01$) indicating a rise in its values as other metals increase. However, it correlated negatively with Kx ($p<0.001$), pH ($p<0.01$) and fine sand ($p< 0.01$), showing an inverse relationship. The inverse relationship between Ala and Ka may be due to the inhibiting effect of Al^{3+} on the net uptake of K (Horst, 2010), while its relationship with pH typifies the findings of Kabata-Pendias (2011). In his

opinion, Al has low solubility when soil pH is within 5-8, and decreases with aging. Ala also correlated positively with clay ($p<0.05$). In humid tropics, the soils are often high in the oxides of Fe and Al, and low in K with acid reaction, mainly as a result of the loss of exchangeable basic cations and accumulation of Fe and Al oxides of which Al doubles as a dominant elements in kaolinites. Soil dominance of 1:1 phyllosilicates, oxides of Fe and Al can lead to severe K deficiency (Rheinheimer *et al*. 2018). Previous studies by Akpan-Idiok and Ogbaji (2013), Ofem and Esu (2015), Osabor et al. (2009) and Kingsley et al. (2020) obtained quartz and kaolinite as dominant minerals with traces of illite and micaceous minerals in the soils of Cross River State. Nonetheless, Ala correlated positively with exchangeable Mg ($p<0.01$) and Ca ($p<0.05$). One would expect an inverse relationship with Mg and Ca as Al gets accumulated upon Mg and Ca's loss. The correlation of Ala with Kx is corroborated by the MRL model describing Ala.

4.4. Factor analysis for the distribution of AR extracted metals

A factor analysis was applied to the existing data to compress the number of variables to three principal components. The three factors explain 74.4 % of the existing variation using eleven variables in the analysis (Table 4) and shown on the score contribution plot (Fig. 4). The low contribution of Alx and SMC to data variation placed them in PC3 masks their appearance in the score contribution plot of PCs (Fig. 4).

Table 4
Result of factor analysis showing relative Loadings from element concentration

Variables	PC1	PC2	PC3
Fea	73.81	34.55	-26.17
Ka	41.72	-61.28	-37.17
Mga	91.52	-12.73	-14.40
Mna	68.86	52.77	2.66
Ala	84.35	-20.60	-32.94
Alx	-9.18	16.64	-58.13
Kx	-89.91	3.75	-19.39
OC	50.28	14.66	62.29
Mg	79.94	18.99	-4.97
CEC	73.36	-34.93	-7.56
SMC	14.38	-10.02	80.54
% total variance	44.2	17.3	12.9
Cumulative % total variance	44.2	61.5	74.4
Eigenvalue	6.18	2.43	1.80
Location {IH}	74.95	57.44	4.69
Location {AI}	-77.47	41.35	-16.90
Location {MF}	9.45	-93.49	12.64

'a' (aqua regia extracted), 'x' (Determined by XRF), SMC (soil moisture content), OC (organic carbon)

Fig. 4
Score Contribution plot of Principal components
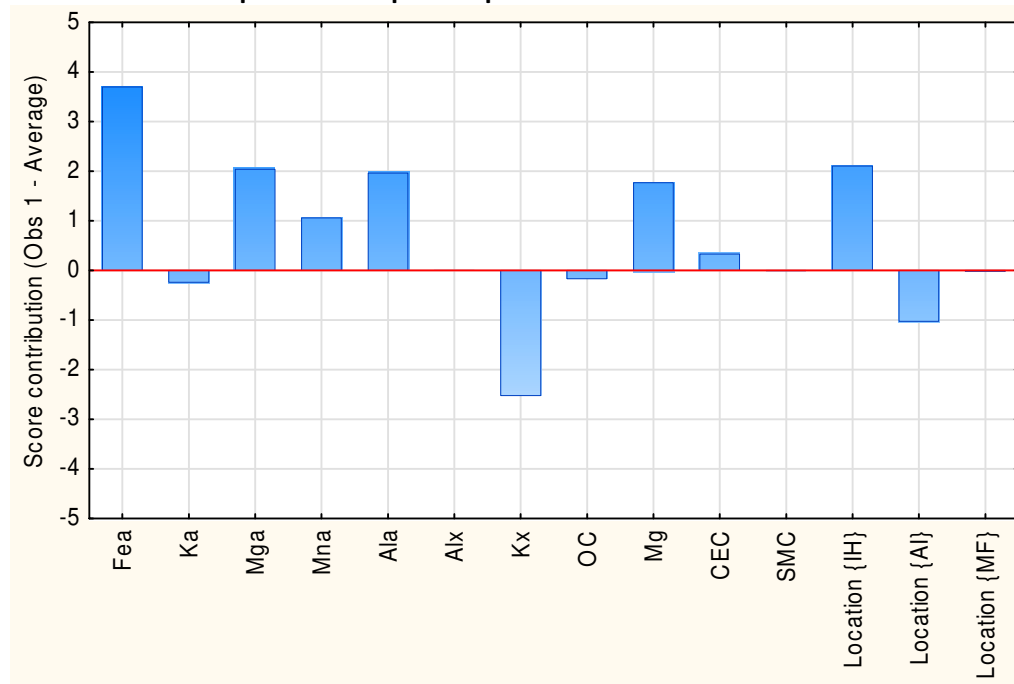
The first loading (PC1) explains 44.2 % of the total variance and returns as the most important principal component. PC1 finds its loadings from the concentrations of Mga, Ala, Kx and Mg (>80 %) as well as Fea and CEC (> 70 %). The high loadings of the above components are consistent with their significance in the MLR models (Table 4) and further emphasizes Kx, Mg and CEC's relevance when modeling AR extractable metals. However, PC2 accounted for only 17.3 % of the total variance related to other soil properties. Ka and Mna contributed most to the loading with individual loadings of 61 and 53 %, respectively. The close loadings of Ka and Mna in PC2 are linked to their similarity in the respective MLR models' performance. Both response variables were significantly related to same predicted variables; Kx, OC, Mg and CEC.

Factor III (PC3) is of less importance and insignificant (Table 4), and accounts for only 12.9 % of the data's variation. However, relatively large loadings to PC3 are linked to SMC (80 %) as well as OC (62 %) and Alx (58 %). The MLR models (Table 2) also indicate, that these predicted variables were the least significant with the models' response variables and may be regarded as less important in the modeling of AR extracted metals.

The per cent total variance of PC1 (44.2 %) is the most significant, while PC3 (12.9 %) is the least significant; consequently, the three factors may be retained since their eigenvalues exceeded 1. However, PC1 maximized variation in the data set with resultant highest eigenvalue, and should be retained.

4. Conclusion

The soils were dominated by AR extractable Fe with mean concentrations greater than 12000 mg/kg for medium loamy soils with the trend such that; Fea> Ala> Mga> Mna≈Ka. Iron may therefore be a threat to the safety of the environment. The dominance of Kx and Alx over corresponding elements digested by AR is due to limitations associated with AR extraction of elements in silicate minerals; hence the necessity for extracting soil mineral elements by more than one method. The distribution of AR metals in the entire soils was quite similar; however, higher values of Fea in the 0-37 cm thickness in IH1P1 (Fig. 1a) is due to seasonal uplifting of soluble Fe or poorly weathered Fe containing minerals in the epipedon. All the MLR functions were within acceptable and best prediction criteria ($R^2 = 0.55–0.77$). The best performing model functions were Ka and Mna, which produced a smaller error when compared with others. The models selected Kx, Mg and CEC as the most important predictor variables to explain the locations' AR metals variability. An increase in sample density per site and the possible removal of insignificant soil properties from the models is proposed in subsequent studies.

Declarations

Conflicts of interests: There are no competing interests.

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Multivariate modeling of some metals concentrations in agrarian soils: distribution and soil fertility implications in the tropics

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