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Soil Health Implications of Some d-block Metals in Selected Agricultural Soils in Southeast Nigeria

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Highlights:

- Mn and Mo threaten the environment the most.
- Soils in the Southern Guinea Savannah are most prone to d-block metals contamination.
- BD, pH, Mg, and CEC are the best predictors of d-block metals in the soils.
- The linear model was best performing in the estimation of V and Mo, respectively.

Abstract

Soil fertility, soil health and environmental management through the estimation of background concentration of potentially toxic elements was required for environmental safety. This study aims at investigating the concentration, fertility and potential health risks of some d-block metals (Ti, V, Fe, Mn, and Mo) in some agricultural soils, and establishes the relationship between the metals and some soil properties. Eight elevation ranges resulted from the digital elevation models of the study area; two in Ishibori (NG1, NG2), three each in Agoi-Ibami (CG1, CG2, CG3) and Mfamosing (SG1, SG2 and SG3). One soil profile pit was sunk along each of the elevations. Thirty-five composite soil samples were collected at 0-30, 30-60, 60-90, 90-120, 120-150, 150-180 and 180-200 cm depending on soil depth. Only the profile means of Mn (660.82 ± 612.89 mg/kg) and Mo (2.61 ± 0.73 mg/kg) exceeded permissible concentrations and would pose threats to the environment. Also, the concentrations of the d-block metals exceeded permissible values in Ishibori making them prone to toxicity. The metals were irregularly distributed with depth; however, Mn and Fe were concentrated in the subsurface soils. Clay and sand contents correlated positively and negatively, respectively with all the d-block metals at $p < 0.05$. The linear model was more efficient in estimating V and Mo via soil properties with adjusted R^2 of 33 – 67 % for the metals. In conclusion, agricultural activities and geology may influence the accumulation of d-block metals, hence the call for environmental monitoring to curtail metals' assimilation by crops.

Keywords: d-block metals. Soil fertility. Agricultural soils. Soil health. Linear regression

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1. Introduction

The ability of the soil to sustain plant growth and optimize crop yield by providing nutrients to plants in proper amounts and proportion with a focus on enhancing the soil for crop production and minimizing environmental impact describes the concept of soil fertility. Despite the relevance of nutrient elements to crop growth and development, they pose a threat to the environment when present in the soil in excess concentrations. This forms the basis for increased soil health inclusion in fertility studies. Soil health is the continued 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 (Ofem et al. 2021a). Such soils maintain diverse communities of soil organisms that help regulate soil functions for food security and environmental safety. There is need to consider the effects of heavy metals on soil organisms, crops, nutrient sufficiency, and environmental sustainability. This could create a balance between metal concentration, crop and animal uptake and food security. The nutrient elements react with other environmental components, resulting in toxic substances that may antagonize nutrients and cause problems to soil fertility.

Determining the background concentration of heavy metals otherwise referred to as potentially toxic elements (Pourret & Hursthouse, 2019) is a complex procedure as the influence of anthropogenic, pedogenic and geologic sources of heavy metals pollution on the soil constitute a significant setback to accurately measuring heavy metal concentration. Long-range transportation of heavy metals *via* air, underground seepage, surficial erosion, and intentional movement of materials containing heavy metals has further complicated the background concentration. Some studies have identified agricultural practices, industrial activities, and associated biological and chemical cycles as influencers of heavy metal concentration (Lončarić et al. 2010). These influencers have contributed to the bulk of heavy metals from anthropogenic sources (Ukpong et al. 2013, Madhav et al. 2023), resulting in elevated soil concentrations (Demetriades et al. 2010). Others have mentioned parent materials (Baize and Sterckeman 2001), organic matter content (Rashid et al. 2023), soil particle size, and chemical analysis methods as factors that influence heavy metal background concentration (Horckmans et al. 2005; Salminen and Gregorauskiene 2000).

Soil pH, cation exchange capacity, particle size distribution and organic matter have been identified as the main soil parameters that govern the processes of sorption and desorption of trace elements (Kabata-Pendias 2011). However, metals' concentrations vary with soil types, parent materials and climate (Sumner, 2000). These properties interact with heavy metals to affect enzymes that are responsible for plant growth and development. For instance, Ti stimulates

the growth of rhizobium strains (Simon et al. 1991), seed germination and root uptake of other nutrient elements, and strengthens plant stress tolerance (Lyu et al. 2017). Furthermore, Fe is required for enzymatic electron transport and is often linked with enzymes in chlorophyll formation. In contrast, Mn is necessary for photosynthetic redox reactions in plants, accelerates germination and maturity and is an important constituent of respiratory enzymes (Kabata-Pendias 2011). Molybdenum is also a component of legume nodules which assists in converting nitrates to ammonium, and leaches easily from the soil but gets absorbed into Fe and Al oxides. Vanadium helps stimulate growth and flowering in pepper, enhances the content of amino acids, sugars and chlorophylls, and modifies nutrient content (García-Jiménez et al., 2018).

Vegetables and forages in contaminated soils absorb heavy metals in concentrations sufficient to cause health risks to the consumers (Singh et al. 2010; Yang et al. 2007). Threat of elevated concentration of metals in the d-block of the periodic table to human health is noticed by a prompt on the native concentration in soils. Such soils act as potential sources of metals to the environment. A high concentration of Ti is phytotoxic and may have adverse effects on human health (Eg. pleural disease). Raised contents of Fe and Mn cause contamination in agricultural lands and food crops (Maina et al. 2016), and are essential as metallo-enzymes or as the cofactors of large number of enzymes (FDA 2001). Fe and Mn are essential to the human body within 8-18 mg/ day for Fe, and 1.8-2.3 mg/day for Mn. Beyond these levels, toxic effects are observed (FDA 2001; Singh et al. 2006) and may cause pathological signs such as the iron oxides deposition in Parkinson's disease (FDA 2001; Powers et al. 2003). However, when Fe is present in chelated form, it is effective in reducing Fe chlorosis than the inorganic forms (Charlson et al. 2005), while its deficiency results in a decline in grain nutritional quality (Welch 2001). The addition of vanadium to the tune of 2.5 - 3.0 mg V L^{-1} in soil inhibits radicle elongation in some crops (Eg. turnip and cabbage) (Carlson et al. 1991) and reduces plant biomass by 50 % at 21 - 180 mg kg^{-1} soil (Smith et al. 2013). Vanadium pollution harm ecological systems and can lead to animal poisoning and human disease (Teng et al. 2006). Carcinogenicity, neural disorders and brain disorders have been reported as a result of the toxicity of these metals (Madhav et al. 2023). Phyto-accumulation of Mo in forages results in physiological Cu deficiency in ruminants (Axelson et al. 2018), especially when present as thio-molybdate (Gould and Kendall 2011). Values of Mo within 58.7 mg kg^{-1} in the dry matter of forages have exposed animals to molybdenosis (Axelson 2011).

Portable X-ray fluorescence (pXRF) has advantages in the speed of analysis, ease of sample preparation, high stability and precision, and a more comprehensive range of detection levels of elements in samples. It does not generate

chemical residues (Weindorf et al. 2014; Stockmann et al. 2016) and has minimal interference on the chemical makeup of soil materials, hence its adoption for the study. However, the limitations of the use of pXRF are centered on matrix and interference effects as well as background noise and calibration standards. The d-block metals are non-biodegradable and concentrate in the environment, entering the food chain and indirectly consumed by man and animals (Mattsson et al. 2017). As crucial as these metals are to the soil's fertility and the environment's safety, there have not been many accessible reports on the concentration, profile distribution, fertility and health implications of the-block metals in the soils of Southeast Nigeria. The importance of evaluating the concentration of d-block metals in agricultural soils cannot be understated. By understanding these concentrations, it becomes possible to manage the risks associated with heavy metal pollution more effectively (Zhao et al. 2022). In scenarios where the origins and levels of these metals remain unidentified, their gradual accumulation can result in the formation of detrimental compounds that degrade soil health and adversely affect plant development (Liu et al. 2017; Liu et al. 2019). Therefore, conducting assessments on soil heavy metal pollution is crucial. Not only does it offer a strategic advantage in controlling the spread of such pollutants, but it also serves as a foundational step in lessening the threats posed by heavy metal contamination. The authors further suggest that lands identified with high toxicity from these metals should be avoided for grazing or agricultural activities.

Currently, few or no studies are available demonstrating the interaction of some selected soil properties with the d-block metals from a soil health standpoint, except for the report of Ofem et al. (2021a), which showed variations of some metals in the soils derived from diverse lithologies. The poor background detection of d-block metals via a reliable procedure like pXRF has simplified the identification of potential problems related to the toxicity of Ti, V, Mn, Fe, and Mo. Therefore, the present research seeks to ascertain the concentration, vertical distribution, fertility and potential health risks of some d-block metals (Ti, V, Fe, Mn, and Mo) in some agricultural soils in southeast Nigeria. The study also established the relationship between the d-block metals and some soil properties.

2. Materials and Methods

2.1 Location, geology, soils, and climate of the study area

The study was carried out in Cross River State, located at 5º31′60″ and 4º27′0″ N, 7º49′60″ and 9º28′0″ E, in Southeastern Nigeria. Areas in northern (NAGZ) (Ishibori; 06°39′17″ N, 08°47'51″ E), central (CAGZ) (Agoi Ibami; 05°43′27″ N, 08°10′37.2″ E), and southern (SAGZ) (Mfamosing; 05° 04′’41.8″ N; 08° 27′49.8″ E) agricultural zones

of Cross River State were selected for the study. Ishibori, Agoi Ibami and Mfamosing are located at approximate distances of 96, 87 and 40 km, respectively away from Calabar, the capital city of Cross River State (Fig. 1a).

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Cross River State has a combination of Basement Complex rocks and Sedimentary lithologies of Cretaceous and Tertiary ages. The Sedimentary geologic formation is basically shale, siltstone, and fine-grained sandstone intercalated with limestone, with alluvium dominating the low lying areas (Ofem et al. 2020). Well-developed limestone beds and caves, that intercalate with sandstone dominate the Agoi Ibami and Mfamosing areas. The study was focused on the Sedimentary formations, with intercalations of sandstone, shale, and limestone. However, Basement Complex rocks occur in the Oban-Obudu hills of Cross River State and are made up of Precambrian Schist and Gneiss with intrusives of igneous rocks and a wide spread of granite-gneiss and hornblende granite-gneiss as well as porphyritic granite.

Soils in the study area are reportedly dominated by kaolinite, quartz, muscovite and biotite, illite, nacrite, montmorillonite, chlorite-vermiculite-montmorillonite interlayered structure, and sparingly vermiculite and palygorskite (Ofem and Esu 2015; Akpan-Idiok and Ogbaji 2013; Ofem et al. 2022). The well-drained soils have been classified as Typic Rhodustult {Ferric Rhodic Acrisols (Ochric)}, Rhodic Paleudults {Ferric Acrisols (Ochric)} and Vertic Paleudalf {Vertic Ferric Luvisols (Differentic, Loamic, Ochric, Profondic)}, while the poorly-drained soils are either Humic Endoaquept {Stagnic Gleyic Cambisol (Humic)} or Humic Endoaquept {Dystric Gleyic Cambisols (Humic, Loamic)} in the USDA Soil Taxonomy and World Reference Base for Soil Resources Systems (Ofem et al. 2020).The soils are deep, weathered, highly leached and high in sesquioxides (Esu 2010).

Ishibori is within the southern guinea savannah and characterized by drier and hotter climatic conditions, while Agoi Ibami and Mfamosing are located within the tropical rainforest zone. The tropical rainforests have a humid tropical climate with all year-round precipitation, high humidity and surface temperatures. The Koppen climate classification system qualifies the areas as tropical moist climate with temperatures greater than 18 ^{o}C all year-round, while precipitation exceeds 1500 mm/year. Rainfall amounts are 1251–3348 mm/year in Ishibori, and 1760–3771 mm/year in Agoi Ibami and Mfamosing. Mean annual temperature varies from 23.0–34.0 ^{o}C in Ishibori to 22.6–32.0 ^{o}C in Agoi

Ibami and Mfamosing (Sambo *et al*. 2016). Oilpalm, teak, gmelina, plantain and cassava constitute dominant tree and food crops grown in the study area, whereas paddy rice is dominantly grown in the poorly drained areas.

2.2 Field investigations

Digital elevation models (DEMs) (30 m × 30 m spatial resolution) of Ishibori, Agoi Ibami and Mfamosing in Cross River State, Southeast Nigeria were obtained from United States Geological Survey Explorer SRTM 1 (Shuttle Radar Topography Mission). Delineations of elevation ranges of the study areas from high to medium and low were obtained using ArcGIS 10.8 software. One soil profile pit was randomly sited along each elevation range, resulting in two profile pits (NG1 andNG2) in NAGZ, three each in CAGZ (CG1, CG2, CG3) and SAGZ (SG1, SG2 and SG3). The profile pits were dug to represent the eight (8) soil units (Fig. 1b). Soil sampling was done at predetermined depths of 0-30, 30-60, 60-90, 90-120, 120-150, 150-180 and 180-200 cm depending on the depths to water table or impenetrable layer. Soil samples were collected from three (3) different points of a depth range and bulked to represent a composite. A total of 35 composite soil samples were obtained and used for the study.

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2.3 Laboratory procedures

Composite soil samples were processed into < 2mm air-dry size fraction and used for laboratory analyses.

Determination of particle size distribution: The particle size distribution was determined by Bouyoucos hydrometer method. In this method, 50 grams of <2 mm air-dried soil sample was transferred to a dispersing cup containing a mixture of 450 ml of water and 50 ml of calgon and stirred on a milk shaker machine for 15 minutes. In a glass cylinder, the sample was made up to 1 L mark with distilled water and stirred vigorously for 2 minutes using a plunger. The hydrometer was carefully lowered into the suspension and read at 40 seconds and the temperature of the suspension taken at a depth of 5 cm. The cylinder was allowed to stand undisturbed for another 2 hours and hydrometer and temperature readings were taken. Percent sand, silt and clay were then determined by calculation.

Soil bulk density was determined by expressing the soil oven-dried at 105 ^{o}C for 48 hours as a ratio of volume of soil (internal volume cylindrical core: $\pi r2h$). Where, π is a constant with value of 22/7, r2 = square of the internal radius of the core, h = height of core.

Soil pH (H_2O) was determined by weighing 20 g of air-dried soil into a 50 ml beaker containing distilled water and allowed to stand for 30 min with occasional stirring with a glass rod. The electrode of the pH meter was inserted into the partially settled suspension and the pH reading was taken. This was done after standardizing the pH meter with a buffer of pH 7.

Total nitrogen was determined by the macro-Kjeldahl digestion method, whereas organic carbon was obtained by the Walkley–Black modified acid–dichromate technique. In the acid–dichromate procedure, diphenol amine was used as an indicator and potassium dichromate as the oxidizing agent.

Cation exchange capacity (CEC) by NH_4OAc at pH 7.0 was obtained by saturating the soil exchange sites with an index cation (NH^-_4) at pH of 7.0 by treating the soil with 1 *M* NH_4OAc at pH 7.0 and the concentration of NH^-_4 in the extract was determined by distillation and titration.

Exchangeable Ca^{2+}, Mg^{2+}, K^+ and Na^+ were determined by leaching the soil sample with 1 *N* neutral NH_4OAc at pH 7.0. Exchangeable K^+ and Na^+ were determined by flame photometry, whereas Mg^{2+} and Ca^{2+} were determined by atomic absorption spectrometry. All analyses were executed by the use of standard laboratory procedures as outlined in Soil Survey Staff (2014).

An automatic mill was used to pulverize and homogenize the < 2 mm air-dry soil materials into fine powder of 3–4 μm. The powder samples were analyzed with the 2019 version of portable x-ray fluorescence (pXRF) Delta Premium Spectrometer (Olympus Innov-X, USA) for metal oxides (Tejnecky et al. 2015). By the guidelines of the United States Environmental Protection Agency, a pXRF installed computer was used to scan each soil sample in triplicate for the oxides of Ti, V, Mn, Fe and Mo, and the results were presented in mg/kg. The average was obtained and used for interpretation. For easy rating of the oxides, conversion was made to their elemental forms using a standard excel sheet for conversion. Laboratory analysis was done in the Department of Soil Science and Soil Protection, Czech University of Life Sciences, Czech Republic.

2.3 Modeling approach, factor analysis and basic statistics

Multiple linear regression (MLR) is a statistical technique that uses several explanatory variables to predict the outcome of a response variable (Wallisch et al, 2022). MLR was performed in the STATISTICA 12 software environment to predict d-block metals (i.e., Ti, V, Mn, Fe and Mo) using the best correlated soil properties. The

Multiple linear regression model used to predict the d-block metals obtained by XRF via selected soil properties is expressed in equation 1:

$$XRFmetaloxides(\text{mg/kg}) = \beta 0 + \beta 1x1 + \beta 2x2 + \cdots \beta \text{k}xk + \epsilon j \ldots Eqn\ 1$$

where XRF is the response variables indicated by Ti, V, Mn, Fe and Mo. x_1, x_2 … x_k are predictor variables: clay, sand, bulk density (BD), soil pH, Mg, K, and CEC. ϵ = residual terms of the model, and β_0 represents regression intercept, while β1 and β2 represent regression coefficients.

Significance statements were obtained from null (Ho) and alternative (Ha) hypothesis such that:

Ho: $\beta 1 = \beta k = 0$.

Ha: $\beta j \neq 0$; for at least one j.

F_{value} (calculated) > $F_{statistics}$; reject null hypothesis.

The selected general soil properties were subjected to multivariate modeling. In this case, root mean square error (RMSE), and coefficient of determination (R^2) were used to explain model performance.

Principal Components Analysis (PCA) enabled the grouping of the d-block metals and general soil properties on the basis of agricultural zones. The principal components(PCs) that account for the grouping enabled the extraction of principal factors accounting for the variability.

Correlation, model computation ($p< 0.05$), principal components analysis, and descriptive statistics were performed using STATISTICA version 13.3.

3 Results and Discussion

3.1 Concentration, profile distribution, and health implication of d-block metals in the studied soils

The overall statistics of the general soil properties and d-block metals concentrations of the studied soils are presented in Table 1, while Table 2 is the summary statistics of individual soil profiles indicating the soils with values that exceed permissible levels. The profile distribution of the d-block metals at various depths is presented in Fig. 2.

a. Titanium: Titanium had a mean of 4593.5 mg/kg for the entire studied soils, with values that ranged from a minimum of 1851.2 mg/kg in the SAGZ (SG2) to a maximum of 10503.0 mg/kg in the NAGZ (NG2) (Table 1). Values of Ti decreased continuously with increasing soil depth in the entire soil profiles and increased at depths over

150 cm in NG1 and SG2, 180 cm in CG1, and 90 cm in CG2 as the impenetrable rock layer is being approached (Fig. 2a). Values of Ti were quite high in the northern agricultural zone. The coefficient of variability of over 50 % for Ti indicates a greater level of dispersion away from the overall mean value.

On the whole, the concentration of Ti does not indicate soil pollution except for values in NG1 and NG2 (NAGZ) which exceeded the mean worldwide (WW) value of 7,038 mg/kg (Kabata-Pendias 2011), and CG1 and CG2 with maximum values exceeding crustal average (Hedrick 1995; Reimann and de Caritat 1998). However, most values exceed 200-2400 mg/kg for WW surface values (Kabata-Pendias and Mukherjee 2007).

The order of concentration of Ti in the soils was NG2> NG1> CG1> CG2> CG3>SG2> SG3> SG1, indicating a decrease in the concentration of Ti from the NAGZ (NG1, NG2) to the CAGZ (CG1, CG2, CG3), and SAGZ (SG1, SG2, SG3).

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At all depths, the concentration of Ti in NG1 and NG2 exceeded the WW average. This may have been due to aerial depositions from distant transportation of the metal from industrialized areas, particularly the Makurdi and Otukpo areas of neighboring Benue state. The supply of Ti in low concentrations has a positive effect on plant growth but causes phyto-toxicity at high concentrations (Wallace et al. 1977). Hence, Ti application for plant nutrition requires utmost monitoring and care. Ti application improves crop quality and increases the concentration of β-carotene and xanthophylls in red pepper (Biacs et al. 1997). Despite the relevance of Ti in plant nutrition, Ti does not meet the criteria for essentiality (Arnon and Stout 1939), and plants can complete their life cycle without it.

Oxides and hydroxides of Ti are formed during the weathering of primary minerals and pedogenesis and are common components of many rocks. Ti concentration in the studied soils falls within the range of 100-25000 mg/kg (Kabata-Pendias 2011) and may not be a threat to the environment. The element does not threaten the environment due to its stability and resistance to weathering but has been used to assess the genesis of several soils. However, the mean value of Ti in the northern agricultural zone (NG1 and NG2) of Cross River State exceeded the WW average of 7,038 mg/kg

(Kabata-Pendias 2011), thus enhancing the co-occurrence relationship and improving the stability of the soil micro-ecological structure, due to their ability to enrich microorganisms (He et al. 2022). The enhancing impact of the Ti ions on the soil micro-ecological structure is an indication of improved soil health condition. Titanium is not readily mobile in most plants but has some beneficial effects on the yield of plants (Pais 1983). According to Anke and Seifert (2004), and Kabata-Pendias (2011), soil properties and origin of lithology, control the content of Ti in plants, hence the variability in the concentration of the metal in the studied soils. In an earlier study, Ofem et al. (2020) described the well-drained soils in the NAGZ as highly weathered. The abundance of Ti in the soils, and particularly in NG1 and NG2, may be due to its mobile nature orchestrated by the strong tropical weathering conditions (Cornu et al. 1999).

b. Vanadium: Mean of 125.2 mg/kg was obtained for the studied soils with minimum value of 76.7 in the CG3 (CAGZ) and maximum value of 174.6 mg/kg in CG2 (CAGZ). Similar soils have been reported by Tume et al. (2011) to have a mean of 52 mg/kg and range of 39-61.4 mg/kg for the concentration of V. Profile distribution of V in the soils indicate irregular distribution (Fig. 2). However, its values seem to be lower in layers of high sand contents. Coefficient of variation of 24 % indicates relative similarity in the distribution of V across the three locations. The distribution of V in most soil profiles is uniform (Kabata-Pendias 2011), and it is often inherited from parent rocks and has a WW average of 129 mg/kg and range of 69-320 mg/kg. Mean of V in the current study is lower than the WW average. Low V concentration is reported for light textured soils, while considerable amounts have been reported in concretions and nodules formed in soils; 400 in Fe – rich and 440 mg/kg in Mn – rich nodules (Kabata-Pendias 2011). This may have been responsible for the negative correlation of V with sand ($p< 0.05$). In sand dominated soils, 80 mg/kg V can reduce plant growth, whereas in loamy soils, < 100 mg/kg V does not affect plants (Kabata-Pendias 2011), hence the need to monitor background values of metals in agricultural soils. The use of V for crop production favours crop development, contributes to human health, and also accumulates in plant tissues (Chongkid 2007). The growth and development of pepper is stimulated by vanadium and enhances mineral and chlorophyll concentration in pepper (García-Jiménez et al. 2018).

Overall mean of V in the entire soils does not indicate accumulation, except for the means recorded in NG1, NG2, CG2, and SG1 which exceeded the WW average of 129 mg/kg (Kabata-Pendias 2011). Values of V at all depths in NG1, NG2, CG2 and SG1 exceeded the WW average. Such high values may be harmful when released into the environment. Vanadium toxicity to plants varies with soil types due to its availability to plants. Shaheen and Rinklebe

(2017) described V as a toxic metal which may cause potential environmental risks when transferred into ground water, vegetation and food chain. The order of profile mean concentrations was such that CG2> NG1> NG2> SG1> SG2> CG1> SG3>CG3 and indicates that poorly drained soils in the tropical rainforests least experienced V accumulation and are less potentially toxic. Soil microorganisms could adapt to the soil environment containing low levels of V, and evolve a stable structure; however, the high concentration of V in soils of northern agricultural zone (NG1 and NG2) could impact the balance of microbial community (Wang 2020). This way, microbial activities are reduced, organic matter decomposition is affected, and the soil's health is threatened.

c. Manganese: An average value of 660.8 mg/kg was obtained in the studied soils, with the values exceeding 35 mg/kg and reaching a maximum of 2151.7 mg/kg in the NAGZ (NG2). A high coefficient of variation of 90 % indicates high variability between values of Mn in the soils of the various locations. In the entire studied soils, the values of Mn regularly increased in all the soil profiles except in CG3 and SG3 (Fig. 2) where values decreased with increasing soil depth. Most crop plants may not be affected by Mn toxicity at such depths of the soil profile. Mn oxides occur in soils as coatings on primary soil particles, fillings, veins, concretions and nodules and tend to concentrate at lower depths, and crops do not suffer Mn deficiency at concentrations above 15-25 mg/kg but are affected by concentrations above 400 mg/kg (Kabata-Pendias 2011), probably due to toxicity effects. The increase in the concentrations of heavy metals at lower depths can be associated with the parent material (Srinivasarao et al. 2014). High Mn in the study area may reflect high availability for plant uptake. Mn in the current study exceeds the WW average of 488 mg/kg (Kabata-Pendias 2011). Also, at all profile depths, the concentration of Mn in NG2 exceeded the WW average, making it more toxic and threatening relative to other studied soils. The order of concentration of Mn was such that; NG2> NG1> CG1> SG2> CG2> SG1> CG3> SG3, with relatively more concentrated values in the NAGZ. The observed concentration ranges of Mn suggest either contamination from agrochemicals or the influence of pedological factors. This is a sign of warning to environmentalists, as adjoining water bodies may already be witnessing raised proportions. Mn toxicity can be prevented by conventional liming, soil drainage, or, at best, the growth of plants with high tolerance to excess Mn (Foy et al. 1988). Manganese is associated with silicate clays and is present in soils in large quantities (Srinivasarao et al. 2014). When Mn is consumed via exposed crops and animals, it causes neurotoxicity in the form of Parkinsonism (Harmanescu et al. 2011). Tume et al. (2011) reported a mean of 454 mg/kg and a range of 171-755 mg/kg in similar soils. Mn acts as an activator and cofactor of various metallo-enzymes and catalyzes various enzyme reactions like redox reactions, phosphorylation,

decarboxylation and hydrolysis (Schmidt and Husted 2019). When Mn is available within prescribed ranges, its catalytic role supports basic soil functions and creates a conducive environment for soil microorganisms to thrive.

d. Iron: Fe content in the soils exceeded 2,500 mg/kg reaching a peak of 66,874.4 mg/kg in the 0-30 cm depth of NG1 (NAGZ) and an average of 28,126.6 mg/kg in the entire soils. The coefficient of variation of over 60 % indicates a wide variation in the concentration of Fe between the soils of the agricultural zones, such that NG1> NG2> SG2> CG2> CG1> SG1> CG3> SG3. The order of concentration of Fe is controlled by the vegetation/climate factor of soil formation, with soils in NAGZ being more prone to toxicity. For instance, NG1 and NG2 decreased with soil depth, whereas its values in the tropical rainforest areas (CG1, CG2, CG3, SG1, SG2, SG3) fluctuates with soil depth. The mean Fe concentration in some soils was reported as 21,329 mg/kg and ranged from 13,310-30,198 mg/kg (Tume et al. 2011). The concentration of Fe at about 500 mg/kg in paddy soils reportedly kills rice seedlings (Foy et al. 1978). The use of Fe as an energy source of bacteria brings about its accumulation by bacterial cells in the form of hydroxides. The biogenic Fe deposits are transformed into ortsteins and then limonite and goethite (Aristovskaya 1974), which have the capacity to influence the properties of dissolved organic matter. The interactions of such mineral particles with degrading bacterial cells are important for biodegradation.

The overall mean concentration of Fe in the soils, irrespective of the agricultural zone, was less than 50,000 mg/kg, reported as the permissible concentration of Fe. However, the profile mean of Fe in NG1 exceeded the permissible concentration of Fe set by WHO (1996) and presented it as a potential threat to the environment. Also, the maximum values of Fe in NG1, NG2 and SG2 exceeded the maximum permissible concentration set by WHO (1996). High values of Fe in NG1 and NG2 are due to the natural concentration in soils. In contrast, relatively low concentrations in CAGZ and SAGZ indicate that Fe may not pose a severe problem to the environment at the moment. However, there is a need to be cautious as continuous accumulation may threaten crops and animals. High concentrations of Fe oxides in the soils have been attributed to intense weathering conditions (Ofem et al. 2020). At relatively low concentrations, Fe, Mn and Mo can enhance some cellular functions in crops. For example, pigment biosynthesis, photosynthesis, respiration, enzyme activities, sugar metabolism and nitrogen fixation (Tiwari & Lata, 2018, Bashir et al. 2016). When concentrations of the metals exceed threshold levels, adverse effects may affect plant growth, development, and reproduction (Shahid et al. 2015).

e. Molybdenum: Molybdenum in the studied soils had values of 1.3 – 4.2 mg/kg with an average of 2.61 mg/kg. A coefficient of variation of < 30 % suggests low variability in the concentration of Mo. The concentration of Mo decreased with soil depth and increased in the basal layers of the soil profiles. This indicates that Mo may have been deposited on the surface soils from industrial or agricultural sources or may be due to geologic sources. An average concentration of 1.5 mg/kg is reported for Mo in the upper earth's crust, while the WW average content in soils is reported as 1.1 mg/kg with a range of 0.9 – 1.8 mg/kg (Kabata-Pendias 2011). Mo requirements in most plants are often met at soil concentrations of 0.2-5.0 mg/kg (Kabata-Pendias 2011), which satisfies the results of the current study. In the production of vegetables in British-Columbia, 24 mg/kg is considered very high (Pieri et al. 1996). Very high contents of 410 mg/kg have been reported for Mn nodules (Kabata-Pendias and Sadurski 2004), whereas more elevated concentrations in soils have been attributed to industrial pollutions such as mining, processing of metals and oil refining (Kabata-Pendias 2011). He further reported that soils with Mo concentration exceeding 5 mg/kg are associated with growth retardation and may lower reproduction in cattle due to the Mo-Cu nutritional relationship (Kabata-Pendias 2011). Despite its relevance in the enzyme system of plants (Nicholas 1975), excess of Mo in the soil may pose a serious challenge to human and animal health. Scouring of cattle and sheep may occur in areas where the pastures contain raised levels of Mo (Underwood 1976). Such raised concentrations of Mo can be tolerant to the growth of carrots, potatoes, sorghum, rice and cotton (Lucas and Knezek 1972; Shorrocks 1984). Molybdenum is one of the least abundant essential nutrients found in plant tissues but is required by nitrate reductase, xanthine dehydrogenase, aldehyde oxidase and sulfite oxidase for their activities (Kaiser et al. 2005). Below threshold values, Mo in soils may not perform its catalytic function effectively, resulting in delayed soil biological processes and poor soil health condition.

The concentration of Mo was in excess of the WW average of 1.1 mg/kg in all the studied soils at all depths. This sends important information to environmental agencies, as humans, animals and crops may be at risk of Mo toxicity. Since the observed concentration of Mo was greater than the baseline limit, the soils may have been contaminated or influenced by pedogenesis. In alkaline soils, molybdenum becomes more soluble and is accessible to plants mainly in its anion form as MoO^{4-}. In contrast, in acidic soils (pH <5) molybdenum availability decreases as anion adsorption to soil oxides increase (Reddy et al. 1997). According to Kang and Osiname (1985), the problems associated with Mo pollution are less common in the humid zone than semi-arid zones. This may have led to the trend; CG2> NG1> CG1> NG2> SG1=SG2> SG3=CG3. Molybdenum toxicity in plants under most agricultural conditions is rare. Tomato and

cauliflower grown on high concentrations of Mo will have leaves that accumulate anthocyanins and turn purple, whereas, in legumes, leaves have been shown to turn yellow (Bergmann 1992; Gupta 1997). Peyue (1963) reported very low total Mo contents (0.44 – 0.75 mg/kg) for some Malian surface soils, while Cottenie et al. (1981) found a range of 3 – 4.2 mg/kg for total Mo in selected Nigerian soil profiles.

3.2 Correlation matrix between the d-block elements and soil properties

The relationships existing between the metals determined by XRF and general properties of the soils are presented in the Tables of correlation matrix (Table 3). Some of the selected soil physical and chemical properties include clay, sand, BD, pH, K, Mg, and CEC.

a. Titanium: Significant correlations were obtained between Ti and clay (r= 0.478), sand (r = – 0.499), exchangeable Na (r = 0.459), K (r = 0.452) and cation exchange capacity (r= 0.753). This indicates that soils dominated by sand have Ti content easily lost or leached. This is probably due to the sand grains' low cation exchange capacity and surface area. In contrast, clay has a high cation exchange capacity, and high values will likely increase the capacity of the soil to hold more Ti in the soils' exchange complex. High CEC will also result in high Ti concentration in the soil. Soil pH significantly affects the absorption of Ti in plants (Lyu et al. 2017), however, Ti concentration was not significantly correlated with soil pH (r= 0.159) at $p< 0.05$. The soil had soil pH ranging from 5.1 to 7.2. These values are within acceptable values for optimum soil microbial activities. However, Ti seems not to be dependent on soil pH. Low soil pH (<4.5) has been attributed to soil aging due to the weathering of minerals, as well as the leaching of exchangeable Ca^{2+} and Mg^{2+}, and subsequent replacement by H^{+} (VandenBygaart and Protz 1994).

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b. Vanadium: Vanadium had significant correlations with silt (r= 0.561) and sand (r = – 0.459) at $p< 0.05$. Therefore, soils with high silt content and less clay are most likely to encourage vanadium accumulation, whereas high sand reduces the concentration of V in the soils. Low V concentration is common in light textured soils, with its mobility in soils being dependent on the soil's host minerals and pH conditions (Kabata-Pendias 2011). Similar results were reported by Shaheen and Rinklebe (2017), as V correlated positively with clay, Fe, and Mn.

c. Manganese: Increase in clay (r= 0.444), Mg (r= 0.371), Ti (r= 0.486), Mo (r= 0.372) and V (r= 0.354) at $p< 0.05$ will result in an increase in Mn concentration due to the positive correlation, whereas an increase in sand content will lead to a decrease in Mn concentration. Mn had inverse and non-significant relationships with total N (r= -0.108), exchangeable Na (r = – 0.032) and K (r= – 0.033). Similar antagonistic relationships have been reported by Kabata-Pendias (2011). Mn has a high level of association with Mo, with its concentration decreasing as the activity and susceptibility to the leaching of Ca increases (Kabata-Pendias 2011). However, in this study, exchangeable Ca seems to be very weakly correlated with Mn concentration and would weakly relate with Mn in the above manner. According to Foy (1983), the excess of Mn induces Ca deficiency because it inhibits the transport of Ca within plants and, under certain conditions, reduces Mn toxicity. Previous studies reported Mn correlation with CEC (r= 0.65) and clay contents (r= 0.79) (Srinivasarao et al. 2014).

d. Iron: An increase in the amount of clay (r= 0.403) and the concentration of Mg (r= 0.611), Ti (r= 0.640), V (r= 0.344), and Mn (r= 0.494) as well as an increase in the soils' cation exchange capacity (r= 0.614) will result in an increase in the concentration of Fe in soils. On the other hand, the concentration of Fe in the soils increases when clay is increased (r= 0.403) and sand content is decreased (r = – 0.401). A significant positive correlation between Fe, Mn and Mg suggests that the elements are closely associated and indicate their common origin (Addis and Abebaw 2017), probably as Fe-Mg and Fe-Mn minerals. Moreover, as Fe and Ti correlate (r= 0.640), Ti may induce the expression of genes related to Fe acquisition, enhancing Fe uptake and utilization when plants encounter Fe deficiency (Lyu et al. 2017). A non-significant correlation was obtained for Fe with organic carbon (r= 0.133) and corroborated with report by Kabata-Pendias (2011), who observed an increase in Fe mobility in soils with high input of organic matter. In calcareous soils, Ca suppress Fe availability and may lead to Fe chlorosis in plants (Kabata-Pendias 2011).

e. Molybdenum: Molybdenum concentration correlated significantly with bulk density (r= 0.443), soil pH (r= 0.497), Ti (r= 0.387), V (r= 0.604), and Mn (r= 0.372), and suggested increasing concentration of Mo when the above parameters are increased. On the other hand, Mo correlated negatively with total N (r = – 0.378) and indicated decreasing Mo concentration with an increasing value of total N. Molybdenum's availability for plant growth strongly depends on soil pH, the concentration of Fe oxides, and organic compounds found in the soil colloids (Reddy et al. 1997). Though not significantly correlated, the relationship between organic C and Mo in the current study (inverse relationship) negates the direct relationship reported by Bloomfield and Kelso (1973). Inverse relationship between Mo and sand aligns with the views of Bloomfield and Kelso (1973), Karimian and Cox (1978) and Riley et al. (1987)

that sandy soils are subject to molybdenum leaching. Furthermore, non-significance in the correlation between Mo and the primary soil particle sizes corroborates with the findings of Kadunas et al. (1999), that Mo does not show any distinct association with soil texture. The direct relationship of Mo with soil pH is indicative that the metal is least soluble in acid soils and readily mobilized in alkaline soils as its Phyto-availability increases with soil pH. Though all the metals were positively correlated with soil pH except Fe ($r = -0.045$), only Mo was significantly correlated with soil pH ($r=0.497$) at $p< 0.05$. This affirms an earlier report that the adsorption capacity for metals increases with increasing soil pH (Wilson et al. 2001). Furthermore, in the current study, Mo seems to have a higher affinity for clay than organic carbon and negates reports by Cˇumakov (1988) that organic substances have a greater affinity for Mo than clays.

3.3 Estimation of d-block elements with some selected soil properties via a linear regression model

Table 4 and Fig. 1S show the results of the linear regression analysis using highly correlated soil properties as independent variables and the variable importance for the d-block metals. In this study, we demonstrated that d-block elements can be estimated using selected soil physical and chemical properties (clay, sand, BD, pH, K, Mg, and CEC) as input data.

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The linear regression model between Ti and selected soil properties indicates that the adjusted R^2 value of 0.67 suggests that these soil properties account for approximately 67% of the variability in Ti levels within the studied soils. Among all the predictors, only the cation exchange capacity (CEC) was statistically significant at the 0.05 level. This positive coefficient for CEC indicates a direct relationship with Ti, implying as CEC increases, Ti also tends to increase. The ANOVA p-value is highly significant, supporting the overall fit of the model in predicting Ti levels based on the chosen soil properties. In addition, the variable importance plot revealed that CEC, K and clay content are the best variables in estimating Ti (Fig. 1S).

For V, the linear model yielded an adjusted R^2 value of 0.375 suggests that these soil properties can explain for approximately 37.5% of the variability observed in V levels within the soils being studied. From the predictors, only clay, sand, and BD were statistically significant at the 0.05 level, indicating they are key factors in predicting V levels.

Specifically, as the proportions of clay and sand in the soil increase, there is a decrease in the V concentration, while an increase in BD corresponds to an increase in V. Although this model showed no statistical significance for CEC in relation to V, previous research has highlighted its importance. A study by Hanus-Fajerska et al. (2021) has documented that vanadium determination is influenced by particle size distribution and CEC. Furthermore, Morakinyo et al. (2016) elucidated that soil particles tend to adsorb vanadium cations, forming complexes with humic acids across varied pH ranges. Overall, the variable importance plot revealed that sand, clay and BD contributes more in the prediction of V (Fig. 1S).

In the case of Mn, the linear model accounted for approximately 32.9% of the variability in manganese concentrations within the studied soils, as evidenced by an adjusted R^2 of 0.329. Among the predictors, pH and exchangeable Mg emerged as statistically significant ($p < 0.05$) with a positive relationship to manganese. The variable importance plot revealed that Mg, clay and pH contribute the most in prediction of Mn (Fig. 1S). The result further suggests that as the values for pH and exchangeable Mg increase, the manganese concentrations in the soil are also expected to rise. When soil becomes more acidic (i.e., a decrease in pH), cations like Mg and K can be displaced by H^+, Al^{3+}, and Mn^{2+} ions. This displacement may, in turn, reduce the cation exchange capacity (CEC) of the soil, as pointed out by Ofem et al. (2021b). A lower CEC can compromise soil fertility, which could have consequential impacts on plant growth and health. Moreso, while the variable importance plot highlights the contribution of Mg, clay and pH in determining soil manganese levels, it also underscores the interconnected nature of soil properties and their collective impact on soil health.

For Fe, the model explained approximately 65.1% of the variability in Fe concentrations within the investigated soils, as illustrated by an adjusted R^2 of 0.65. Of the various predictors included in the model, Mg and cation exchange capacity CEC emerged as statistically significant, both exhibiting positive coefficients. This implies that as the values of Mg and CEC in the soil increase, so do the concentrations of Fe. It is important to note that Mg, CEC and sand contribute the most in predicting Fe. CEC's significance aligns with known soil science principles: soils with high CEC values have an enhanced ability to exchange cations at their exchange sites, often leading to increased fertility and the capability to support a diverse range of crops (Ofem et al. 2021b). In this context, a higher CEC suggests more exchange sites available for Fe absorption.

In the case of Mo, the model indicated an adjusted R^2 of 0.362, suggesting that the selected soil properties account for 36.2% of the variability in Mo concentrations in the investigated soils. Among the various predictors, BD, pH, and exchangeable potassium (K) emerged as statistically significant at the $p < 0.05$ level. This evidence supports rejecting the null hypothesis that these variables have no relationship with Mo concentrations. Notably, each of these variables exhibits positive coefficients, implying that as their values increase, Mo concentrations tend to rise correspondingly. The significance of exchangeable K is particularly noteworthy in tropical soils. Higher values of exchangeable K often signal soils rich in fertility, possibly indicating regions less impacted by advanced weathering processes where micaceous minerals remain untransformed into clay phases. Additionally, as soils become more acidic (evidenced by a decrease in pH), the common cations like K are often displaced by H^+, Al^{3+}, and Mn^{2+}. This ion replacement typically diminishes the soil's CEC, as supported by Ofem et al. (2021b). A broader understanding from recent research (Rashid et al., 2023) indicates that the bioavailability of heavy metals to crops usually increases in soils with a more acidic pH, reduced organic matter, and a lower CEC.

3.3 Principal Components Analysis for the Distribution of XRF Metals and other soil properties

Factor analysis was used to reduce the existing data to three (3) principal components (PCs). The PCs explained 67 % of the existing variation using seventeen soil variables (Table 5) and shown on the biplot (Fig. 3) and scree plot (Fig. 4). The percent total variation of principal component 1(PC1) (31 %) is the most significant and influential, followed by PC2 (25.6 %), while the least significant PC was PC3 with a total variation of 10.4 %. Silt (3 %) and soil pH (11.7 %) had the lowest contributions to data variation in PC1, giving rise to relatively high score contributions in PC 3 (Fig. 3).

The first loading (PC1) contributed 31 % of the total variation and was the most important PC. Its loadings emanate principally from BD, OC, total N, Na and K with each contributing loadings greater than 80 %. Also, every XRF metal made a contribution within the range of 15 - 39 % to data variation in PC1. This is quite low and suggests low contribution of the metals to variation between the soils. Also, all the metals correlated with clay ($p< 0.05$) and either with sand or BD. These properties are therefore very significant in the multiple linear regression (MLR) models. The low contribution of silt and soil pH (< 12 %) to the loadings in PC1 undermines their relevance in metal modeling in the study area.

The second loading (PC2) accounted for 25.6 % of the total variation related to other soil properties. The loadings were dominated by Ti, CEC, sand, clay, Mn and Fe with each contributing a minimum of 60 % to sample variation. Principal component 3 was the least important PC with contribution to variation in the soils arising principally from silt (> 74 %).

The eigenvalues of PCs 1-3 were retained as the values exceeded 1 in each case. However, variation in soil properties was maximized in the data set in PC1 where the highest eigenvalue (5.3) was obtained.

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<<<<<<<<<<<<<<<<<<<<<<<<**SPACE FOR FIGURE 3** >>>>>>>>>>>>>>>>>>>>>>

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4. Conclusion

Among the five studied d-block metals (Ti, V, Mn, Fe, Mo), the profile means of Mn (660.82 ± 612.89 mg/kg) and Mo (2.61 ± 0.73 mg/kg) exceeded the World-wide permissible concentrations. Also, the concentration of Ti, V, and Fe all exceeded their permissible values in soils of NAGZ (NG1 and NG2) making the soils to be most prone to metal toxicity. Mn and Fe were either concentrated in the subsurface depths or increased continuously with increasing soil depth. These findings indicate a pedogenic and geologic source of the metals. Low concentration of Ti and V in the soils is beneficial to plant growth but may result in phyto-toxicity in raised concentrations in the southern guinea savanna area. In low amounts, Fe, Mo and Mn may enhance cellular function in crops but will affect crop growth, development and reproduction when present in raised concentrations. Such raised amounts may result in phyto-accumulation leading to neurotoxicity. Soils in southern guinea savanna were most prone to d-block metals toxicity.

Clay and sand contents correlated positively and negatively with the d-blocks metals, respectively. Organic carbon and exchangeable Ca were not significantly associated with the d-blocks metals. All the linear regression models showed that the d-block metals could be estimated efficiently using soil properties. Overall, the linear model performed higher in estimating V and Mo with the soil properties. The principal component analysis also revealed that BD, OC, total N, Na and K dominated principal component 1 and, as such, had the most contribution to the variation in the dataset.

In conclusion, agricultural activities as well as pedogenic and geologic processes influence the accumulation of d-block metals. As such, prior to crop establishment, farmers must often ascertain these metals' concentration and vertical distribution of the d-block metals. Broad-range study to include more agrarian communities, greater number of soil samples as well as the assessment of plant and animal exposure to the metals is proposed in future studies.

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Declarations

Ethics approval: All authors have read, understood, and complied as applicable with the statement on “Ethical responsibilities” as found in the instructions for Authors.

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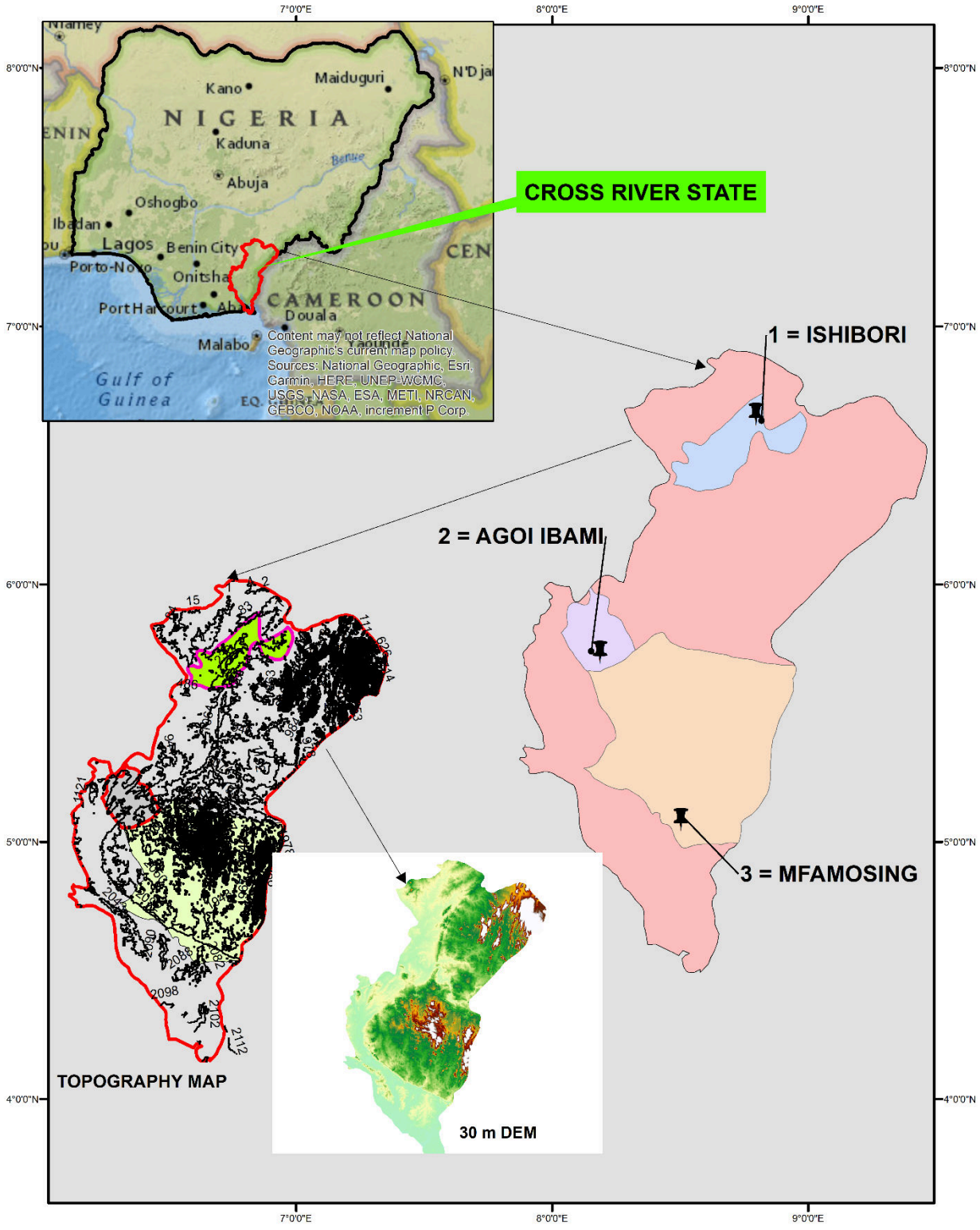


Fig 1a: Map of Cross River State showing the study areas, topography map and 30 m digital elevation model

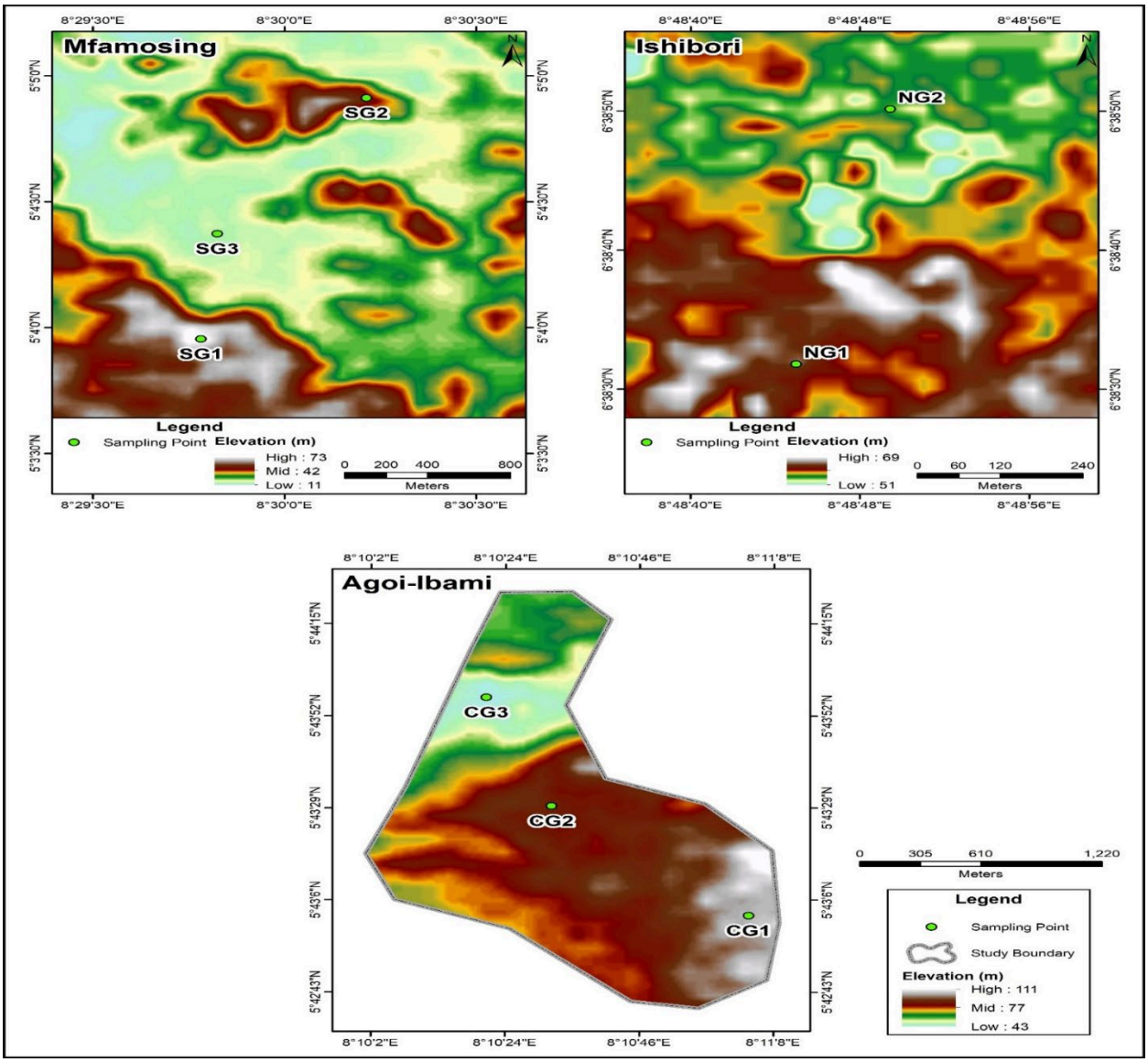


Fig. 1b: Digital elevation models of the study areas indicating sampling points

Table 1: General soil properties and d-block metals concentration in the studied soils

N=35	Mean ±SD	Minimum	Maximum	Coeff. Var.	Std. Error
Clay (g/kg)	187.7±61.4	100.0	320.0	33	10.4
Silt (g/kg)	99.3±31.3	40.0	180.0	32	5.3
Sand (g/kg)	713.0±70.0	560.0	840.0	10	11.8
BD (Mg/m^3)	1.38±0.21	0.85	1.70	16	0.036
pH	6.0±0.62	5.1	7.2	10	0.105
OC (g/kg)	7.88±10.06	0.69	46.34	128	1.70
TN (g/kg)	1.52±1.13	0.50	5.58	74	0.19
Na (cmol/kg)	0.04±0.05	0.01	0.28	113	0.008
K (cmol/kg)	0.07±0.05	0.01	0.29	69	0.009
Mg (cmol/kg)	2.73±1.33	0.20	6.80	49	0.225
Ca (cmol/kg)	5.05±1.97	2.20	9.20	39	0.333
CEC (cmol/kg)	15.95±12.12	4.00	54.40	76	2.05
Ti (mg/kg)	4593.45±2398.56	1851.20	10503.00[a]	52	405.43
V (mg/kg)	125.21±29.84	76.70	174.60[a]	24	5.04
Mn (mg/kg)	660.82[a]±612.89	35.60	2151.70[a]	93	103.59
Fe (mg/kg)	28126.6±17852.2	2576.8	66874.4	63	3017.58
Mo (mg/kg)	2.61[a]±0.73	1.30[a]	4.20[a]	28	0.123

SD: Standard Deviation, a: values are less than the worldwide average, Ti (7038 mg/kg), V (129 mg/kg), Mn (488 mg/kg), Mo (1.1 mg/kg) (Kabata-Pendias 2011), c: above WHO soil permissible level of 50,000 mg/kg (WHO 1996)

Table 2: Mean, maximum and minimum values of d-block metals in the studied soil profiles

		NG1	NG2	CG1	CG2	CG3	SG1	SG2	SG3
n=		6	3	7	4	3	4	6	2
		→			mg/kg	→			
Ti	Mean	7819.483[a]	9011.033[a]	4312.343	3617.675	2957.967	2422.575	2955.95	2931.85
	Max	9880.7[a]	10503[a]	4705.8[b]	4912.3[b]	3141	3088.7	4328.8	3694.6
	Min	6647.3[b]	7876.3[a]	3835.7	2506.7	2736.7	1956.3	1851.2	2169.1
V	Mean	147.35[a]	144.1[a]	102.7	165.1[a]	83.1	136.8[a]	112.4	108.0
	Max	173.5[a]	153.7[a]	150[a]	174.6[a]	92.6	147.7[a]	135.2[a]	127.6
	Min	123.8	132.9[a]	79.5	149.4[a]	76.7	127	85.5	88.3
Mn	Mean	1074.1[a]	1295.6[a]	901.8[a]	306.4	109.5	193.6	680.5[a]	36.5
	Max	1936.5[a]	2151.7[ac]	1933.9[a]	404.5	157.2	235.7	1844[a]	37.4
	Min	432.9	840.9[a]	394	192.1	51.1	156.2	133.2	35.6
Fe	Mean	50208.2[c]	44770.1	16008.0	21888.3	8206.2	15101.7	42001.6	6114
	Max	66874.4[c]	55916.4[c]	28852.2	29084.2	11474.2	17038.3	63897.3[c]	9651.2
	Min	39371.2	38790.9	5362.7	10465.1	5898.4	14030	33929	2576.8
Mo	Mean	3.2[a]	2.6[a]	2.7[a]	3.6[a]	1.9[a]	2.2[a]	2.2[a]	1.9[a]
	Max	4[a]	2.9[a]	3.2[a]	4.2[a]	2.3[a]	2.7[a]	3[a]	2.5[a]
	Min	2.7[a]	2.2[a]	1.8[a]	2.7[a]	1.3[a]	1.8[a]	1.3[a]	1.3[a]

a: values exceed the worldwide average, Ti (7038 mg/kg), V (129 mg/kg), Mn (488 mg/kg), Mo (1.1 mg/kg) (Kabata-Pendias, 2011), b: values are less than worldwide average but greater than crustal average, Ti (4400 mg/kg) (Hedrick 1995; Reimann and de Caritat 1998), c: above WHO soil permissible level, Fe (50,000 mg/kg), Mn (2000 mg/kg) (WHO 1996)

Table 3: Correlation between XRF d-block metals and general soil properties

	Clay	Silt	Sand	BD	pH	OC	TN	Na	K	Mg	Ca	CEC	Ti	V	Mn	Fe
Silt	0.04															
Sand	-0.89‡	-0.48‡														
BD	0.69‡	-0.13	-0.55‡													
pH	0.03	0.09	-0.06	0.11												
OC	-0.36‡	-0.06	0.34‡	-0.64‡	-0.05											
TN	-0.38‡	0.07	0.30	-0.61‡	-0.05	0.74‡										
Na	-0.23	0.10	0.15	-0.68‡	-0.10	0.78‡	0.53‡									
K	-0.30	0.10	0.21	-0.74‡	-0.09	0.81‡	0.65‡	0.96‡								
Mg	-0.07	-0.12	0.11	-0.06	-0.09	0.30	0.16	0.23	0.19							
Ca	-0.02	0.36‡	-0.14	-0.15	0.29	0.44‡	0.44‡	0.36‡	0.32	0.24						
CEC	0.17	0.14	-0.21	-0.26	0.14	0.64‡	0.52‡	0.66‡	0.65‡	0.32	0.59‡					
Ti	0.47‡	0.17	-0.49‡	-0.01	0.15	0.21	0.12	0.45‡	0.45‡	0.17	0.29	0.75‡				
V	0.23	0.56‡	-0.45‡	0.28	0.25	-0.29	-0.28	-0.08	-0.12	-0.03	0.17	0.06	0.27			
Mn	0.44‡	-0.05	-0.36‡	0.33	0.23	-0.14	-0.10	-0.03	-0.03	0.37‡	0.04	0.19	0.48‡	0.35‡		
Fe	0.40‡	0.10	-0.40‡	0.15	-0.04	0.13	0.09	0.23	0.22	0.61‡	0.25	0.61‡	0.64‡	0.34‡	0.49‡	
Mo	0.30	0.10	-0.31	0.44‡	0.49‡	-0.25	-0.37‡	-0.16	-0.17	0.04	-0.09	0.07	0.38‡	0.60‡	0.37‡	0.28

N/B: ‡Significant at $p < 0.05$,BD: Bulk density, K: Exchangeable K, Mg: Exchangeable Mg, CEC: Cation exchange capacity

Table 4: Prediction of metals concentration via multivariate modeling

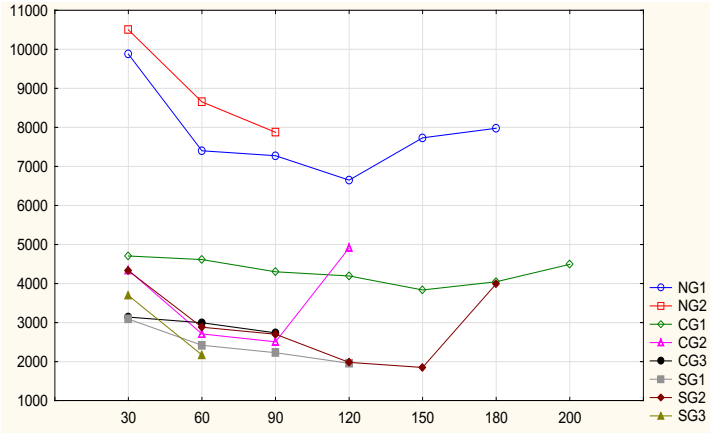
Response variable	Predicted model	Adjusted R^2	Standard error of Establishment
Ti	-69.2 + 0.41 (Clay) – 0.12(Sand) -0.03(BD) + 0.11(pH) + 0.31(K) + 0.03(Mg) + 0.42(CEC)*	0.670	1377.1
V	477.9 – 1.4 (Clay)* - 1.4(Sand)* + 0.68(BD)* + 0.18(pH) + 0.33(K) + 0.05(Mg) – 0.08(CEC)	0.375	23.6
Mn	-4031.9 + 0.57 (Clay) + 0.06(Sand) + 0.17(BD) + 0.33(pH)* + 0.38(K) + 0.46(Mg)* - 0.30(CEC)	0.329	502.07
Fe	49490.5 + 0.01(Clay) – 0.28(Sand) + 0.16(BD) – 0.01(pH) + 0.01(K) + 0.5(Mg)* + 0.44(CEC)*	0.651	10549.7
Mo	-1.7 - 0.44 (Clay) – 0.36 (Sand) + 0.87(BD)* + 0.47(pH)* + 0.54(K)* + 0.09(Mg) - 0.15(CEC)	0.362	0.582

*Significant at 5 % level of significance

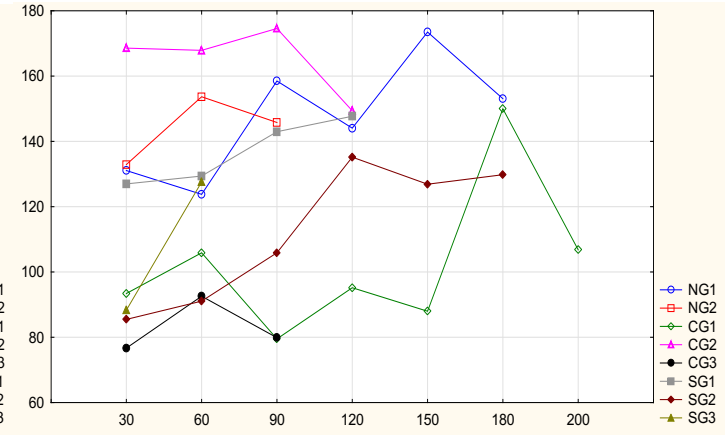
Table 5: Result of factor analysis indicating relative loading from XRF metal and general soil properties

Variable	PC1	PC2	PC3
Clay	49.6	64.3	-22.2
Silt	-3.0	35.4	74.5
Sand	-42.2	-72.2	-13.9
BD	82.6	30.7	-21.2
pH	11.7	28.7	40.4
OC	-91.0	4.4	-5.4
TN	-81.4	-2.4	5.8
Na	-86.4	22.9	3.6
K	-90.4	18.4	4.5
Mg	-30.6	30.8	-55.3
Ca	-45.9	41.0	32.6
CEC	-64.6	65.1	-5.0
Ti	-25.1	83.6	-7.7
V	31.4	58.4	47.3
Mn	18.2	63.6	-34.1
Fe3+	-14.9	77.7	-37.4
Mo	39.2	54.6	14.7
% Total variance	31.0	25.6	10.4
Cumulative % total variance	31.0	56.6	67.0
Eigenvalue	5.3	4.4	1.8

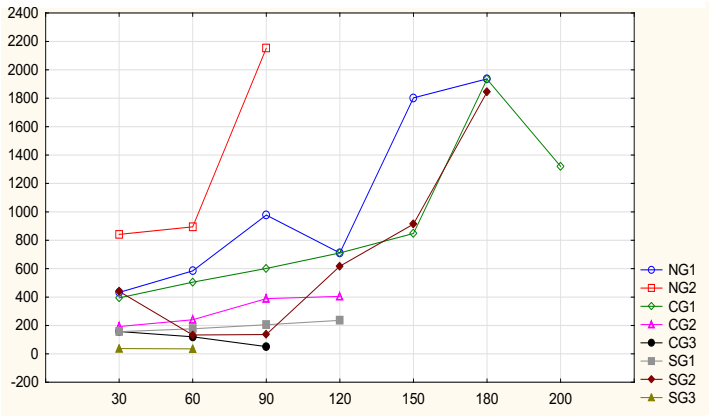
PC: Principal component



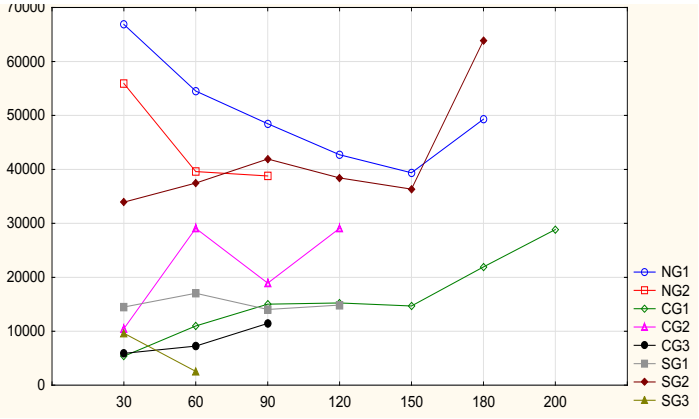
a: Vertical distribution of titanium in the studied soil profiles



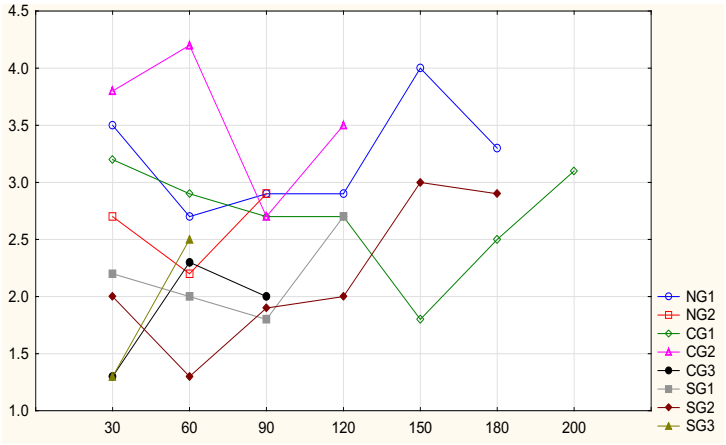
b: Vertical distribution of vanadium in the studied soil profiles



c:Vertical distribution of manganese in the studied soil profiles



d: Vertical distribution of iron in the studied soil profiles



e: Vertical distribution of molybdenum in the studied soil profiles

Fig. 2: Distribution of the d-block metals concentrations in the studied soils

N/B: Vertical axis is concentration in mg/kg, horizontal axis is soil depth in cm

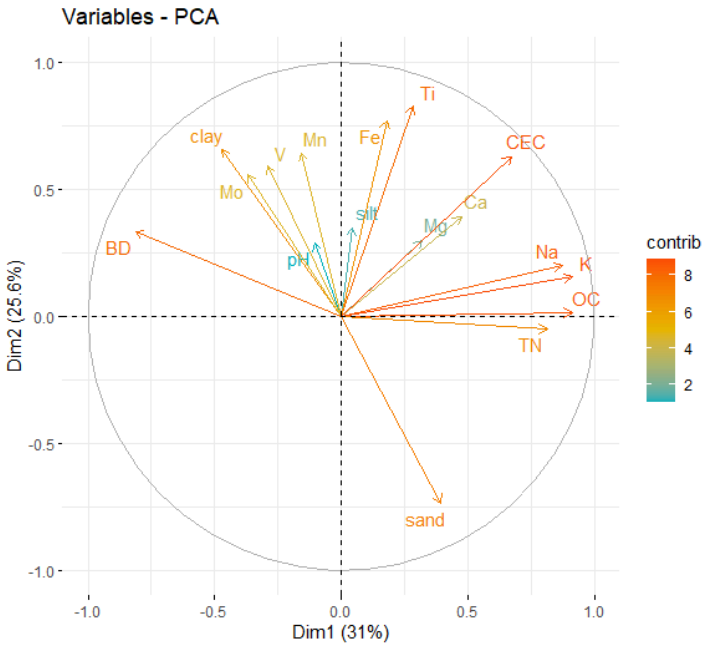


Fig. 3: Biplot of variables contributions to each PC

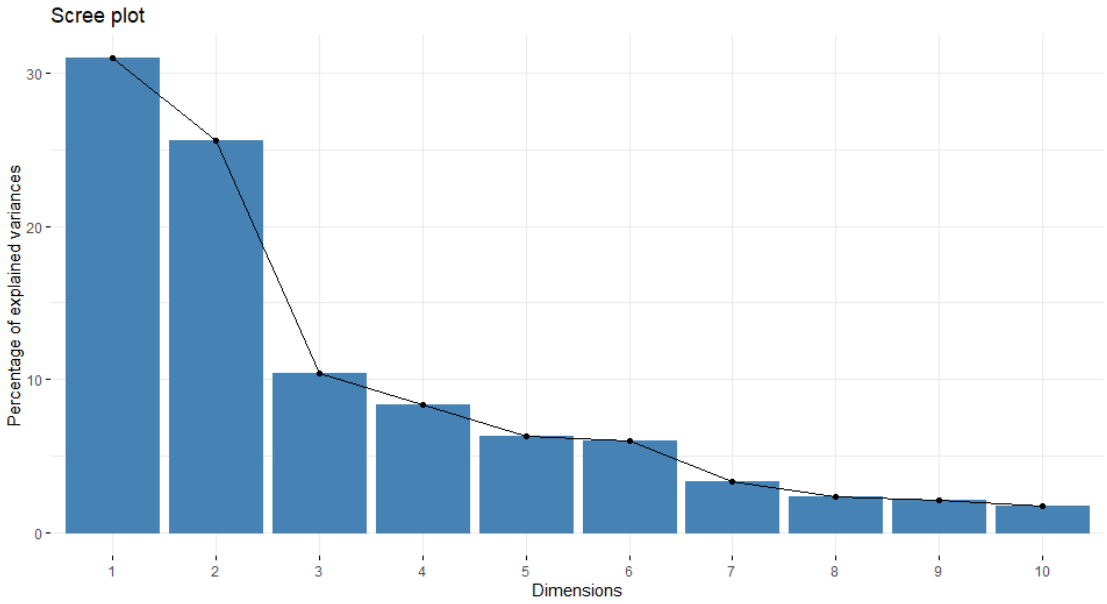


Fig. 4: Scree plot showing the distribution of Principal Components

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Soil health implications of some d-block metals in selected agricultural soils in Southeast Nigeria

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