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Spatial distribution and relative enrichment of some upper-group trace elements in rhizosphere of highly anthropized and rapidly developing tropical environment

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Abstract
Most upper-group (Groups 13-17) trace elements, some of which are micronutrients, are toxic. Soil concentrations, distribution and relative enrichment of 10 of these elements were studied at Ikwo, southeastern Nigeria, representing largely disturbed and rapidly evolving humid tropical ecosystems. Sampling collection,done in the dry season, was from the 0-50-cm soil layer of fallow lands in the four cardinal zones (with marked agricultural/mining activities) and a reference central zone. Elemental concentrations were determined using Inductively Coupled Plasma Atomic Emission Spectroscopy. Enrichment factor was calculated as the ratio of each element to that of Fe (a reference element) in the soil. The central and north zones had the highest and lowest concentrations (21.00-10.75, 1.83-0.93, 10.90-5.58, 4.05-2.05, 4.97-2.54, 2.20-1.12, 17.75-9.09, 26.74-13.69, 4.41-2.26 and 1.89-0.96 mg kg^{-1}, respectively for Se, As, B, Al, Si, S, Sn, Sb, I and Br), implying that agricultural/mining activities rather reduced their accumulation in the rhizosphere. Enrichment factors showed extreme-to-significant levels in the soils for five of the elements (Si > Sb > B > Al > Se) and moderate-to-insignificant levels for the rest (Br > Sn > I > S > As). However, the elements showed similar distribution/enrichment patterns across the five zones including the reference zone. These patterns together suggest greater dependence of the enrichment levels of especially those with extreme-to-significant enrichments on the relative abundance of the elements in the earth's crust than on the agricultural/mining activities in the agroecosystem. Thus, these activities at their current modes and intensities in the humid tropics apparently may not constitute any ecological risks.

Keywords
disturbed ecosystem, micronutrient enrichment, relative distribution, humid tropics

Introduction

The status of most trace elements in the soil has ecological implications as some of them are micronutrients for plant growth. Loss of micronutrients from agricultural soils is gaining global attention. Soils lose micronutrients via topsoil erosion that reduces soil organic matter (SOM), thereby limiting their capacity to accumulate nutrients. This situation is indeed threatening agricultural sustainability (Obalum et al., 2012a; Borreli et al., 2015; Rodrigo-Comino et al., 2016). The loss of plant nutrients in the soil is facilitated mainly by anthropogenic activities like farming, mining and industrial use of soil. These

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activities not only cause lossess of nutrients but also disrupt the balance of nutrients and other ions in soils, and this disrupts the normal functioning of the soil (Parjono et al., 2019; Tyopine et al., 2020). All agricultural soils suffer micronutrients deficiency, but the extent of such deficiency depends on soil type, cropping system and anthropogenic activities (Shukla et al., 2014, Nieder et al., 2018). There exists a very thin margin between deficiency, adequacy and toxicity of micronutrients in the biosphere. Nutrient concentration above or below a critical range may lead to toxicity or deficiency of an element which may adversely affect plant physiological functions and productivity (Nieder et al., 2018). High availability of micronutrients in soil could hamper plant growth and reduce crop yields. For example, high tissue concentrations of B are toxic to plants, although they can maintain tissue B concentration within an optimum range by modulating B transport processes (Miwa and Fujiwara, 2010). Conversely, B deficiency inhibits the growth of vegetative and reproductive parts of plants. During vegetative growth, B deficiency causes stunted root and shoot tips. In root crops, B deficiency has been associated with breakdown of internal tissue (Dugger, 1983; Marschner, 1995; Cakmak and Romheld, 1997). Ikwo is a popular agrarian community in the southeastern region of Nigeria. Crop farmers in the area depend heavily on synthetic fertilizers which are micronutrient-free but rich in macronutrients mostly the primary plant nutrients of N, P and K. In Ikwo and the environs, these synthetic fertilizers and/or organic amendments including assorted ashes used as soil amendments often affect critical soil 'physical' and chemical fertility indices as well as crop yields (Nwite et al., 2011a, b, 2012a, b, c, d, 2013, 2016, 2017, 2019). With extensive cultivation involving ample use of synthetic fertilizers, it is expected that levels of micronutrients will reduce given the age of the soil and that of the prevailing farm practices. Scanty vegetation and yellowing of leaves on trees, shrubs and grasses at Ikwo in the rainy season raises serious concerns about soil fertility status in the area.

Agro-wastes generated from the agronomic enterprises such as rice-mill waste which is usually dumped at strategic places in the area when harnessed as organic fertilizers could help to rejuvenate the soils including their Si-fertility (Ifejimalu, 2018; Nwite and Azuka, 2019; Nwite et al., 2019). This suggests that the abundant generation and poor disposal of this waste may also contribute to soil accretion of the oundesirable trace elements in the area. In the derived savanna of southeastern Nigeria where Ikwo is located, the sequence of soil pH and SOM concentration within the upper part of the soil profile often varies according to the extent and time since last cultivation-related disturbance to the agricultural soil (Obalum et al., 2013; Onah et al., 2021). The availability of nutrients to plants is influenced by soil pH and SOM concentration, for unit changes in soil pH from 4 to 9 are known to alter the solubi- lity of soil compounds, availing the ions in soil solution to varying extents. For example, a decre-ase in pH increases Fe availbility far more than the effect of pH change on such other micronutrients as Mn, Cu and Zn (Lindsay, 1979). The SOM provi-des ligands that chelate nutrient ions thereby incre-asing their solubility and bioavailability to growing plants (Shukla et al., 2016). Against this backdrop, any decreases in soil pH and SOM status due to the intensive crop farming activities at Ikwo may imply increases in the soils' contents of non-micronutrient trace elements whose accumulation above certain critical limits constitutes ecological risks, but this notion needs to be supported with empirical data. Besides agronomic production, Ikwo is also known to have active mines and the mining activities have increased surface area of broken rocks, and these flooded mines set the stage for topsoil erosion (Chukwuma, 1993; Oti-Wilberforce et al., 2012; Tyopine et al., 2020). The ecologically hazardous effects of such an anthropogenic disturbance to the environment may wane with time, as has been reported for heavy metals in sandy soils affected by crude oil spillage (Umoren et al., 2019). In the case of Ikwo, however, there exists to date both active and abandoned mine sites. The holistic review by Eyankware and Obasi (2021) implicates the mining and the associated quarrying activities as the major source of accumulation of heavy metals in soil and water resources of Ebonyi State in southeastern Nigeria where Ikwo is located. It is possible, therefore, to have some reasonable quantities of upper-group trace elements some of which qualify as heavy metals (e.g., As and Sn) in the agricultural soils of Ikwo due to mining and associated quarrying activities. As a major crop production and mining area in the south-eastern part of Nigeria, Ikwo deserves research attention as regards assessment of responses of the

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environment to these economic activities, in terms of soil accumulation of trace elements. There is paucity of data, however, on spatial availability and distribution of trace elements in Ikwo soils. This study thus had as its objectives to assess the availability of some upper-group trace elements among Ikwo soils, and to evaluate the enrichment levels of these trace elements using enrichment factor scheme. This preliminary study intends to add to the data pool on the assessment of soils of Ikwo typifying an area of heavy anthropogenic activities for ecological risks.

Materials and Methods

Study Area

Ikwo is located in southeastern Nigeria. It has humid tropical climate with two distinct seasons; rainy and dry seasons which begin in April and November respectively. Asu River supplies shale which is the major geologic material of Ikwo (Tyopine et al., 2020). Being lateritic and with mud-stony features, shale often gives rise to sandy-loam and clayey soils (Igwe et al., 2013). Ikwo lies in the lower Benue trough and within the mineralised Pb-Zn deposits of the Benue trough situated within the savannah belt of Nigeria (Obaje et al.,1999; Tyopine et al., 2018). There is plethora of active mining sites in Ikwo and the environs, and these mining activities in the past have left some open and abandoned pits. These have altered the physiographic features of Ikwo. The lowlands here are usually flooded in most times of the rainy season and this favours cultivation of rice (Nwite et al., 2017). Other crops commonly grown in Ikwo include: yam, cassava, cocoyam, maize, etc.

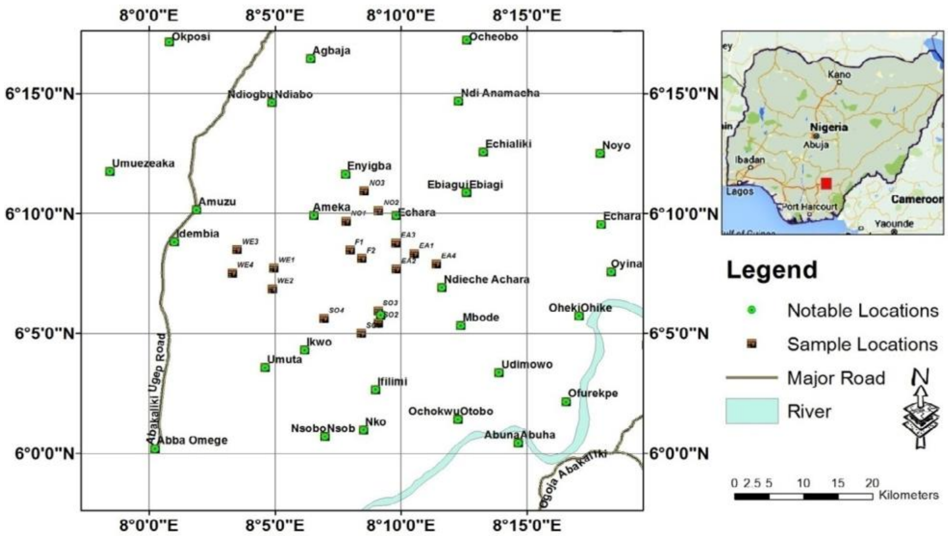

Figure 1. *Map showing sampling spots and other notable locations in the study area of Ikwo, southeastern Nigeria.*

Soil sampling, processing and analyses

The map showing the sampled sites is shown in Figure 1. The area sampled covers over 300 km^2 which represents 3/5th of Ikwo land mass. The sampling scheme covered five geographic zones; the North (N), South (S), East (E), West (W) and Centre (F). The N zone and, to a lesser extent, W zone are areas of active mining. The F zone is devoid of mining and agricultural activities and, therefore, serves as a reference point. Soil samples were obtai- ned from fallow grasslands in the dry season of 2017. Four soil samples were collected from each of N, S, E and W zones and two from F zone, giving a total of 18 samples. These samples were collected from 0-50 cm soil depth (root zone) using using a screw auger depth. The soil samples were homogenised and the sample sizes were obtained by cone and quartering method. The samples were air-dried to constant weight, crushed and passed through 2-mm sieve. Soil fine-earth materials of < 2 mm were preserved for laboratory analyses which were carried out at the International Institute of Tropical Agriculture (IITA) in Ibadan, southwestern Nigeria. The quality of the analyses was checked by calibration using known standard reference materials (SRM) after analysing every 20 or more

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samples. Where duplicate values differed by more than ±5%, a third replicate analysis was conducted. Two out of the three replicates with a difference of less than ±5% were then selected. This approach ensured an agreement between measured certified values within an error limit of ±5%. Soil pH and electrical conductivity (EC) were determined in 1:1 (w/v) soil-water suspensions. The SOM was determined following the standard procedure as outlined in IITA's (1981) manual. For elemental analyses, duplicate portions of 0.50 g each were cold-digested overnight in 2 mL conc. HNO_3. The digest was dried to remove carbon. Each time the digest dried leaving black carbon, extra conc. HNO_3 was reintroduced. This step was repeated until the solution became clear. The clear solution was dissolved using 1:1 HNO_3-$HClO_3$ mixture heated to dryness and then allowed to cool. The resulting ash was dissolved with 1 mL conc. HCl and 10 ml 5% HNO_3 in a centrifuge tube (IITA, 1981). The resulting solution was subjected to Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES) (Questron Technologies Corp. TL 6000) for the determination of the metals (Se, As, B, Al, Si, S, Sn, Sb, I and Br). The instrument was calibrated using various concentrations (2, 4, 6, 8 and 10 ppm) of the standards for these 10 elements, following which the regression of absorbance on concentration showed an *r* value of 99.99 ($P \leq 0.01$). All the elements have their analytical limits of detection and quantitation by the instrument as 0.0001 mg kg^{-1}. The measurement techniques involved the use of element-specific wavelengths, which enabled the reading of the elemental concentrations in the samples. The enrichment factors (EF) of the elements in the soils were calculated to determine the influence of the anthropogenic activities in the study área on their relative enrichment as well as for inference on the sources of these elements in the environment. The method followed the procedure of Tyopine et al. (2020):

$$EF = {(E/R)\ sample}\Big/{(E/R)\ baseline} \qquad [1]$$

where E is the concentration of the element considered in the sample and R is the concentration of a reference element in the sample. Similarly, E and R in the baseline retain their definition in the formula for EF. The values of E and R in the baseline were obtained from the literature – Table 3. In this study, iron (Fe) was selected as the reference element because element enrichment in soils is associated with intrusions of ferrocarbonatite (Romero-Freire et al., 2018). For inferences on the extent of enrichment of the various trace elements in the soils, five enrichment categories defining EF were adopted; < 2 as minimal, between 2 and 5 as moderate, between 5 and 20 as significant, between 20 and 40 as very high, and of > 40 as extremely high enrichment (Topine et al., 2020).

Statistical analyses

Descriptive statistics was used to present the results as means with standard deviations. These means and standard deviations were generated using the software Statistical Package for the Social Sciences (SPSS) version 21.0 for Windows.

Results and Discussion

Physicochemical properties of the Ikwo soils under investigation

Table 1 shows selected physicochemical properties of the Ikwo soils. Soil texture influences hydraulic properties of soils. The particle sizes were distributed as follows, sand: N > E > S > W > F, silt: S > E > W > F > N and clay: W > S > E > F > N (Table 1). The N zone is rather sandy and experiences active mining and, as such, showed the lowest SOM. Soils in mining zones elsewhere were characterised by high sand content and low SOM,concentration (Rachman et al., 2019; Nnabude et al., 2021). Sandy soils are usually low in SOM, a situation that is often linked to inadequate amounts of clay to foster clay-SOM aggregation and to associated excessive leaching (Obalum et al., 2012b; Oguike et al.,2022). The W, S and E zones were flood-prone probably due to the lateritic features giving rise to the clayey soils of Ikwo. This aligns with the high SOM in these zones since they are where rice cultivation is done in Ikwo and agricultural residues decay to supply SOM to the soil. Mean soil pH values in the sampled área at Ikwo ranged from 7.0 in F zone to 7.6 in N zone. With this narrow range, soil pH here was the least variable soil property. This observation on soil pH, which has been made elsewhere in the derived savanna of southeastern Nigeria (Obalum et al., 2013), suggests that it would have little or no influence on the spatial distribution of especially especially epiphytic plant species in the area (Adubasim et al., 2018). There was a decrease in soil pH values towards the centre, F zone.

The closeness in soil pH values recorded in this study

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across the sampled zones may suggest existence of a common soil parent material in the area (Jie et al., 2019). Electrical conductivity (EC) values were lowest (185.88 S cm^{-1}) in N zone and highest in W zone (323.06 S cm^{-1}). Ikwo soils are generally classified as saline since EC values were far greater than 4S cm^{-1} (Shukla et al., 2020). The distribution of soil pH and EC showed opposite patterns, as soil pH increased outwards (F towards W) while EC decreased from W towards F zone. Soil organic matter (SOM) had similar pattern of distribution as EC. The SOM was highest in W zone (50.67 g kg^{-1}) and lowest in N zone (38.02 g kg^{-1}).

Mean concentrations of the trace elements in the soils

Table 2 shows the mean soil concentrations of the 10 trace elements of the study including selenium (Se), arsenic (As), boron (B), aluminium (Al), silicon (Si), sulphur (S), tin (Sn), antimony (Sb), iodine (I), and bromine (Br). The highest in concentration was Sb (26.74 mg kg^{-1}) while the lowest was As (0.93 mg kg^{-1}). Their relative abundance in Ikwo soils was of the order Sb>Se > Sn > B > Si > I > Al > S > Br > As. All 10 trace elements followed similar pattern in all the sampled zones. They all had their highest concentrations in F zone and lowest in N zone. Their distribution pattern was of the order F > W > S > E > N. Selenium may reach 1200 mg kg^{-1} in seleniferous soils (Quang et al., 2018). Concentrations of Se in soils are usually classified under five categories: deficient (< 0.125 mg kg^{-1}), marginal (0.125-0.175 mg kg^{-1}), sufficient (0.175-0.40 mg kg^{-1}), rich (0.40-3.0 mg kg^{-1}) and excessive (> 3.0 mg kg^{-1}). The soil concentra- tions of Se as observed in the present study (10.75-21.00 mg kg^{-1}) greatly exceded 3.0 mg kg^{-1} thereby making Ikwo soils seleniferous. The concen- tration of Se is influenced by weathering of parent rock material (Long and Ino, 2017; Wang et al., 2017), anthropogenic activities like coal mining (Huang et al., 2009) or Se deposition (Sun et al., 2016). The seleniferous nature of the soils across the sampled zones could be attributed to geologic factor or farming activities (Wang and Gao, 2001; Hartikainen, 2005). The atmosphere could be a source of Se due to Se cycle (Winkel, et al., 2014). Selenium toxicity was reported where Se concentrations were 3.71, 4.50 and 3.44 mg kg^{-1} (Ren et al., 2012; Zhou et al., 2014). Mean As concentrations were much lower than the permissible limits of 25 mg kg^{-1} prescribed by Environmental Protection Administration of China (Zhang et al., 2018). The values obtained in the present study (0.93-1.83 mg kg^{-1}) were far lower than those (9.22-1026.05 mg kg^{-1}) reported by Zhang et al. (2018). These As levels reported by Zhang et al. (2018) suggest contamination of topsoil by As. Arsenic is usually added to pesticides, herbicides and insecticides applied to crops to improve biocidal efficiency, but their application also increases As concentration in the topsoil (Cai et al., 2015). The low As levels recorded in Ikwo soils reflect the low content of As in herbicides, pesticides or fertilizers applied to the soils for cropping purpose. Comparing results in this study with those reported by Zhang et al. (2018), the concentrations of As in Ikwo soils are due primarily to their parent material. The distribution of B in soils depends on physicochemical properties of the soil, climate and management practices. Other factors include soil pH, SOM, clay minerals, aluminium oxides and tillage (Tsalidas et al., 1994; Yermiyahu et al., 1995). Boron concentration in soils varies with degree of weathering of parent material. It can reach 100 mg kg^{-1} with higher degrees of weathering (Barber, 1995). The concentrations of B in the soils were much lower than this value (100 mg kg^{-1}). Far greater concentrations of B reaching 630 mg kg^{-1} have been reported in some agricultural soils of India (Padbhushan and Kumar, 2017). By the rather low concentrations of B in the present study, B may be said to be deficient in Ikwo soils, its concentration in these soils dictated mainly by the weathering.of parent material. Aluminium and SOM form stable organo-mineral complexes that influence soil tensile strength which often provides cohesion between soil aggregates (Zhao et al., 2017). This, which involves absorption of SOM into clay through multivalent bond sites of Al, is the process of composite formation (Bronick and Lal, 2005). Organo-mineral complexes of Fe and Al are argued to be the most active components in soils (Amézketa, 1999). The Al had a direct relationship with SOM in the present study. Both Al and SOM were lowest in N zone. Greater SOM implies more humification compensating for the adverse effects of high sand content (Parjono et al., 2019). Mean Si levels in agricultural soils of the sampled zones ranged from 2.54 to 4.97 mg kg^{-1}. Availability of Si in soils is affected by soil pH. It is known that increasing pH reduces concentration of Si in soil solution (Haynes, 2019), but it is unclear how this phenomenon avails Si to plant roots under field conditions.

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Table 1. *Mean physicochemical properties of the soils*

Samples	Sand	Silt	Clay	SOM	Soil pH	EC (S cm–1)
	(g kg-1)					
N01	89.00	3.00	8.00	40.16	7.9	196.33
N02	91.00	4.00	5.00	36.66	7.3	179.24
N03	90.00	3.00	7.00	38.59	8.4	188.62
N04	88.00	3.00	9.00	36.68	6.9	179.33
Mean	89.50	3.25	7.25	38.02	7.6	185.88
SD±	1.29	0.50	1.71	1.69	0.66	8.24
S01	71.00	17.00	12.00	62.24	7.9	304.24
S02	68.00	19.00	13.00	53.47	6.6	261.37
S03	72.00	16.00	12.00	59.60	8.1	291.37
S04	70.00	17.00	13.00	61.62	7.3	301.24
Mean	70.25	17.25	12.50	59.23	7.4	289.55
SD±	1.71	1.26	0.58	4.00	0.67	19.58
E01	75.00	14.00	11.00	54.07	6.5	264.33
E02	77.00	16.00	7.00	57.13	5.9	279.27
E03	74.00	14.00	12.00	59.69	8.7	291.77
E04	69.00	21.00	10.00	56.72	7.6	277.27
Mean	73.75	16.25	10.00	56.90	7.1	278.16
SD±	3.40	3.30	2.16	2.30	1.23	11.24
W01	65.00	14.00	21.00	66.34	8.2	324.33
W02	68.00	15.00	17.00	61.24	6.7	299.37
W03	67.00	14.00	19.00	69.81	6.9	341.27
W04	67.00	13.00	20.00	66.95	6.6	327.27
Mean	66.75	14.00	19.25	66.08	7.1	323.06
SD±	1.26	0.82	1.71	3.57	0.74	17.44
F01	71.00	19.00	10.00	74.96	6.9	366.42
F02	65.00	18.00	17.00	73.49	7.1	359.24
Mean	45.75	12.61	9.57	50.67	7.0	247.70
SD±	38.65	10.22	7.66	40.80	0.14	199.44

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Table 2. *Mean concentrations of the 10 trace elements of the study*

Samples	Se	As	B	Al	Si	S	Sn	Sb	I	Br	Fe (mg kg⁻¹)
	(mg kg⁻¹)										
N01	11.36	0.99	5.89	2.16	2.68	1.19	9.60	14.46	2.38	1.02	93.58
N02	10.37	0.90	5.38	1.98	2.45	1.08	8.77	13.20	2.17	0.93	85.44
N03	10.91	0.95	5.66	2.08	2.58	1.14	9.22	13.89	2.29	0.98	89.91
N04	10.37	0.90	5.38	1.98	2.45	1.08	8.77	13.21	2.18	0.93	85.48
Mean	10.75	0.93	5.58	2.05	2.54	1.12	9.09	13.69	2.26	0.96	88.60
SD±	0.47	0.04	0.24	0.09	0.11	0.05	0.40	0.60	0.10	0.04	3.92
S01	17.60	1.53	9.13	3.36	4.16	1.84	14.88	22.41	3.69	1.58	145.0
S02	15.12	1.31	7.84	2.88	3.57	1.58	12.78	19.25	3.17	1.36	124.6
S03	16.86	1.47	8.75	3.21	3.98	1.77	14.25	21.46	3.54	1.51	138.9
S04	17.43	1.52	9.04	3.32	4.12	1.82	14.74	22.19	3.66	1.56	143.6
Mean	16.75	1.46	8.69	3.19	3.96	1.75	14.16	21.33	3.52	1.50	138.0
SD±	1.13	0.09	0.58	0.21	0.26	0.11	0.95	1.44	0.23	0.10	9.33
E01	15.29	1.33	7.93	2.92	3.61	1.60	12.93	19.47	3.21	1.37	126.0
E02	16.16	1.40	8.38	3.08	3.82	1.69	13.66	20.57	3.39	1.45	133.1
E03	16.88	1.47	8.76	3.22	3.99	1.77	14.27	21.50	3.54	1.51	139.1
E04	16.04	1.39	8.32	3.06	3.79	1.68	13.56	20.43	3.37	1.44	132.2
Mean	16.09	1.40	8.35	3.07	3.80	1.68	13.61	20.49	3.38	1.44	132.6
SD±	0.65	0.05	0.33	0.12	0.15	0.06	0.54	0.82	0.13	0.05	5.35
W01	18.77	1.64	9.74	3.58	4.44	1.97	15.87	23.90	3.94	1.69	154.6
W02	17.33	1.51	8.99	3.31	4.10	1.82	14.65	22.06	3.64	1.56	142.7
W03	19.75	1.72	10.3	3.77	4.67	2.07	16.70	25.15	4.15	1.78	162.7
W04	18.94	1.65	9.83	3.62	4.48	1.99	16.01	24.12	3.98	1.70	156.0
Mean	18.70	1.63	9.70	3.57	4.42	1.96	15.81	23.81	3.93	1.68	154,0
SD±	1.01	0.09	0.52	0.19	0.24	0.11	0.85	1.28	0.21	0.09	8.31
F01	21.21	1.85	11.0	4.05	5.01	2.23	17.93	27.00	4.46	1.91	174.7
F02	20.79	1.81	10.8	3.97	4.92	2.18	17.58	26.47	4.37	1.87	171.24
Mean	21.00	1.83	10.9	4.01	4.97	2.20	17.75	26.74	4.41	1.89	172.96
SD±	0.29	0.03	0.15	0.06	0.07	0.03	0.25	0.37	0.06	0.03	2.42

This is because silicic acid is highly mobile in soils at reduced pH and is easily leached in this form (Sommer et al., 2006; Cornelis et al., 2011). Silicon is considered to be weakly adsorbed by soil colloids at elevated pH, thereby promoting available Si to be retained in soil and not easily leached. However, this proposition is yet to be fully investigated (Haynes, 2019). With the foregoing, it is not clear if liming Ikwo soils will increase their Si levels since the prevailing soil pH was already neutral. The mean values of soil concentration of S across the sampled zones ranged from 1.12 to 2.20 mg kg^{-1}. The concentration of S in the root zone of Ikwo soils may be due to the nature of parent material, types of crops grown and type of fertilizers applied in the area. Organic acids released into the soil during the decomposition of crop residues as well as the action of soil microbes facilitate the weathering of minerals contained in the soil, and this is the mechanism by which S is introduced into the soil (Shukla et al., 2020).

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Mean Sn values across the sampled zones ranged from 9.09 to 17.75 mg kg^{-1}. Tin (Sn) concentration in the earth's crust ranges from 2 to 3 mg kg^{-1} with its organic form dominating over the inorganic form. Tin in unpolluted soils have concentrations less than 5 mg kg^{-1} (Budavari 2001; De Vos et al. 2006). In Europe, Sn in soils could be up to 106 mg kg^{-1}. Tin is least absorbed in sandy soils and highest in clayey soils (Kabata-Pendias and Szteke, 2012). This is consistent with the results in this study (Table 3). The lowest concentration of Sn was in N zone with fairly high sand fraction. The ranges of Sn content in agro-topsoils reported in other areas were < 0.2-96.3 mg kg^{-1} (Cohen et al., 2012) and 2.1-12.8 mg kg^{-1} (Adamo et al., 2014). Both studies concluded that Sn levels above 5 mg kg^{-1} were judged as polluted levels. Tin levels recorded in the root zone at Ikwo are higher than background value of 5 mg kg^{-1}; so, the soils may be said to be polluted. Tin is anthropogenically introduced to soil through application of pesticides, land filling with Sn-containing waste and use of urban refuse as soil amendments (ATSDR, 2005). Therefore, the concentration of Sn in Ikwo soils is more of a geologic than anthropogenic factor.

Table 3. *Background values for enrichment evaluation in Ikwo soils.*

Background value (mg kg^{-1})		Reference
Fe	216.3	Tyopine et al. (2018)
Se	4.0	Garcia Moreno et al. (2013)
As	25	Zhang (2018)
B	0.87	Jeena et al. (2018)
Al	0.5	Parjono (2019)
Si	0.09	Tubana and Heckman (2015)
S	9	Van Biljon et al. (2004)
Sn	5	De Vos et al. (2006)
Sb	3.0	Zhou et al. (2019)
I	5.56	De Vos et al. (2006)
Br	0.5	Wishkerman (2006)

Mean values of Sb in the soils (13.69-26.74 mg kg^{-1}) exceeded global average of 0.80 mg kg^{-1} (Amereih et al., 2005). Antimony (Sb) is released into the atmosphere and it eventually settles on topsoil increasing its concentration in topsoils. In areas of high traffic, topsoils near roads often have high Sb concentration due to traffic emissions which settle on the topsoil (Amereih et al., 2005). The high values of Sb observed in this study were probably due to anthropogenic contamination at Ikwo. Iodine generally accumulates more in órgano-rich soils and less in sandy soils (Smyth, 2011). Iodine in soils typically ranges from < 0.10 to 10 mg kg^{-1} (Kabata-Pendias and Pendias 1992). The values obtained in this study fall within this range, and are also comparable to the average value of 5.56 mg kg^{-1} in European topsoils (De Vos et al., 2006). Iodine is usually influenced by bedrock geology, superficial deposits retaining atmospheric iodine, and soil type and topography; so its concentrations in Ikwo soils were deemed pedogenic. Johnson (2003) classified iodine enrichment based on accumulation in soil type as follows: clayey soils (4.30 mg kg^{-1}), silty soils (3.00 mg kg^{-1}) and sandy soils (2.20 mg kg^{-1}). This classification is consistent with iodine enrichment among Ikwo soils. Hence, the zones with fairly high SOM concentrations namely W, S, E and F zones were those that showed elevated iodine levels. In a study of iodine and bromine (Br) contents in some Austrian soils, Gerzabek et al. (1999) reported that iodine was accumulated less than Br in the soils. Contrary to this assertion, Ikwo soils were enriched more with iodine compared with Br. The latter (Br) is easily volatile and it is enriched more in surface soils in comparison with underlying geologic material. This is due to the precipitation of Br with rain (Kabata-Pendias and Pendias, 1992). Bromine is also known to accumulate more in organic soils and coal. The accumulation of Br was least in N zone where SOM concentration was lowest. The concentration of Br is affected by geological material, losses to leaching and amount of wet deposition in the soil.

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Extent of enrichment of the trace elements in Ikwo soils

The enrichment level of the trace elements in Ikwo soils is presented in Table 4. The values of EF ranged from minimal (< 2) to extremely high (> 40). Silicon (Si) and antimony (Sb) were extremely enriched. Being the second most abundant element in the earth's crust, Si showing the highest EFs is understandable.

Table 4. *Enrichment factors of the trace elements*

Samples	Se	As	B	Al	Si	S	Sn	Sb	I	Br
N01	6.7	0.1	15.7	11.5	71.6	0.3	5.1	51.5	1.3	5.4
N02	6.7	0.1	15.7	11.6	71.7	0.3	5.1	51.5	1.3	5.4
N03	6.7	0.1	15.7	11.6	71.7	0.3	5.1	51.5	1.3	5.4
N04	6.7	0.1	15.7	11.6	71.7	0.3	5.1	51.5	1.3	5.4
S01	6.7	0.1	15.7	11.6	71.7	0.3	5.1	51.5	1.3	5.4
S02	6.7	0.1	15.7	11.6	71.6	0.3	5.1	51.5	1.3	5.5
S03	6.7	0.1	15.7	11.6	71.6	0.3	5.1	51.5	1.3	5.4
S04	6.7	0.1	15.7	11.6	71.7	0.3	5.1	51.5	1.3	5.4
E01	6.7	0.1	15.7	11.6	71.6	0.3	5.1	51.5	1.3	5.4
E02	6.7	0.1	15.7	11.6	71.7	0.3	5.1	51.5	1.3	5.4
E03	6.7	0.1	15.7	11.6	71.7	0.3	5.1	51.5	1.3	5.4
E04	6.7	0.1	15.7	11.6	71.7	0.3	5.1	51.5	1.3	5.4
W01	6.7	0.1	15.8	11.6	71.8	0.3	5.1	51.5	1.3	5.5
W02	6.7	0.1	15.7	11.6	71.8	0.3	5.1	51.5	1.3	5.5
W03	6.7	0.1	15.8	11.6	71.8	0.3	5.1	51.5	1.3	5.5
W04	6.7	0.1	15.8	11.6	71.8	0.3	5.1	51.5	1.3	5.4
F01	6.7	0.1	15.7	11.6	71.7	0.3	5.1	51.5	1.3	5.5
F02	6.7	0.1	15.8	11.6	71.8	0.3	5.1	51.5	1.3	5.5

The extremely high EF values for Si and Sb were most likely due to accelerated degree of weathering, otherwise they were anthropogenically introduced to the soils. For Si (which is merely an essential nutrient), it may also mean that most crops cultivated around Ikwo do not need it for normal growth, thereby sparing it in the soils. For Sb, we infer that these crops may be highly susceptible to Sb toxicity, subject to verification in the future. The EF values for Se, Al and B were within the range of 5-20, implying that they were significantly enriched. Their concentrations in the soils may have been introduced from farm activities other than fertilizer application. The high enrichment levels of Se and B both of which are plant micronutrients are in spite of the fact that modern farm practices now involve heavy use of micronutrient-free fertilizers while relying on improved varieties and intensive cultivation that aggravate micronutrients deficiencies for increased yields (Kabata-Pendias, 2001).

Whether continuous cropping would elevate or reduce soil micronutrient status may depend on crope type, micronutrient considered, and farming system adopted together with its intensity (Alarima et al., 2020).

The EF values for As, S, I, Sn and Br ranged from < 2 to 5. This is a range from minimal to moderate enrichment. Considering the positive relationship between SOM and S in soils (Obalum et al., 2017), and the fact that the latter is a plant macronutrient, increases in SOM would be needed to enhance its enrichment for sustained S-fertility of the soils. The EFs of these five trace elements suggest that their concentrations in the soils are pedogenic in nature. As noted earlier, the trace elements exhibited similar pattern of distribution in the soils of the five sampled zones. The data presented in Table 4 also show uniformity in EFs of the trace elements in soils. Though the reason for these similarities in both the distribution of the trace elements and the EF values is not clearly understood, they are most likely due to uniformity in soil pedogenesis. Under such a condition, the imprint of the underlying geological

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material in supplying and enriching the rhizosphere with nutrient elements is usually evident (Ukabiala et al., 2021). Based on the observed similarities and the implications of the uniformity in pedogenesis, we infer that the enrichment levels of the trace elements in the soils depended far more on their relative abundance in the earth's crust than on the agricultural and mining activities in this humid tropical agroecosystem. This is particularly true for Si, Sb, Se, B and Al with extreme-to-significant enrichment levels.

Conclusions

The trace elements in this study showed their abundance within and across the sampled zones in Ikwo. All the trace elements showed highest concentrations in F zone and lowest in N zone. It could be said that all of them exhibited reasonable similarities in distribution patterns across the sampled zones. The distribution pattern followed the order Sb > Se > Sn > B > Si > I > Al > S > Br > As. The EFs showed uniformity across the áreas; nevertheless, there were variations. The enrichments as evaluated were as follows Si > Sb > B > Al > Se > Br > Sn > I > S > As, with the first two and the next three showing extreme and significant enrichments, respectively. The rest showed insignificant-to-moderate enrichments suggesting that they are deficient in the soils such that, at the current scale of agricultural production, other practices that would improve their availability might be needed. This study has provided baseline data for future assessment of the impact of agricultural and mining activities on the environment as regards accretion of trace elements in Ikwo soils. The data attained are expected to apply to similar agro-ecologies with similar sources and level of anthropogenic disturbance in the humid tropics.

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