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Analysis of Anthropogenic Contribution to Natural Concentration of Trace Element in Zaria Soil

***1Idris M.C, 2Okunade I.O, 2Ogunleye P.O. and 3Mohammed L.**

1Ahmadu Bello University,
School of Basic and Remedial Studies, Funtua
2Ahmadu Bello University,
Centre for Energy Research and Training (CERT), Zaria
3Department of Physics,
Ahmadu Bello University Zaria

Abstract

The level of potentially toxic trace element constituents in Zaria soil was assessed using index analysis approach. The indexes employed are enrichment index (EI), geo-accumulation index (I_{geo}) and pollution load index (PLI). The EI of the elements Co, Cr, As, Mn, Fe, Th, U and Sb was found to be less than 1 thus indicating that these elements were derived from crustal materials. The I_{geo} of the metals falls within the class of 0 and 1. Considering permissible levels of metals, this reveals that the soil in Zaria and environ is not enriched in these potentially toxic elements. The calculated PLI values of the studied region range from 0.49-3.15. This further confirms that Zaria soils are in an unpolluted condition. Enrichment factor analysis and the geo-accumulation index method were applied in order to determine the extent of anthropogenic contamination, and both show that Pb, Cd, and Hg have been significantly increased by human activities. Principal component analysis was used to identify the sources of metals in these soil samples.

Keywords: heavy metals, soil, geo-accumulation indexes, pollution load index, Nigeria

1.0 Introduction

The process of physical and chemical weathering of rocks results in the formation of soil and allows the removal of chemical elements from these systems to ground surface waters [1]. Most of the time, the determination of concentration of elements in the soil is not sufficient to estimate whether they are being accumulated or what is their ability to be released in the environment. Thus, determination of the distribution and chemical binding for a given element is very important because it determines its mobility and potential bioavailability throughout the soil profile. Heavy metals and rare earth elements (REE) are particularly of environmental concern because of their potential toxicity. It is,therefore, not surprising that the degree and extent of heavy metal pollution as a result of human activities has been one of the main topics studied by scientists [2].

Apart from anthropogenic metal inputs, high levels of potentially toxic elements of concern to both man and animals, such as Cd and Mo, have been reported in natural soils and rocks [3, 4, 5]. Researches carried out by various environmental scientists have revealed that the occurrence and geographical distribution of certain diseases could be as a result of the presence of toxic elements in the geological environment [6, 7].Bedrock geochemistry, human activity and several anthropogenic processes are, therefore, the main controllers of heavy metals distribution in the earth's crust [8].

*Corresponding author: ***Idris M.C,*** E-mail: myidrismc@yahoo.com, Tel. +2348032934675

In Bassawa, Kufena, Tsibiri, Palladan, Kamphaghi and Kudingi, little has been done to investigate the levels of potentially toxic elements in natural geochemical materials or environment. Background levels of trace elements coupled with data on plant uptake, toxicity and transport of trace elements in soils are important in the policy decisions regarding the application rates of waste materials, inorganic fertilizers and pesticides to agricultural andor forested lands. Most heavy metal and trace element pollution studies have focused on industrial or agricultural (cultivated) areas [9].

Studies on heavy metals (density > 5.54 gcm^{-3}) in ecosystem have revealed indication of silent epidemic of environmental metal poisoning of ever increasing metals in sub humid tropical soils [10, 11]. Most edible crops are indiscriminate in their extraction of nutrients from the soil and thus will extract the non-desirable heavy metals alongside the essential nutrients. This may predispose the populace to heavy metals through the consumption of such agricultural products thereby serving as a point of entry of heavy metals into the food chain. This call for the need to carryout researches on their impact on soil properties as a potential source of introduction of contaminations into the food chain. This can be better achieved by monitoring the sources and the pathway of heavy metals from the undisturbed soil through the edible parts of plants into human. This paper, therefore focuses on determination heavy metals distribution in soils, their mobility and accumulation in plantsin Zaria and environ.

Methodology

The samples were collected from sheet 102 Zaria based on two major rock types underlying the study area. Samples were collected from first horizon 0 - 15 cm soil fraction from the surface and second horizon 15 - 30 cm depth using hand auger and plastic trowel.

The samples were air dried in a dust free environment and the portion of the laboratory sample was then ground to finer particle size using agate mortar and pestle. The powdered samples were packed in small ampules and put in an irradiation container. The samples were irradiated in a reactor with a thermal neutron flux of 5×10^{11} $ncm^{-2}s^{-1}$ at the Centre for Energy Research and Training (CERT), AhmaduBelloUniversity,Zaria. The samples were irradiated with certified reference material (CRM) IAEA-405. the analysis was performed using PC based gamma-ray spectrometry. Details of spectrometry system and analytical measurements are described else where [12, 13]. Table 1 gives the summary of the analytical photopeaks used for the determination of the various elements.

Results and Discussion

The results obtained are as shown in Table 2. The results indicate that the concentration of the elements agree with the certified values within the limit of experimental errors. The reported uncertainties are the standard deviations of at least three replicate analyses. It can be observed that the concentration profiles of most of the elements determined increases with the depth indicating that , the elements are from crustal materials (that is the anthropogenic input in the area where the samples were collected is minimal or even absent). Similar observation was made by Dampare et al., [12] in the soils supporting medicinal plants in the eastern region of Ghana [7] and Luis et al., [14], in lake sediments in Laguna Chica de San Pedro.

Table 1 Radionuclides and irradiation scheme used for the determination of elemental concentration in soil samples

Element	Reaction	Activation Product	Half-life	Irradiation Time	Decay Time	Counting Time (sec.)
Co	$^{59}Co\ (n,\gamma)\ ^{60}Co$	^{60}Co	5.27yrs	6h	10-15d	3600
Cr	$^{50}Cr\ (n,\gamma)\ ^{51}Cr$	^{51}Cr	27.72d	6h	10-15d	3600
Fe	$^{58}Fe\ (n,\gamma)\ ^{59}Fe$	^{59}Fe	-	6h	10-15d	3600
As	$^{75}As\ (n,\gamma)\ ^{76}As$	^{76}As	26.32h	6h	4-5d	1800
Th	$^{232}Th\ (n,\gamma)\ ^{233}Pa$	^{233}Th	27.0d	6h	10-15d	3600
Mn	$^{55}Mn\ (n,\gamma)\ ^{56}Mn$	^{56}Mn	-	2min.	3-4h	600
V	$^{51}V\ (n,\gamma)\ ^{52}V$	^{52}V	3,75min	2min.	2-15min	600
U	$^{238}U\ (n,\gamma)\ ^{239}Np$	^{239}U	23.47min	6h	10-15d	3600
Sb	$^{121}Sb\ (n,\gamma)\ ^{122}Sb$	^{122}Sb	2.70d	6h	4-5d	1800

Table 2 Comparison of certified values (CV) with our results (values are in ppm except otherwise stated)

Element	Concentration 0-15 cm depth	15-30cm depth	CRM IAEA-405 Range (CV)
Co	5.24±1.44	6.42±0.87	13.0-14.4
Cr	34.54±5.24	36.58±3.05	80-88
Fe	2.53±0.14	2.83±0.17	3.7-3.8
As	-	3.90±0.30	22.9-24.3
Th	25.90±3.47	40.09±5.19	12.2-16.4
Mn	270.83±2.61	401.52±1.82	484-506
V	41.26±5.16	30.17±4.31	90-100
U	35.44±5.60	37.41±6.08	-
Sb	0.60±0.12	0.65±0.19	1.6-2.0

The total concentration of all the elements is presented in Table 3, where the mean concentration of Co, Cr, As, V and Sb were mostly well below levels in world average soils/uncontaminated soils reported by Bowen [15]. With the exception of Th and U whose concentration are relatively higher than the world average soils. Worthy of notice is that none of the soils is enriched in the potentially toxic elements considering permissible levels of metals suggested by Kloke [16]. According to some authors [16, 17], the permissible or tolerable level of an element is the approximate concentrations (or the threshold of the element's concentrations) in soils above which crops produced are considered as unsafe for human or animal health. Nevertheless, it is not advisable to interpret data sets that involve analyses of multiple elements on the merit of single element content, as most toxic element contamination in the surface environment is associated with cocktail rather than one element [18]. Consequently, Nishida et al. [19] proposed a pollution index for Japanese river sediment , which many workers have adopted for pollution studies. In this study the revised pollution index (enrichment index) of Lee et al [20] was adopted. The enrichment index (EI) is defined using equation 1.

$$EI = \frac{\sum \left(C_m / C_p \right)}{N} \qquad (1)$$

where,

EI = Enrichment index, C_m = Concentration of the metals in the soil

C_p = Permissible levels for metals, N = Number of metals

Five elements (Co, Cr, As, Mn and Sb) were selected for the computation of the EI . An enrichment index greater than 1 indicates that on average, element concentrations are above the permissible level and any enrichment may be from anthropogenic input or from geological source [3, 18, 21]. In this study the EI was found to be less than 1 and this indicates that the area is not enriched with toxic elements.

Table 3 Total concentration of toxic trace elements in soil

Element	Mean	Normal soil[a]	Permissible[b]
Co	5.83±1.16	8	50
Cr	35.56±4.15	70	100
Fe	2.68±0.16	-	5[d]
As	3.90±0.30	6	20
Th	33.00±4.33	9	-
Mn	336.18±2.22	-	2000[d]
V	35.72±4.74	90	-
U	36.43.±3.84	2	-
Sb	0.63±0.16	1	5[c]

Source: [a]Bowen [15], [b]Kloke [16], [c]Kabata=Pendais and Pendais [17], [d]Ewers [22]

Muller [23] also introduces Geo-accumulation index (I_{geo}) which can also be used to assess metal pollution in sediments besides enrichment index [23, 24]. I_{geo} is defined using equation (2). The I_{geo} which include seven grades is presented in Table 4. It includes various degrees of enrichment above the background value ranging from unpolluted to very polluted soil quality [24].

$$I_{geo} = \log_2\left(\frac{C_n}{1.5B_n}\right) \qquad (2)$$

where,

C_n = measured concentration of heavy metals in the soil, B_n = Geochemical background value or Clarke value [25] and 1.5 is the background matrix correction in factor due to lithogenic effects.

Table 4 Geo-accumulation index of heavy metal concentration [21]

I_{geo}	Class	Pollution intensity
0	0	background concentration
0-1	1	Unpolluted
1-2	2	moderately to unpolluted
2-3	3	moderately polluted
3-4	4	moderately to highly polluted
4-5	5	highly polluted
>5	6	very highly polluted

Source: Sarva et al.[24]

The pollution load index (PLI) proposed by Tomlinson *et al*., [27] that refers the heavy metal concentration (equation 3). The pollution load index is obtained as concentration factors (CF). This CF is the quotient obtained by dividing the concentration of each metal. The PLI of the place is calculated by obtaining the n-root from the n-CFs that were obtained for all the metals [24, 28].

$$PLI = \sqrt[n]{CF_1 \times CF_2 \times CF_3 \times ....CF_n} \qquad (3)$$

where,

$CF = {C_{metal}}/{C_{background}}$

$n = number\ of\ elements$

PLI varies from 0 (unpolluted) to 10 (highly polluted). The calculated I_{geo} presented in Table 5 indicates that the study area is not contaminated with the potentially toxic trace elements. Also the PLI values of the studied region ranging from 0.49-3.15 confirmed that Zaria soils are in an unpolluted condition (Table 6).

Table 5 Geo-accumulation indexes of heavy metal concentration in Zara soil

I_{geo}	Pollution intensity	Heavy metals
0	background concentration	Mn, Cr, Co, Fe
0-1	unpolluted	As, Sb
1-2	moderately to unpolluted	-
2-3	moderately polluted	-
3-4	moderately to highly polluted	-
4-5	highly polluted	-
>5	very highly polluted	-

Table 6 The pollution load index for Zaria soil

Element	CF
Co	0.49
Cr	0.50
Fe	0.76
As	2.29
Mn	0.49
Sb	3.15
PLI	1.19

Conclusion

Different metal assessments were successfully employed in order to assess the level of potentially toxic trace element in Zaria soil.The EI of all the elements (Co, Cr, As, Mn, Fe, Th, U and Sb) was found to be less than 1 and this indicates that the area is not enriched with toxic elements. Thus the most likely source of these elements is the crustal materials. The I_{geo} showed that all the heavy metals are in class 0 and class 1. While the calculated PLI values of the studied region ranging from 0.49-3.15 confirmed that Zaria soils are in an unpolluted condition.

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