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ENVIRONMENTAL GEOCHEMICAL INVESTIGATION OF THE GEOGENIC POLLUTION POTENTIAL OF BIDA FORMATION, NORTHERN BIDA BASIN NIGERIA

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ABSTRACT

The environmental geochemistry of sandstones of Bida formation around Doko, northern Bida Basin Nigeria was studied to assess the potential for the release of toxic elements into the environment. Eight representative samples were collected and analysed to determine the total elemental concentration using X-ray fluorescence spectrometry (XRF). Four sub-samples were analysed for their near-total concentration of selected metals using atomic absorption spectrometry (AAS). The results show that many of the elements are depleted with mean enrichment ratios of less than 1. Ce, W, Nb and Pb are the exceptions with ER values of 116.4, 122.9, 25.26 and 2.22 respectively. A similar pattern was found with *Igeo*, where W, Ce and Nb fall within strongly to extremely polluted and extremely polluted classes. High to very high partition coefficients (KD_i) for four selected PTEs show that metals are strongly held within the sandstone matrix rather than dissolving. Because the elements are not soluble, they will not be readily available for uptake by plant roots, or will not be directly toxic to soil biota. The undissolved metal pool also reflects the sandstone metal fraction that is unsusceptible to leaching and could therefore not contaminate water. We conclude that there is no significant geogenic pollution risk associated with PTE release and uptake from the formation. It is however recommended that further research should be carried out to investigate the phases hosting Ce, W, Nb and Zr in the sandstone in Doko and its environs.

Keywords: Mobility, Geochemistry, Natural contamination, Sedimentary rocks, Trace elements

INTRODUCTION

Metals occur widely in the natural environment and are observed in sedimentary rocks, soils, water, and organic matter (Davies, 1987). The pollution of soil with metals is a global environmental problem (Adamu and Olaleye, 2022). Weathering of rocks and subsequent leaching and erosion are among the sources of environmental pollution of geogenic nature (Grba *et al*., 2015; Wang *et al*., 2023). Mineral dissolution and element release from rocks contribute potentially toxic elements, previously tightly held with rock matrices, into soil and water sources. Igneous and sedimentary rocks are among the most common sources of environmental metal pollutants. In many parts of the world, especially in India and Bangladesh, the geogenic contamination of water with arsenic and fluoride is a serious environmental and human health concern.

Previous work (Peter, 2019; Sakariyau, 2019, Personal communication) in the Doko area of the northern sector of the Bida basin, Nigeria has shown elevated concentrations of some toxic elements in rocks. Weathering of these rocks to soil presents a potential geogenic hazard in respect of soil and water contamination (Grba et al., 2015). Little or nothing is known about their potential for release into the environment through dissolution in water and probable uptake by plants in this area. The aim of this work, therefore, is to investigate the environmental geochemistry of Bida formation in the Doko locality to understand the geogenic pollution potential of the rocks.

MATERIALS AND METHODS

The Study Area

Doko lies about 25 kilometres southwest of Bida, Nigeria, along the Bida-Nupeko road (Figure 1). The area is characterised by low-lying to gently rolling plains, often punctuated by mesas. The area is well drained by river Toro which flows in the NE direction. Streams that enter River Toro as tributaries are seasonal and form a dendritic drainage pattern. The area has two distinct climatic regimes marked by the dry season (November – March) and wet season (April - October) with the highest amount of rain recorded in July. Annual rainfall in the area falls between 1270 mm – 1524 mm, spread over April to October with the highest amount received in July. Annual temperatures are between 22°C and 33°C although there could also be local climatic changes. The vegetation is of the typical Guinea Savanna belt of West Africa rich in grasses of average height of 2 to 3 metres and also fire-resistance trees which reach up to 18 metres in height

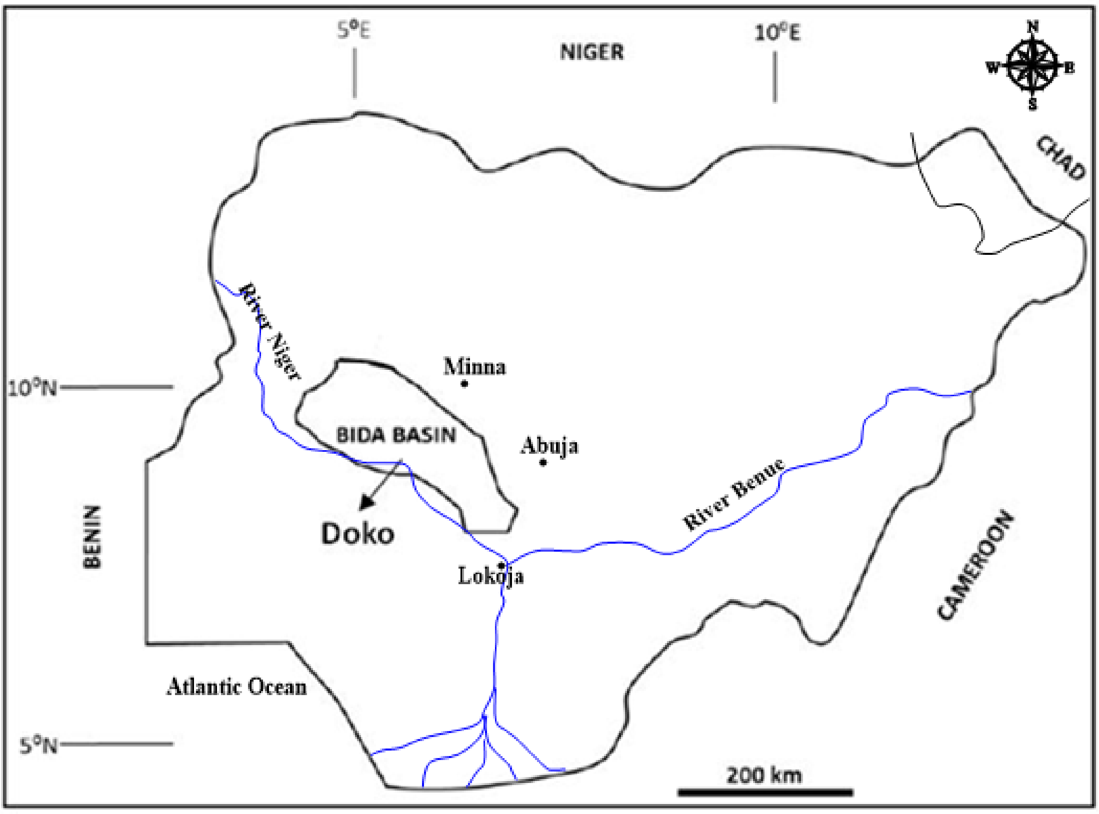

Figure 1: Location of Doko within Nigeria (Modified from Goro *et al.*, 2017)

The sedimentary succession studied belongs to the Bida Formation of northern Bida Basin, Nigeria exposed in a mesa close to Doko village. The Bida basin is a gently down-warped trough trending northwest-southeast perpendicular to the main axis of the Benue Trough and extends from Kontagora in the north to Lokoja in the south. In the northern part of the basin around Bida, four mappable stratigraphic units are recognizable, comprising the Bida Formation, Sakpe Ironstone, Enagi Siltstone and Batati Ironstone Formation. The Campanian-Maastrichtian Bida Formation (Adeleye and Dessauvagie, 1972) consists of two members, the upper Jima sandstone member and the lower Doko sandstone member. The Doko member is reported to be an arkosic unit, consisting of feldspathic and quartzose sandstones. It has small amounts of lithic–feldspathic sandstone, sub-greywackes and sandy siltstone with intra – formational breccia occurring in places (Adeleye, 1973). The Jima member on the other is rich in quartz and exhibits brownish-coloured, massive beds that are cross-stratified with subsidiary greywacke, siltstone, claystone and breccia.

Fieldwork and Sampling

Detailed mapping was carried out in the study area to determine the rock types. This involved sedimentological logging, to characterise different beds or lithofacies. A sedimentological log was produced showing the stratigraphic sequence of rock units in the study area. Eight representative samples of the sandstone were collected and stored in zip-lock bags before laboratory analysis. The samples collected from each horizon were properly labelled to avoid mixing up.

Laboratory Analyses

The sandstone samples were analysed for the total concentration of major and potentially toxic trace elements at the Central Research Laboratory of Umaru Musa Yaradua University, Katsina, Nigeria. The samples were first made into powder form and a 2 g aliquot of each sample was placed into a sample holder and covered with cotton wool to prevent it from spraying. The samples were analysed with an energy-dispersive XRF Spectrometer in air mode for 10 minutes, following calibration with a certified soil reference material (IAEA Soil-7).

The easily extractable (more readily dissolved and available for uptake) concentration of four potentially toxic elements in the four sub-samples was determined at Sheda Science Complex, Abuja, Nigeria. 3 g of sample was digested with 20 mL aqua-regia (nitric and hydrochloric acid) and heated for five hours and cooled until the solution became clear. It was then filtered into a 100 mL volumetric flask and made to the mark with distilled. The extracts were analysed using a flame atomic absorption spectrometer (FAAS), following calibration of the instrument using standard solutions of the elements.

Data interpretation

Minimum and maximum concentration, the mean and median values and the standard deviation were calculated using an MS Excel package. The enrichment ratio was calculated using the formula.

$$\textbf{E.R} = \frac{Cn}{Bn} \tag{1}$$

where C_n is the concentration of an element in a sample while B_n is its background concentration (in this case, the upper continental crust abundances from Taylor and McLennan, 1995). An ER of 1 shows no enrichment or depletion, whereas ER of > 1 or < 1 is an indication of enrichment or depletion (Waziri, 2014). The index of geoaccumulation, I_{geo}, proposed by Muller (1969) is also often used to estimate the enrichment or depletion of elements and to infer pollution levels by PTEs and it has been used by many previous workers, including Grba *et al*. (2015) and Wang *et al*. (2023). This method is used to assess the severity of pollution using seven enrichment classes (Table 1). The index of geoaccumulation was computed using the formula proposed by Muller (1969):

$$I_{geo} = \text{Log2}\,\frac{Cn}{1.5Bn} \quad (2)$$

where C_n and Bn are the same as in equation 1; 1.5 is a constant which accounts for natural fluctuations in the concentration of specific substances in the environment (Shi *et al*., 2011).

Table 1: Pollution severity based on the index of geoaccumulation (I_{geo})

I_{geo} value	I_{geo} class	Pollution intensity
>5	6	Extremely polluted
4–5	5	Strongly to extremely polluted
3–4	4	Strongly polluted
2–3	3	Moderately to strongly polluted
1–2	2	Moderately polluted
0–1	1	Unpolluted to
0	0	Unpolluted

Partitioning method was employed in metal risk assessment to assess the potential leaching of metals, their bioavailability and the ease of mobilisation in stream sediments to the environment. The metals used for the partitioning approach are Pb, Cu, Zn and Cr (Sidi *et al*., 2019). Solid-solution partitioning was evaluated by calculating the ratio between the total metal concentration in solid and the near total concentration of metal in liquid, thus:

$$KD_i = \frac{Total\ metal}{dissolved\ metal} \quad (3)$$

where KD_i is the partitioning coefficient

RESULTS AND DISCUSSION

Geology

The sedimentological log of Bida Sandstone around Doko is subdivided into four lithofacies (Figure 2). The first lithofacies (F1) consists of massive coarse-grained pebbly sandstone with lots of burrows and rounded concretions within it (Bed 1). The bed is 2-8cm thick with basal conglomerate. The second lithofacies (F2) is made up of moderately sorted, trough and planar cross-bedded medium to coarse-grained sandstone with scanty burrows (Bed 2 and Bed 3). It is arkosic with wave-like structures and parallel bedding. The third lithofacies (F3) is a well-sorted cross-bedded, medium-grained sandstone; its upper part consists of whitish clay minerals. Some units display cross-lamination (Beds 4, 5 and 6) while one unit appears bioturbated (Bed 7). Some parts of this sandstone are reddish-brown with whitish particles. Overlying the F3 is F4 lithofacies with well-sorted trough-cross bedded fine-grained sandstone (Bed 8) with ripples within it (Plate II).

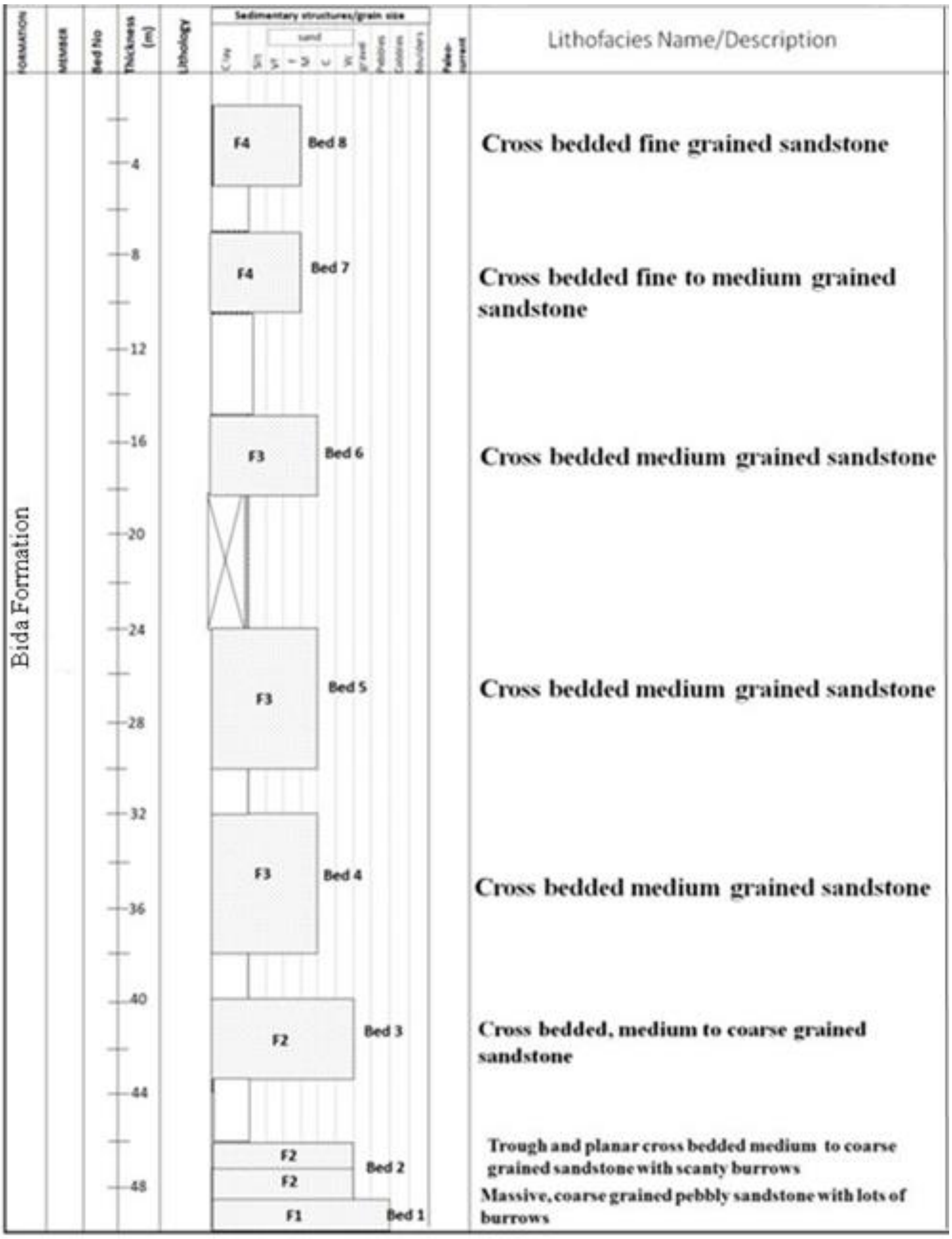

Figure 2: Lithofacies and the stratigraphical sequence of the rock units on a mesa, west of Doko community, northern Bida Basin, Nigeria

Geochemical Characteristics

Table 2 presents the summary of the major and trace element concentrations, along with the crustal averages (Taylor and McLennan, 1995). The results for Si, Ti, Al and Fe are 26.78± 2.3, 0.22 ± 0.1, 12.62 ± 1.2 and 0.69 ± 0.2 respectively. The results further show that the mean concentrations of Ca, K, Mn and P are 0.02±0.01, 0.09±0.02, 0.02±0.0 and 0.09±0.02 respectively.

Table 2: Summary of the chemical composition of Sandstone around Doko, Northern Bida Nigeria (major elements are in wt. %, while trace elements are presented in mg/kg).

	This Study					UCC
Elements	Minimum	Maximum	Mean	Median	Standard Deviation	
Fe	0.4	0.94	0.69	0.67	0.17	3.5
Si	23.74	30.98	26.78	27.29	2.33	30.8
Al	10.17	14	12.62	13.05	1.16	8.04
Mg	1.04	2.41	1.75	1.77	0.45	1.33
P	0.06	0.11	0.08	0.09	0.02	0.2
Ti	0.09	0.43	0.22	0.18	0.11	0.3

Mn	0.01	0.03	0.02	0.02	0	0.1
Ca	0.01	0.05	0.03	0.02	0.01	3
K	0.06	0.12	0.09	0.09	0.02	2.8
Cu	5.6	11	8.1	8.7	1.98	25
Zn	19.1	34.1	25.21	23.75	4.72	71
Cr	17.6	35.8	24.53	23.15	5.62	35
V	17	52.5	34.33	32.95	11.25	60
Pb	27.5	59	44.43	42.1	10.01	20
Rb	2.99	6.6	4.48	4.495	1.11	112
Ga	9.19	13.84	11.66	12.09	1.55	17
Ni	5.49	11.1	8.7	9	1.68	20
Zr	62.5	1156	404.44	272.5	352.09	190
W	123	332	245.75	254	64.47	2
Ce	5640	11560	7451.25	7020	2065.48	64
Y	12.74	15.98	14.5	14.34	1.03	22
Nb	604.7	654	631.59	632.5	20.25	25
Cs	ND	3.98	3.18	3.53	1.3	3.7

A major feature of these results is the elevated Aluminium concentration is elevated while the rocks are depleted in Fe, Na and K to their crustal average values (Taylor and McLennan, (1995). This observation can be attributed to advanced chemical weathering in the source area, which lead to the leaching of the alkalis accompanied by an enrichment of oxides and or hydroxides of iron and manganese (Tijani *et al.*, 2006). The mean concentrations of Pb, Ce, Nb and Zr are above the published crustal abundances. While it is not clear what caused the elevated concentrations of these elements in the rocks of the Doko area, refractory phases like zircon and monazite are thought to be likely sources of Zr and Nb. It is concluded that the high concentration of W may have been contributed by feldspars. These may not have been highly concentrated in the parent rocks but were instead concentrated by paleo-weathering and leaching processes. A modern analogue of this was reported by Key *et al. (*2012) in Nigeria, where intensive chemical weathering, accompanied by the physical breakdown of minerals was thought to effectively remove most of the clay minerals. This resulted in sediments enriched in zircon and the other refractory minerals that contribute to high levels of the aforementioned elements. The concentration of Pb in these rocks is very low, compared with the 110 $\mu g g^{-1}$ total Pb reported by Davies (1983) as a toxic level.

Enrichment Ratio

Table 3 is the summary of enrichments ratios (ER) for selected PTEs and the values indicate that many of the elements, like Cu, Ni, Zn, and Rb have been depleted in the Bida sandstones relative to their average crustal abundances. Ce and W were found to be the most enriched relative to the baseline values, with mean ER of about 116 and 123 respectively. The concentration of Nb is about 25 times its upper crustal concentration. Unlike the case for Nb, Pb and Zr are only slightly enriched (2 and 6 times respectively). Cs on its part is depleted relative to the continental crust with an ER of 0.8.

Table 3: Summary of Enrichment Ratios

Element	Min	Max	Mean
Cu	0.22	0.44	0.32
Zn	0.27	0.48	0.36
Cr	0.50	1.02	0.7
V	0.28	0.88	0.57
Pb	1.38	2.95	2.22
Rb	0.03	0.06	0.04
Ga	0.54	0.91	0.71
Ni	0.28	0.56	0.43
Zr	0.33	6.08	2.13
W	61.50	166.00	122.88
Ce	88.13	180.63	116.43
Y	0.58	0.73	0.66
Nb	24.19	26.16	25.26
Cs	0.00	1.05	0.82

Index of Geoaccumulation (*Igeo*)

The Igeo values for this area are presented in Table 4 which when compared to Table 1 show that the rocks may have problems relating to Ce, W and Nb contamination. The mean I_{geo} value of 6.23, 6.3 and 4.07 for Ce, W and Nb falls within class 5 of the Muller (1969) scale, indicating that the sandstone from this area is strongly polluted with respect to Ce, W and Nb. Some of the samples fall within class 6 which indicates extremely strongly polluted conditions, as indicated by maximum I_{geo} values > 5. The rocks were found to be unpolluted to moderately polluted with Pb, where the *Igeo* values are generally less than 1. This shows that the area has no problem concerning possible Pb contamination of surface water and stream sediments. Similarly, the mean indices of geoaccumulation for Cu, Zr, Ni, V, Rb, Cs, Cr, Zn, Y and Ga of below 0 indicate no pollution concerning these elements.

Table 4: Summary of indices of geoaccumulation, I_{geo} for trace elements in Sandstone around Doko, Northern Bida Nigeria

	Indices of geoaccumulation, I_{geo}		
Element	**Min**	**Max**	**Mean**
Cu	-1769	-0.2	-222.93
Zn	-2.48	-1.64	-2.1
Cr	-1.58	-0.55	-1.13
V	-2.4	-0.78	-1.46
Pb	-0.13	0.98	0.53
Rb	-5.81	-4.67	-5.27
Ga	-1.47	-0.12	-1.02
Ni	-2.45	-1.43	-1.81
Zr	-2.19	2.02	0.06
W	5.36	6.79	6.3
Ce	5.88	6.91	6.23
Y	-1.37	-1.05	-1.19
Nb	4.01	4.12	4.07
Cs	-0.67	0.66	-0.37

Extractable concentration and Geochemical Partitioning
The result from the AAS is tabulated for Pb, Cu, Cr and Zn in Table 5. The extractable metal concentrations were found to be generally low, indicating that none of the metals is likely to be easily leached into the wider environment. Similarly, the PTEs may not be easily taken up by plants, especially crops growing in soils derived from weathering of the Bida formation and passed through the food chain. It shows that the mobility of these elements in the sandstone is very low, given the high to very high partition coefficients (KD_i) obtained for the elements (Table 6). It, therefore, shows that even if the total concentration of each of the elements is passed onto the residual soils as discrete grains through physical weathering, they are unlikely to pose serious geogenic environmental pollution problems. Although most existing environmental risk assessment indices use the total concentration of contaminant elements, a knowledge of the easily solubilized or biogeoaccessible fraction is key to understanding the scale of the problem (Adamu and Olaleye, 2022; Waziri, 2013; Ullrich *et al*., 1999).

Table 5: Extractable concentration of selected potentially toxic elements in sandstone around Doko, Northern Bida Nigeria (µg/mL)

Elements	B1	B2	B7	B8
Cr	0.45	ND	0.04	0.69
Zn	0.09	0.04	0.05	0.01
Cu	0.35	0.33	0.37	0.35
Pb	1.57	1.17	0.32	0.74

Because the metals are not soluble and they partition strongly to the solid phase, they will not be readily available for uptake by plant roots, or will not be directly toxic to soil biota. The undissolved metal pool also reflects the sandstone metal fraction that is unsusceptible to leaching and could therefore not contaminate groundwater or surface water.

Table 6: Partition coefficients of four potentially toxic metals in sandstone around Doko, Northern Bida Nigeria.

Elements	B1	B2	B7	B8
Cr	51.56	ND	577.5	30
Zn	247.78	477.5	480	2230
Cu	26.29	24.85	24.86	16.86
Pb	32.48	33.25	126.25	55.68

CONCLUSION
This study assessed the possibility of geogenic pollution of soil and water resources in the Doko area due to elevated concentrations of potentially toxic elements in rocks of the Bida Formation. We found that most of the PTEs studied are only slightly enriched or within normal levels expected in sedimentary rocks like the Bida formation. However, levels of Pb, Ce, W and Nb are above their crustal abundances and are therefore said to be enriched in the formation. Except for Pb, the enrichment of the other three elements is thought to be a result of paleo-weathering in the source area and leaching, which effectively removed most labile fractions, leaving the sediments rich in refractory phases. It was further established that the solubility of four selected PTEs (Cu, Zn, Cr and Pb) in the rock is very low and that the elements partition very strongly to the solid phase. This implies that even for Pb which is relatively enriched in the Bida Formation, the chance of getting into the mobile phase is very low. It, therefore, shows that there is very little, if any risk of geogenic contamination of water with these metals in the area. Similarly, plant uptake of these PTEs and their transfer through the food chain is unlikely to be a human health concern. It is concluded, therefore, that this study has not found any significant geogenic contamination risk, arising from PTE levels in the Bida Formation.

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