https://dx.doi.org/10.4314/dujopas.v9i3a.7
ISSN (Print): 2476-8316
ISSN (Online): 2635-3490
Dutse Journal of Pure and Applied Sciences (DUJOPAS), *Vol. 9 No. 3a September 2023*

Assessment of Levels of Contamination and Estimation of Ecological Risk by Potentially Toxic Elements in Chanchaga River of Minna, Nigeria

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Abstract
This research investigated the geochemical characteristics, contamination indices and *ecological risk assessment of stream sediments from Chanchaga area of Minna Metropolis, North-Central Nigeria. Eight samples were collected from River Chanchaga and its tributaries and sieved to less than 2 mm grain size following air drying for 48 hours. The samples were subsequently analysed for the concentration of major and trace elements using X-ray fluorescence (XRF) spectrometry. Contamination indices (enrichment ratio, enrichment factor and index of geoaccumulation) and potential ecological risk index (PERI) were used for assessing the level of risk that exists with respect to potentially toxic elements (PTEs). The research has found significant enrichment of Pb and Cu in stream sediments of Chanchaga area, indicating possible contamination by human activities. Based on the indices of geoaccumulation, the sediments are considered to be moderately to heavily contaminated with respect to these two PTEs. Potential ecological risks exist with respect to PTEs in these sediments, with PERI values in the range of 12.88 to 167.76, averaging 58.63. Pb presented higher monomial ecological risk index, falling within the considerable risk band and contributed significantly to the PERI values, compared to that of Cu. It is therefore concluded that human activities within Chanchaga area of Minna metropolis, Nigeria have had a negative impact on stream sediment quality and there is likelihood of mobilisation of PTEs into the water column from sediments under right environmental conditions. It is recommended that the partitioning of PTEs, especially Pb and Cu in these sediments be studied in order to ascertain their ease of dissolution and eventual biogeoaccessibility.*

Keywords: Sediments, urban streams, environment, toxic elements, pollution

INTRODUCTION
Stream sediments are important sinks and potential future sources of potentially toxic elements in the environment (Hudson-Edward, 2007). Streams as fluvial systems receive materials from different sources, both close and from far areas upstream, including geogenic and anthropogenic inputs. Weathering, erosion and eventual dissolution of minerals contribute elements to stream loads, in both clastic and hydromorphic forms. Human activities, including agricultural, municipal and industrial operations are also significant contributors of extraneous materials to fluvial systems, through run-off from different areas. Streams draining or located in urban areas are particularly at risk of being contaminated with PTEs and other deleterious substances because they receive inputs from different sources within the catchment. Discharges of various nature emanate from municipal areas and end up in the streams, thereby affecting or modifying their chemical composition and the quality

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of both water and bottom sediments. Road deposited sediments (RDS) are one of the major source of toxic metals that end up in streams draining an urban area. Robertson *et al*. (2003) reported high concentrations of toxic metals in RDS within Manchester, UK. Such sediments may eventually end up in the fluvial system and get deposited in streams, altering their chemistry. Metals are discharged in both dissolved and solid phases in proportions that vary greatly depending on the element properties, pollution sources and chemistry of receiving river waters (Salomons and Forstner, 1984). In river water, metals tend to precipitate rapidly or to be adsorbed onto solid particles. These processes may be reversed with changes in the redox potential (Eh) and pH, which are master variables that control the partitioning of metals between sediments and the water columns (Salomons and Forstner, 1984).

Sediment-associated with PTEs can be stored in fluvial systems for periods from days to millennia, depending on the river-flow dynamics (Taylor and Owens, 2009). It has been estimated that river channels of mid-sized catchments, of the order of thousands square kilometres, are responsible for the storage of only a small percentage of the annual sediment associated pollutant flux (Walling *et al.,* 2003; Villarroel *et al.,* 2006). The storage of fine grained sediment in channelized urban rivers is of the order of days to months (Taylor and Owens, 2009). In channels of less modified rivers, sediments of fine grained sand and silt fractions can be stored for several to tens of years in shelters, at confluences or in wide channel sections as sediment deposits and sequences many decimetres thick (Skalak and Pizzuto 2010; Famera *et al.,* 2013). These can however get remobilised and become sources of contaminant metals downstream in future when the stored sediments is entrained again. Toxic metal bearing sediment, accumulates in channels during periods of low to mean discharges. These particles are resuspended during floods, transported downstream and redeposited onto flood plains as vertically accreted overbank alluvium (Leenaers, 1989; Macklin and Lewin, 1989), where they can constitute an important human and ecological risk.

Many investigations have been carried out on the geochemistry of sediments in parts of central Nigeria, including the Minna area. The work of Lapworth *et al*. (2012) on stream sediment geochemistry in west-central Nigeria, though has some environmental components, was a more regional exercise. A follow up work by Key *et al*. (2012) in this area was aimed at unravelling the high zirconium concentrations in sediments. Obaje *et al*. (2014) studied the environmental geochemistry of River Gora (Chanchaga River) sediments in Minna using statistical methods and pollution indices and recommended further studies to investigate the possibility of more pollution risks in the area. More recent works in the greater Minna area (Akpotu and Alabi, 2022; Amoo and Alabi, 2021) focused on the search for new mineral deposits. However, the previous studies did not estimate the ecological risk of potentially toxic element (PTE) contamination of stream sediments in the area. This study is therefore aimed at the assessment of levels of contamination and estimation of ecological risk posed by potentially toxic elements in sediments of Chanchaga River of Minna, Nigeria.

METHODOLOGY

The Study Area

Chanchaga area is a part of the greater Minna metropolis, which is the capital city of Niger State in the north-central part of Nigeria. The area studied is bounded by latitude 9° 32′ to 9° 34′ N and longitude 6° 34′ to 6° 36′ E. It is one of the fast developing areas of the sprawling city and is characterised by different forms of human activity, including but not limited to farming, motor vehicle repair, trading and other commercial activities. Artisanal gold mining is actively practiced in this area, including along the channels of the Chanchaga River and its numerous seasonal tributaries (Figure 1). Disposal of domestic and commercial wastes in open dumps and directly into stream channels is common in the area. Geologically, the area is located within the north-central Basement Complex, underlain by the migmatite-gneiss complex and metasedimentary rocks which have been intruded by the older (Pan-African) granites. The metasedimentary rocks include schists of the Birnin-Gwari formation, amphibolite and quartzite and have experienced several cycles of deformation.

Sampling and Sample preparation

Eight representative stream sediment samples were collected from River Chanchaga and its tributaries (Figure 1). The sediments were collected from active stream beds using a plastic hand trowel and placed in cloth bags specifically designed for that purpose to allow water to drain. Prior to bagging the sediments, large pieces, including pebbles and rock fragments together with plant matter were removed by hand. The samples were transported to the laboratory where they were air dried for 48 hours and passed through a BS type 2 mm mesh sieve to remove materials coarser than sand fraction. Finally, the dry < 2 mm materials were each placed in labelled zip lock bags and shipped to the laboratory for analyses.

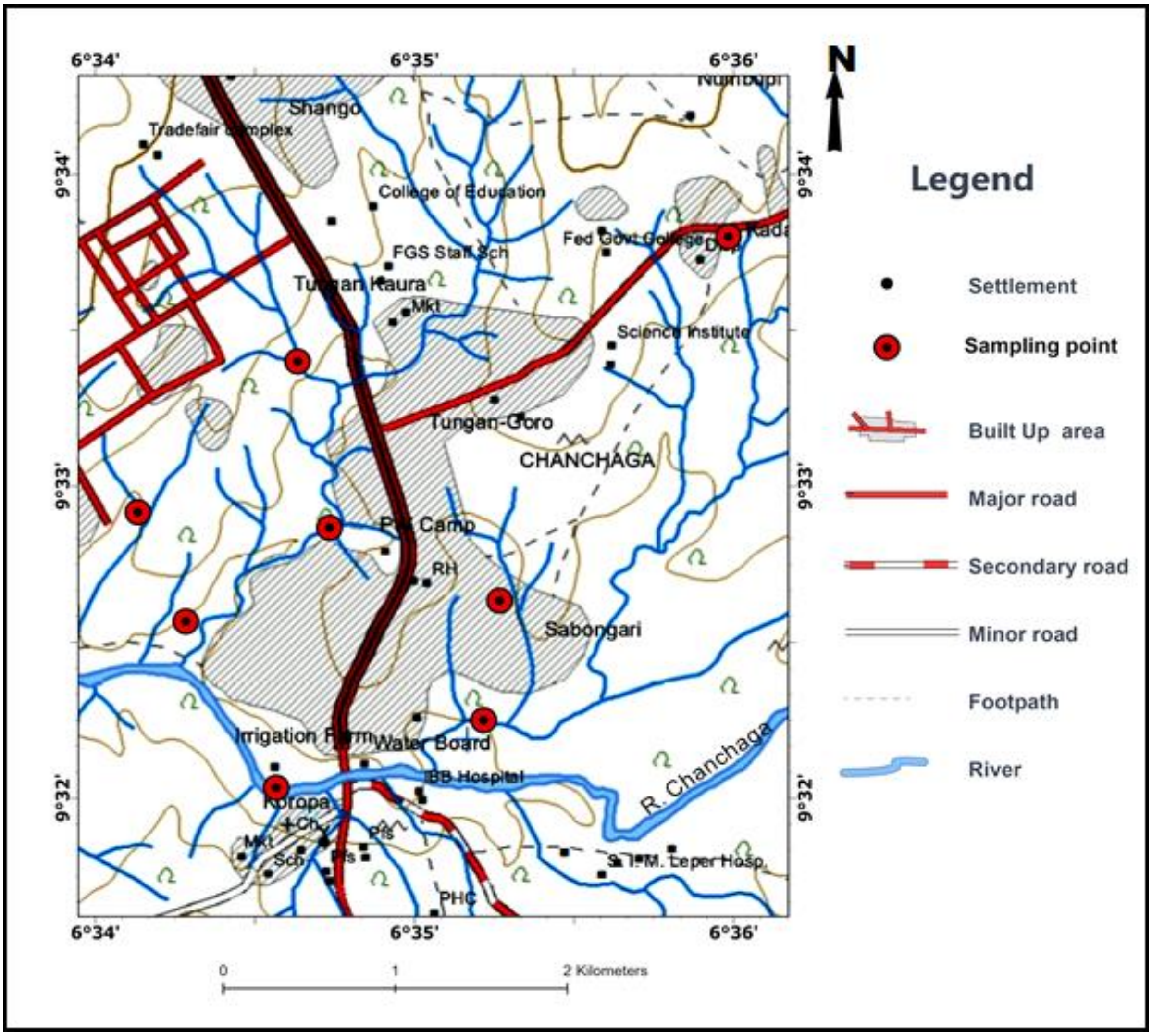

Figure 1: Location of Chanchaga area of Minna metropolis, Nigeria

X-ray Fluorescence Analysis

X-ray fluorescence (XRF) spectrometry was employed for determination of major and trace elements concentrations in sediments of Chanchaga River and its tributaries. The sediments were pulverised using a ball mill to less than 65 µm grain size and 10 g of powder was mixed with approximately 1 g of stearic acid binder and thoroughly homogenized in an agate mortar. The mixture was then transferred into a 40 mm diameter steel disc and pressed into a pellet. The pellets were then analysed in air mode for their major and trace element concentrations.

Contamination Indices and Ecological Risk Index

Contamination indices, including enrichment factor (EF) and index of geoaccumulation (*Igeo*) were computed, along with potential ecological risk index (PERI) for selected PTEs in these stream sediments. The contamination indices were computed in accordance with the methods described by Tijani et al. (2006), Waziri (2013), Odukoya et al. (2021) and Ondayo et al. (2023). PERI on the other hand was developed by Hakanson (1980) and has been applied by other workers (including Ahdy and Khaled, 2009; Manoj and Padhy, 2014).

$$EF = \frac{(Ci/Cref)sample}{(Ci/Cref)background} \quad (1)$$

$$Igeo = \log_2\left(\frac{Cn}{1.5Bn}\right) \quad (2)$$

$$PERI = \sum_{i=1}^{n} E_r^i \quad (3)$$

$$E_r^i = T_r^i \times CF_i \quad (4)$$

$$CF_i = \frac{Cn}{Bn} \quad (5)$$

RESULTS AND DISCUSSION

Geochemical Characteristics

The summary of chemical composition of stream sediments of Chanchaga area is presented in Table 1. The concentration of Fe_2O_3 ranges from 1.59 % to 4.99 %, with an arithmetic mean of 2.98 %, which is consistent with the behaviour of clastic sediments from felsic rocks that have experienced intense tropical weathering. Alumina is somewhat depleted in the sediments of the area, averaging about 7 %, indicating the paucity of feldspars and other aluminosilicates relative to quartz. Among the features of this result is the preponderance of magnesia (1.20 to 3.63 %) over lime (0.76 to 1.95 %).

Potash content is very low, ranging from 0.30 to 0.76 %, buttressing the earlier observation about reasons for low alumina concentration. Finally, the concentration of titanium oxide was found to range from 0.42 to 3.74 %, with an average of 0.90 %, which is generally above the Upper Continental Crustal abundance for the oxide. The concentration of Cu, one of the potentially toxic metals ranges from 19.57 to 290.22 ppm, with a mean of about 114 ppm (Table 1). On a general note, Cu concentration in this area is several orders of magnitude above the upper continental crust value (UCC) of 25 ppm. Similarly, in most of the sediment samples, the concentration of Pb is much higher than its average crustal abundance of 20 ppm. These values for Pb and Cu are significantly higher than those reported in sediments of Brahmaputra River in Bangladesh (Hossain, 2022). Worthy of note also, is the distribution of Bi in the sediments of this area; its concentration averages about 201 ppm. The relatively elevated concentrations of these three metals may be attributed to both natural and anthropogenic sources, mainly from gold ores mined by artisans in the area and human activities, including waste disposal and vehicular emissions. Copper, Pb and Bi are known to be geochemically associated with gold and have been used as pathfinder elements for the mineralisation of the latter. It is therefore plausible to attribute gold mineralisation in the Chanchaga area and upstream as the main source of these metals in stream sediments of the area. This observation is to some extent validated by the strong positive correlation (**r =0.75**) between Cu and Pb in the sediments (Table 2).

Table 1 Summary of chemical composition of stream sediments from Chanchaga area, together with sediment quality guidelines (SQLs) for four potentially toxic elements.

	Min	Max	Mean	Median	St Dev	TEL[1]	LEL[1]	EC-TEL[2]
Fe_2O_3	1.59	4.99	2.98	3.12	1.18			
SiO_2	73.98	80.53	76.98	76.72	2.11			
Al_2O_3	6.02	8.58	7.01	6.94	0.92			
MgO	1.20	3.63	2.18	2.21	0.76			
P_2O_5	0.25	0.46	0.32	0.31	0.07			
SO_3	0.03	0.13	0.09	0.08	0.03			
TiO_2	0.42	3.74	0.90	0.51	1.15			
MnO	0.22	0.80	0.40	0.36	0.19			
CaO	0.76	1.95	1.35	1.23	0.41			
K_2O	0.30	0.72	0.41	0.36	0.14			
Cu	19.57	290.22	114.01	97.70	89.98	35.7	16	18.7
Zn	41.21	349.63	96.93	60.57	103.57	123	120	124
Cr	0.00	75.47	44.06	44.06	23.86	37.3	26	52.3
V	24.98	198.30	97.56	96.94	52.58			
Pb	0.00	429.15	127.79	106.56	136.36	35	31	30.2
Rb	8.60	538.59	183.09	93.41	222.47			
Ga	3.85	8.05	6.01	6.01	1.17			
Zr	311.45	2974.57	804.70	442.71	898.27			
Sr	0.00	761.03	167.00	0.00	313.20			
Nb	875.90	1127.55	927.98	902.11	82.50			
Bi	0.00	399.07	201.12	292.15	170.12			
Sn	0.00	2024.26	941.24	827.03	1011.98			
Ba	0.00	12992.28	6371.24	6329.61	6812.01			

[1]Threshold effect level & Lowest effect level (Macdonald et al., 2000), [2]Environment Canada threshold effect level (Smith et al., 1996)

Less prominent are the concentrations of Zn, Cr and V in the sediments of these urban streams, their average concentrations been just above the UCC values.

However, the data shows a significant enrichment of Zr, Nb and Sn. This is perhaps due to surficial geochemical enrichment of refractory minerals by intense tropical chemical weathering and leaching of labile species, rather than the influence of zircon, columbite and cassiterite mineralisation in the country rocks within the basin. This interpretation, is in part, further corroborated by the very strong positive correlation (**r = 0.97**) found between Nb and Zr (Table 2), and a very low mean Rb/Sr ratio of about 0.34 obtained from available data.

Similar scenarios have already been reported, particularly with respect to Zr concentration in sediments and soils from other parts of Nigeria (Lapworth *et al*., 2012; Waziri, 2013, Obaje, 2014). Overall, the concentration of four selected potential toxic elements in these sediments decrease in the order Pb>Zn>Cu>Cr, indicating a probable anthropogenic input of lead into the streams from municipal activities (Hossain, 2022). Mean concentrations of Cr, Cu and Pb were found to be above the sediment quality guidelines (SQLs; Table 1) but that of Zn is within the effect levels. This goes to show that sediments of Chanchaga area have unacceptable levels of PTEs that could potential be harmful to the ecological system.

Contamination Indices

Pollution indices for the selected potentially toxic metals are presented in Figure 2. Contamination levels of the sediments range from 0.00 to 21.46; 0.58 to 4.92; 0.78 to 11.61 and 0.00 to 2.16 for Pb, Zn, Cu and Cr respectively. Based on these values the stream sediments of Chanchaga area are adjudged to be generally moderately to highly contaminated with respect to the elements (Hakanson, 1980; Ahdy and Khaled, 2009; Manoj and Padhy, 2014). Enrichment factors were found to be in the range 0.00 to 67.36 for Pb, 2.46 to 36.44 for Cu, 1.82 to 15.46 for Zn and 0.00 to 6.24 in the case of Cr. These are several orders of magnitude higher than those for sediments in parts of Bosnia and Hezgovina (Grba *et al*. 2015). In a study of stream sediments in southwest Nigeria, Sikakwe et al. (2021) reported that Pb showed extremely high to significant enrichment in some locations, while the enrichment of Cr, Cu and Zn was classified as moderate. According to the scheme of Sinex and Helz (1981) and Sutherland (2000), these sediments are considered to be moderately to very highly enrich in these metals, particularly with respect to Pb and Cu. Zn and Cr are less severely enriched compared to the previous two. The EF values, especially for Pb and Cu are more likely to be due to anthropogenic input from agricultural and urban sources, rather than just geogenic contribution, in spite of the possible link to gold mineralisation cited earlier.

Calculated index of geoaccumulation (*Igeo*), a third pollution index used in this work shows a similar pattern to the previous two. The values for lead range from 0 to 3.84; those for Cu, Zn and Cr are -0.94 to 2.95, -1.37 to 1.71 and -0.72 to 0.52 respectively.

These again show that the sediments in Chanchaga area of Minna metropolis are not contaminated with Zn and only very slightly with Cr. However, they are moderately to heavily contaminated with respect to Pb and Cu (Muller, 1979; Muller, 1981; Mohiuddin *et al*., 2011). Sikakwe et al. (2021) found that the geoaccumulation index (I-geo) values for Cu, Pb, Zn and Ni in stream sediments in quarrying and mining areas in part of south-western Nigeria fall under unpolluted (0) to moderately polluted (1-2) classes. It is therefore clear that the sediments from this area might have been contaminated with Pb and Cu from external sources due to human activities in the area.

Table 2 Correlation of trace elements in stream sediments of Chanchaga area

	Cu	*Zn*	*Cr*	*V*	*Pb*	*Rb*	*Ga*	*Zr*	*Sr*	*Nb*	*Bi*	*Sn*	*Ba*
Cu													
Zn	-0.07												
Cr	-0.10	-0.25											
V	-0.68	-0.28	-0.26										
Pb	**0.75**	0.12	-0.52	-0.51									
Rb	**0.66**	**0.61**	-0.33	-0.69	**0.80**								
Ga	**0.70**	0.13	0.35	-0.88	**0.58**	**0.69**							
Zr	-0.35	-0.14	-0.80	**0.67**	0.14	-0.23	-0.66						
Sr	0.40	-0.25	-0.65	0.02	**0.78**	0.30	0.12	**0.62**					
Nb	-0.28	-0.04	-0.84	0.70	0.18	-0.13	-0.64	**0.97**	**0.61**				
Bi	0.10	-0.56	0.03	0.16	0.17	-0.31	0.03	0.29	**0.60**	0.24			
Sn	**0.61**	0.43	-0.28	-0.63	**0.67**	**0.87**	**0.58**	-0.26	0.13	-0.20	-0.59		
Ba	-0.56	-0.40	0.25	**0.62**	-0.61	-0.83	-0.55	0.27	-0.07	0.22	**0.64**	-0.99	

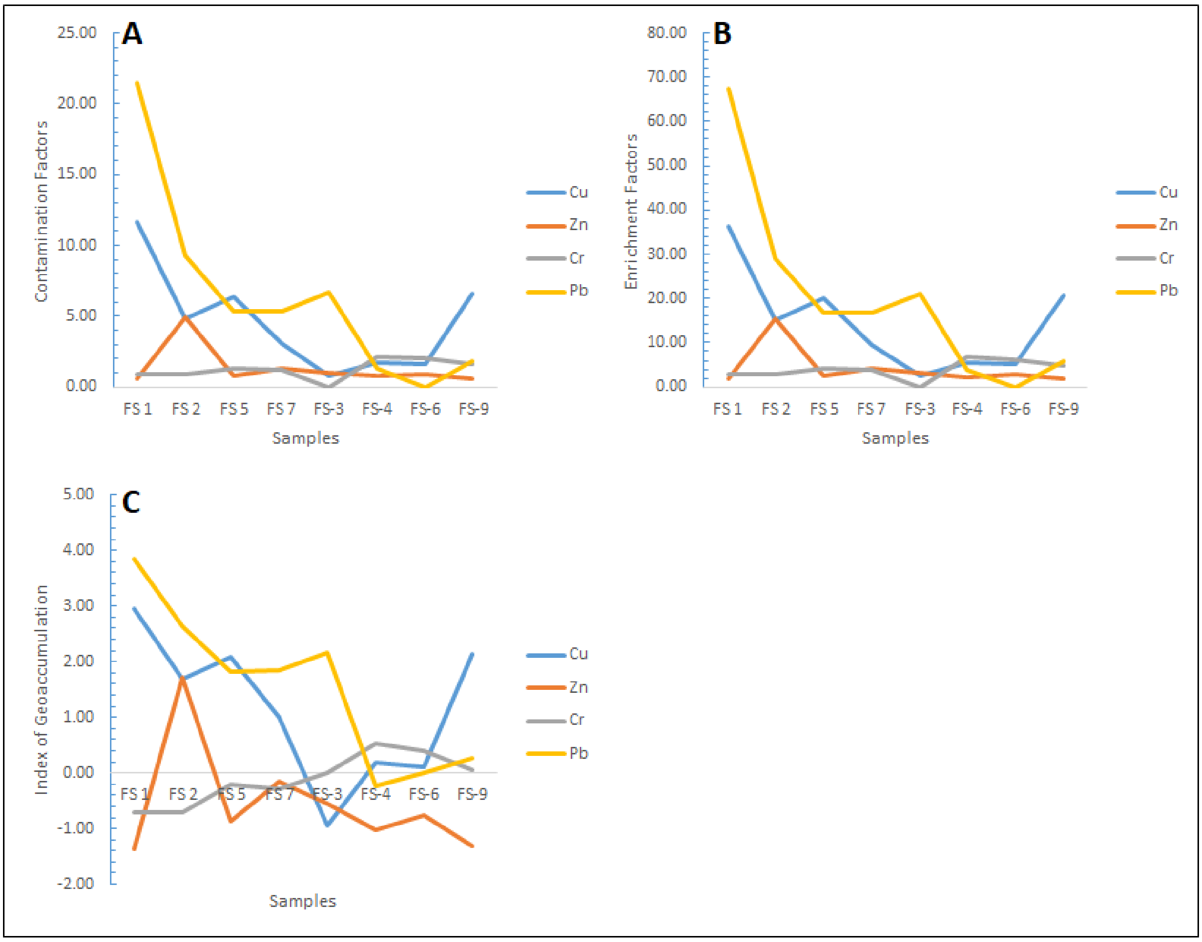

Figure 2: Contamination indices for stream sediments of Chanchaga area of Minna metropolis, Nigeria

Potential Ecological Risk Assessment

In addition to contamination indices (CF, EF and *Igeo*) already discussed above, potential ecological risk index (PERI) is a tool used to assess the ecological risks that potentially toxic elements pose to biological systems in an area (Manoj and Padhy, 2014). The potential ecological risk index (PERI) computed for these elements in the sediments of Chanchaga streams are presented in Figure 3. They range from 12.88 in sample CH7 to 167.76 in CH1, with a mean of 58. 63. These values indicate levels of risk, ranging from low through moderate and high to significantly high (Hakanson, 1980; Wei et al., 2010; Aktaruzzaman *et al.,* 2013). Similar findings have been reported by Nawab *et al*. (2021) for bed sediments from parts of Pakistan, where PERI values were found to range from < 150 to > 300. Pb showed much higher monomial potential ecological risk of between 9.10 and 107.29 (falling within the considerable risk band; Manoj and Padhy, 2014), followed by Cu, Cr with Zn having overall lowest values. This pattern differs slightly from that found for these four elements in sediments in southwest Nigeria, where the reported single element potential ecological risk decreased in the order Pb > Cr > Cu >Zn (Sikakwe et al., 2021).

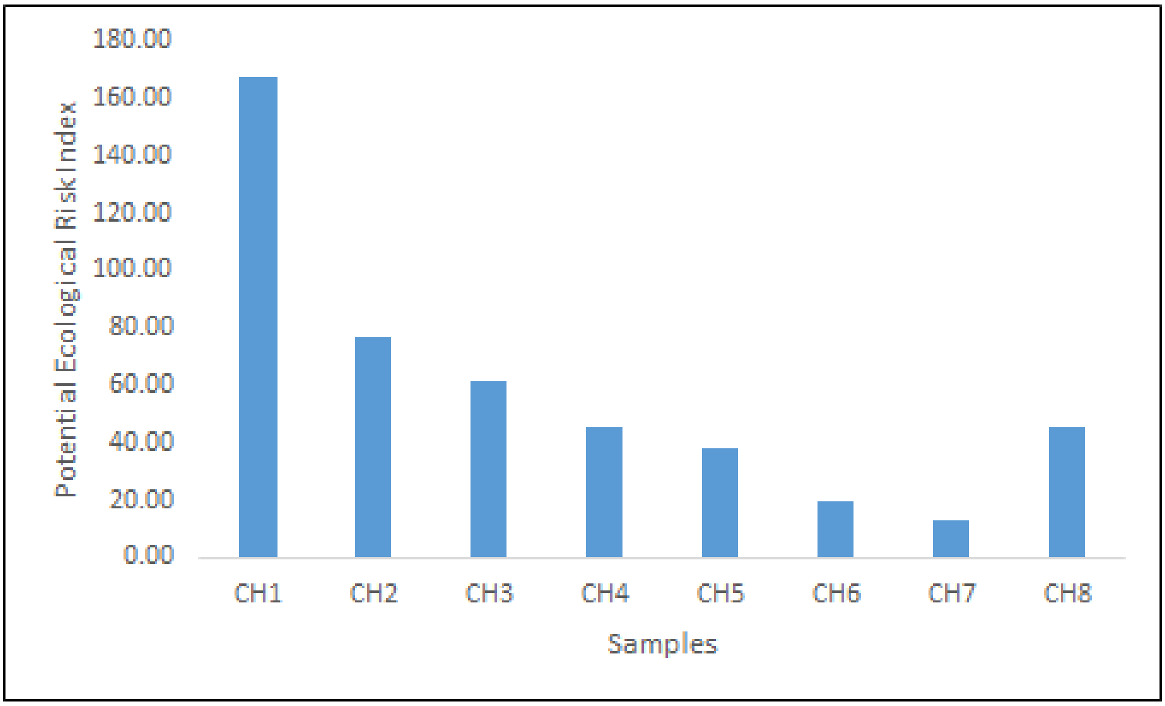

Figure 3: Potential ecological risk indices (PERI) for stream sediments in Chanchaga area

CONCLUSION

Contamination of urban fluvial systems with potentially toxic elements (PTEs) is an environmental problem of global significance. Stream sediments are known sinks and possible future sources of contaminant elements, constituting potential human and ecological risks. This research has found significant enrichment of Pb and Cu in stream sediments of Chanchaga area. The level of contamination fall within the moderate to heavy band, indicating possible contamination by municipal activities. Potential ecological risks have been found to exist with respect to PTEs in these sediments, with PERI values in the range of 12.88 to 167.76, averaging 58.63. These are controlled mostly by Pb, which presented higher monomial ecological risk index falling within the considerable risk band, compared to that of Cu. It is therefore concluded that human activities within Chanchaga area of Minna metropolis, Nigeria have had a negative impact on stream sediment quality and there is likelihood of mobilisation of PTEs into the water column from sediments under right environmental conditions. It is recommended that the partitioning of PTEs, especially Pb and Cu in these sediments be studied in order to ascertain their ease of dissolution and eventual biogeoaccessibility.

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