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ORIGINAL ARTICLE

An evaluation of potential toxic metals in sediments of a tropical watershed in southern Benue Trough, Nigeria

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Abstract

This study assessed heavy metal contamination in sediments within the Anambra drainage basin in Southern Benue Trough, Nigeria. Twelve river sediments were collected from the basin upstream and downstream in two seasons—rainy and dry seasons. The control was collected from the basin source. Samples were analyzed using X-ray fluorescence (XRF) spectroscopy for common major Potential Toxic Metals (PTMs). Concentration of zinc (Zn), nickel (Ni), manganese (Mn), iron (Fe), chromium (Cr), lead (Pb), vanadium (V), molybdenum (Mo), scandium (Sc) and europium (Eu) were detected in trend: Fe > Mn > Zn > Pb >>> Cr > Ni > Mo > Eu > Sc. Contamination trend in rivers shows Adada > Oji > Ezu > Obele > Mamu > Ankpa. The rainy season and the upstream sediments had lower concentrations than the dry season and downstream, respectively. Sediments had higher PTMs concentrations than the background sediments, though most PTMs concentrations were within the recommended standards- USEPA, WHO and Consensus-Based Sediment Quality Guidelines (CBSQGs). Contamination factor (Cf), enrichment factor (Ef), and geo-accumulation index (Igeo) recorded range from 0 to 15, 0 to 6.69 and − 8.43 to 3.32 respectively, signifying significant accumulation and enrichment of PTMs. Pollution load index (PLI) of the heavy metals ranges between 0.24 and 1.34, which suggest that at the different seasons, the basin was enriched with PTMs to a pollution level through anthropogenic activities. In the Anambra drainage basin, concentration and distribution of heavy metals may have been influenced by both non-anthropogenic and anthropogenic processes such as geology of the area, weathering and erosion as well as mining and agricultural activities.

Keywords Sediment · Potential toxic metals · Accumulation and enrichment · Spatial distribution · Heavy metals · Implication

Introduction

Sediments are important in many respects—landscape formation (Walling and Collins 2008), aquatic ecology (Hefni et al. 2006), and biogeochemical processes (Jesus et al. 2015). Sediments are resource (SED 2004) albeit; it harbors heavy metal (Forstener and Wittmann 1983). Undeniably in most basins, heavy metal distributions have witnessed a spectrum of spatio-temporal gradient, whose accumulation index should not be given little regard. Furthermore, heavy metal is sensitive to weathering (Minu et al. 2018) and has an affinity for organic substrates (Saeedi et al. 2011), aqua solution (Aras et al. 2017) and biological tissues (Nwani et al. 2009; Akbulut and Akbulut 2010; Oumar et al. 2018). It also has toxic effects (Pande and Sharma 1999) which poses many health risks to ecosystem (Jia et al. 2018). Undoubtedly, if the accumulation of heavy metals in river sediments is disregarded, it would decimate the extensive population of species, whose survival depends on stream sediments. Such makes river basins an object of scorn and a critical opprobrium in which case, remediating the resourcefulness of rivers, as nature's gift to mankind is left to serendipitous moment.

Heavy metals originate from anthropogenic and non-anthropogenic conditions such as hydrodynamics occasioned by land reclamation (Zhu et al. 2018), socio economic activities (Guan et al. 2018), crustal processes

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(Minu et al. 2018), illegal mining (Duncan et al. 2018), and waste disposal (Ekengele et al. 2017). Nevertheless, appropriate analytical methods which are touch stone for any critical investigation have offered a credible platform for the assessment of sediment status (Muller 1979). Spurred by the drive to unravel the concentration of heavy metal in sediments, Pururshothaman and Govind (2007) revealed that downstream of Ganja is characterized with reducible–organo-sulphide components from natural and man-made processes likewise Aguamilpa basin (Jesus et al. 2015).

Anambra basin traverses middle belt and large section of south eastern Nigeria located in weakly consolidated sedimentary formation (Anyadike and Phil-Eze 1989) and is a province of hydrocarbon (Agagu and Ekweozor 1985). It is situated in West African rift system hosting the Benue Trough (Fairhead and Okereke 1987) that is often over burdened by sedimentation (Nwajide and Reijers 1996). It is confounding to note that the concentration of heavy metal in the surface stream sediments has not been adequately factored in, in most researches. This is in spite of the role of environment in development and the continuous drive to achieve sustainability in all spheres globally (World Commission on Environment and Development 1987; Nzeadibe et al. 2015). Anambra basin supports enormous aquatic life and biodiversity (Awachie and Hare 1977; Awachie and Walson 1978) that had remained vulnerable, since the river sediment is often digested as food by aquatic life, and in some cases, life evolves from it (Hefni et al. 2006). Importantly, Khan et al. (2018) noted histopathological alteration in tissues and organs due to heavy metals. Above all, Jia et al. (2018) enunciated its potential health risk in humans and disclosed that children were more vulnerable. Thus, if this eco risk is unchecked, it could be a threat to life.

Given the above scenario, the appropriateness of a spatio-temporal sediment analysis occupying a prominent position in this study is unbeatable. We envisage that the present study will be relevant in the development of intervention strategies and land mark legislation.

Reinforcing the need for this study is the total eclipse and the palpable neglect of the need to examine and document the stream sediments status in Anambra drainage basin. Unequivocally, alluding such in researches is like "fanning an ember of scourge" and that is infamous. Beyond any contest, central in this paper is the need to identify the seasonal level of concentration of heavy metal in the surface stream sediments, to assess the enrichment metal factor, geo-accumulation index, and heavy metal fractionation and produce a cluster diagram which will delineate the magnitude concentration in space, while the source of heavy metal will not be left in subaltern position.

Materials and methods

Study area

Anambra drainage basin lies within latitudes 6°00′N–7°30′N and 7°00′E–7°30′E (Fig. 1), embracing some parts of southeastern Nigeria—Enugu and Anambra States and Kogi State in North-central Nigeria.

The research area is in the humid tropics with 7 months of rainfall that measures 1750 mm to 2000 mm, while dry season lasts for 5 months with February–April as the hottest months. The mean annual temperature range is 27 ℃–28 ℃ (Monanu and Inyang 1975). The elevations in the basin are less than 50 m in the southwest to about 200 m at the northeast, with low and high slopes ranging between 1° and 80° in the south and north, respectively (Fig. 2).

The entire study area lies within the southern Benue Trough. It is underlain by similar geological succession of quaternary (alluvial plain sand and coastal plain sand) and tertiary rocks–cum-cretaceous sedimentary sequences (Imo, Ajalli, and Mamu formations) (Reyment 1965; Kogbe 1989) with the majority of its vast section on the low lands areas, except at the crest (higher elevated areas) which is dominantly made up of false bedded sandstone (Fig. 3). Following the river catchment, Anambra drainage basin is dendritic and flows southwest, draining into the River Niger (Fig. 1).

Soils that typify the Anambra basin are lithosol, juvenile soil, ferralitic soils, and hydromorphic soils that formed under the dominant influence of the prevailing factors of geological formations of the study area, relief, land use, climate, and weathering processes (Ofomata 1975; Flyod 1969). Within the drainage basin, deforestation without reforestation has defaced the green reserve of the area. Phil-Eze (2001) expressed that deforestation proceeds at the rate of 67.27 km^2 per annum in the northern flank of the study area, while in the other southern section, Igbozurike (1975) and Phil-Eze (2001) described the vegetation to be a formidable bio- geographic zone, though currently, it is being depleted.

Sampling and analysis

Twenty-four (24) sediment samples were collected from the basin upstream and downstream in the rainy and dry seasons. Thus, 12 sediment samples were collected in each season from the sampling locations—upstream and downstream of the six tributaries (Ankpa, Obele, Adada, Oji, Mamu and Ezu) within the Anambra drainage basin (Fig. 4). Samples were collected at the peak

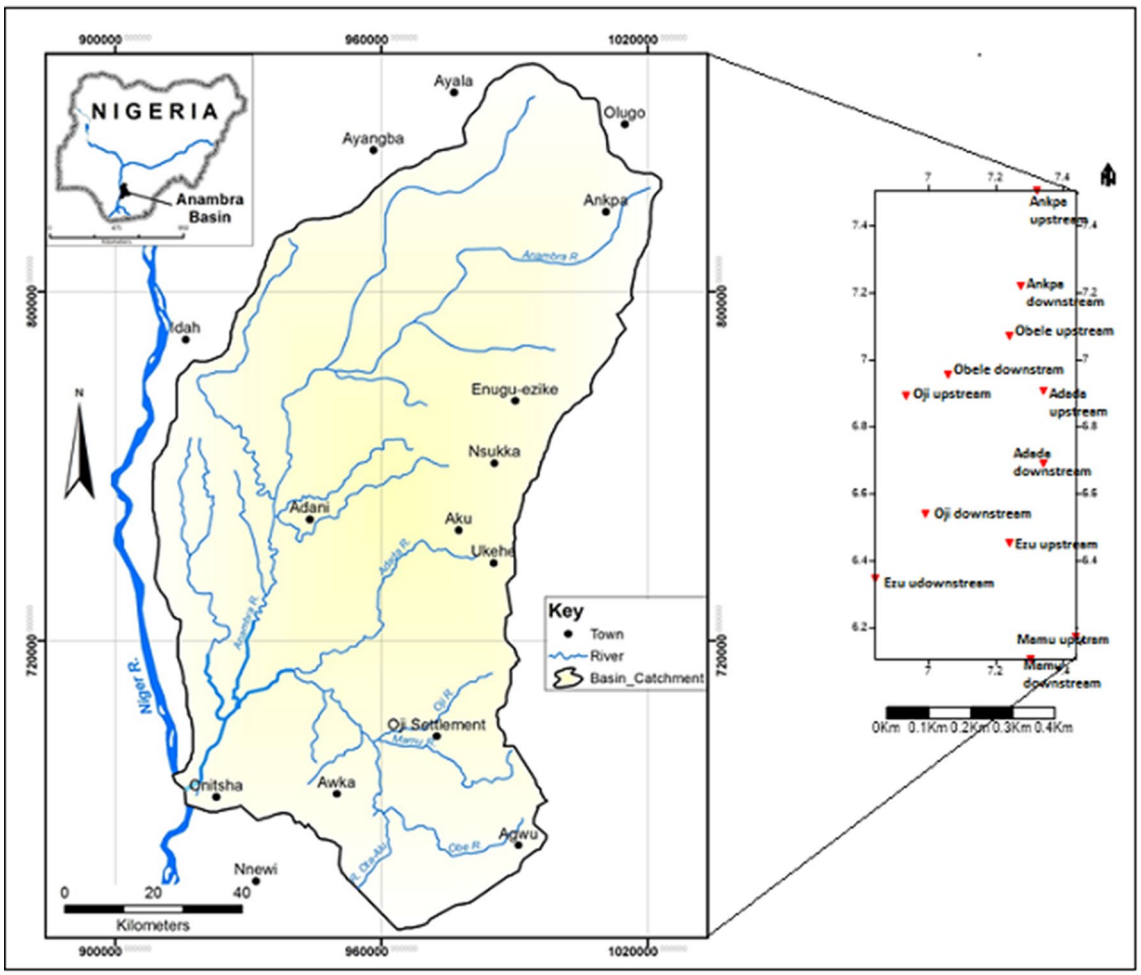

Fig. 1 Map of Anambra drainage basin showing sampling points

of rainy and dry seasons when sediment flux were at its peak and lowest conditions, respectively, and sampling was governed by accessibility to sediments. The control sample was collected at the source of the drainage basin. Each sample weighs one (1) kilogram and sampling was carried out July, 2015 and December, 2015 for rainy and dry seasons' sediments, respectively. Collection was done with a Van Veen grab from the top 10 cm of the sediment layers regarded as the sediments' surface, and the sampling locations were tracked (Fig. 4) using a GPS device. Each sample was carefully packaged and labeled accordingly at the point of collection in black polyethylene plastic bags and transported to the laboratory for analysis within 48 h of collection to avoid microbial activities on sediments' components. The sediment samples were analyzed at the National Steel Raw Materials Exploration Agency, Kaduna, Nigeria, using X-ray fluorescence (XRF) spectrometer.

The method of extracting the total metal concentrations in sediment was based on Igwe et al. (2014). It involves sieving of samples to remove fragments of organic matter, shells, and stones after which the samples were oven dried at 105 °C for about an hour and then allowed to cool. The dried samples were pulverized using agate mortar and later sieved in a 2 mm mesh nylon sieve to ensure the removal of coarse grain and any retained sizeable friable substance. As a sequel, cellulose flake binder was admixed to the sieved samples on a proportion of 1:5 (1 g of binder to 5 g of each dried sample) and pelletized at a pressure of 10 ton/in. in a pelletizing machine. Then, desiccator was used in storing the samples for analysis.

Metallic concentrations in the samples were examined using Advant-X Thermoscientifics X-ray fluorescence spectrometer- model XRF-1200 ARL, with a detention limit of 0.01 mg/kg. In this case, the machine was heated up to 6–8 h, and while the X-ray tube was operating within the range of 25 kV and 50 µA, Samples were radiated and scanned for 15 min for detection of any PTMs. The high energy of an X-ray beam on each sample enabled the production of X-ray features (spikes) of atoms

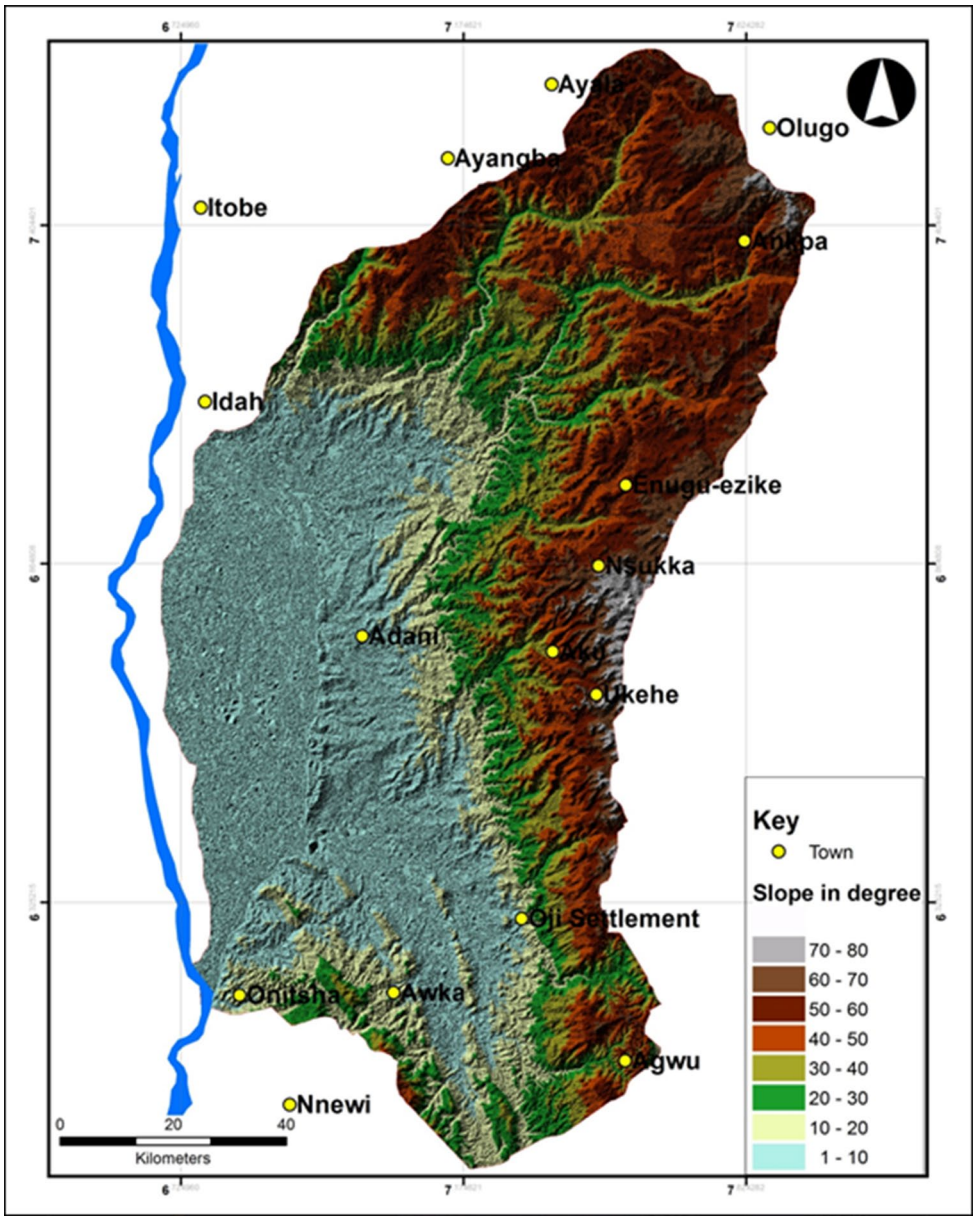

Fig. 2 3D digital elevation model of Anambra basin

and elements present. Their identification was from the energies of their characteristic radiation, while concentration evaluation was from intensity of measurements. Elemental standards were determined using increasing weight of their oxides. The approach has been observed to generate similar and approximate values of result as the atomic absorption spectrometer (AAS) analysis (Igwe et al. 2014). The percentage recoveries for the metals in sediment samples range between 97 ± 5 and $100 \pm 8\%$. Triplicate sediment samples which were obtained by quartering method for each location were analyzed and the average values of each PTM's concentration recorded.

Contamination and pollution analysis

To explore the origin and evaluate the stage of PTMs' contamination in the basin sediments, the enrichment factor (Ef), contamination factors (Cf), geo-accumulation index (Igeo), and pollution load index (PLI) were considered.

The geo-accumulation was calculated using the formula outlined in the following equation:

$$\text{Igeo} = \text{Log}_2\left[Cn/(1.5 \times Bn)\right], \quad (1)$$

where Cn is the concentration value of the metallic element (n) in the sample of sediment. Bn is the geo chemical

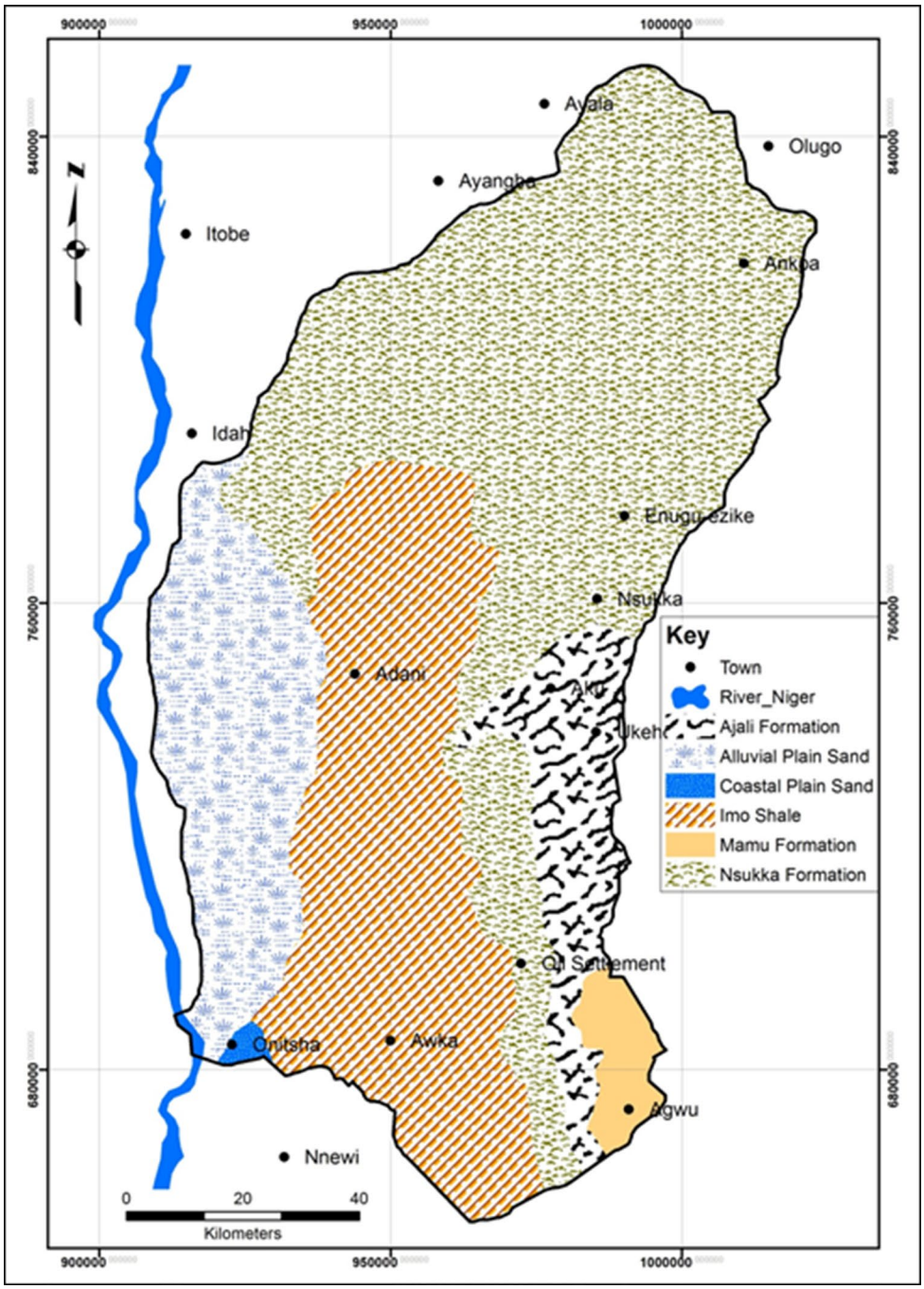

Fig. 3 Geology of the Anambra river basin

background for metallic element (n) of the metal (n) geochemically. 1.5 is the background index correction factor due to the variation in litho-genetics.

With respect to Igeo, seven quality classes were employed in this work as delineated by Muller (1979), Lacutusu (2000), Fagbote and Olanipekun (2010).

Enrichment factor (Ef) detects excesses or abnormality in the metallic assemblage in a composition of sediment, and often times with conservative element such as Al, Fe, or Si (Mucha et al. 2003; Pandey and Singh 2017; Zhang and Liu 2002) due to their virtual availability and abundance in soils and sediment. Iron (Fe) is considered as the normalizer in the present study. This is because, it has been well validated and is commonly used as conventional tracer for distinguishing metal source variability (Young et al. 2013; Mucha et al. 2003; Cevik et al. 2009; Esen et al. 2010; Gerhat and Blomquist 1992; Jesus et al. 2015; Pandey and Singh 2017). Furthermore, Fe is the fourth most abundant major element in the earth crust (which is reflected in the present study as the most available on average in the sampled sediments),

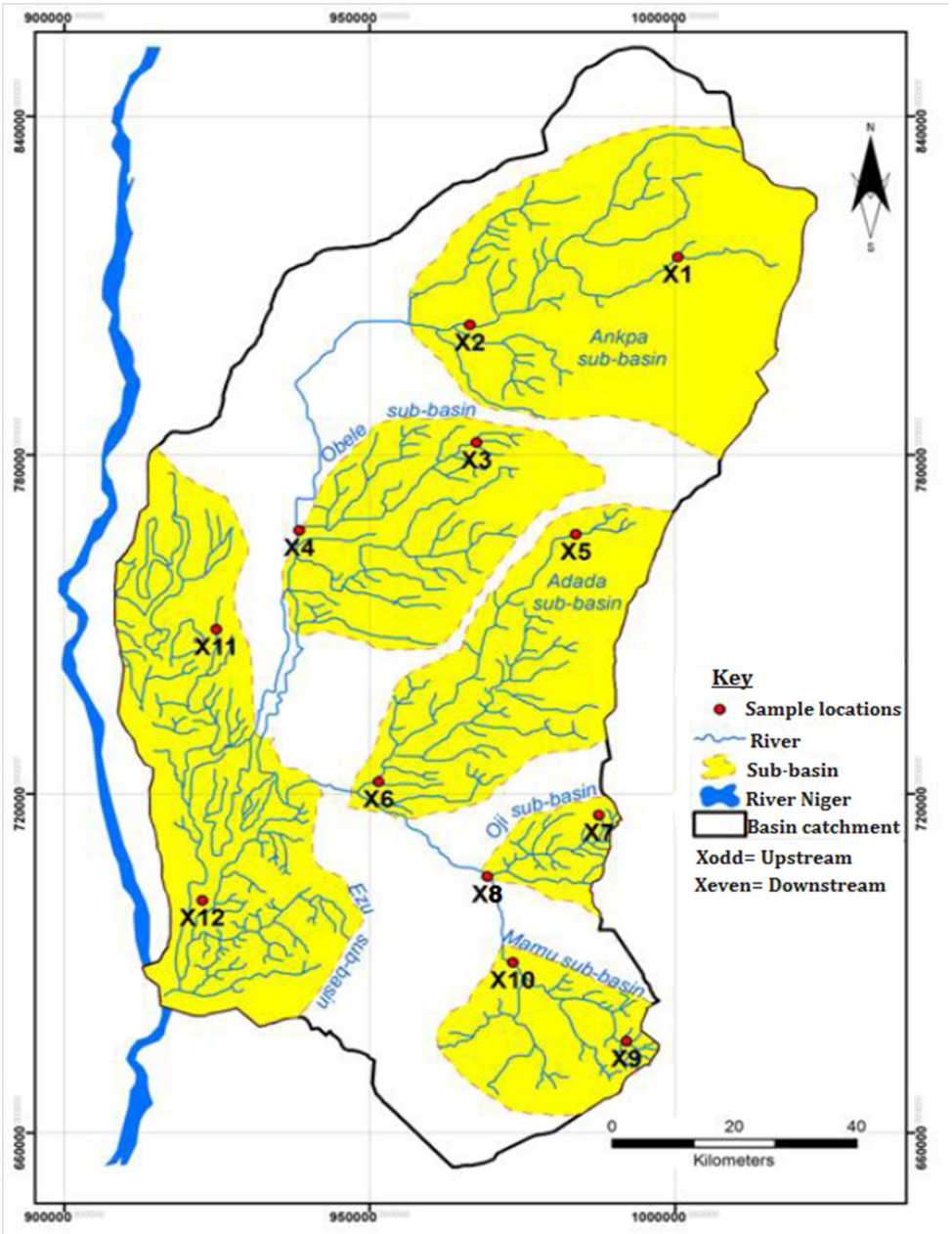

Fig. 4 Map showing sampling locations of the various sub-basins

and it is usually of no contamination concern (Young et al. 2013). Enrichment factor is metrically expressed as

$$\mathrm{Ef} = (\mathrm{M/Fe})\mathrm{sample}/(\mathrm{M/Fe})\mathrm{background}, \quad (2)$$

where $(\mathrm{M/Fe})_{\mathrm{sample}}$ signify the ratio of heavy metal and Fe concentration of the sample. $(\mathrm{M/Fe})_{\mathrm{background}}$ indicate the ratio of heavy metal and Fe concentration of the background. Egbareuba and Odjada (2002) EF grading was adopted in this work.

Contamination factor (Cf) reveals the degree of concentration status of a metal in the sediment taking cognizance of the background index of the metal in the sediment sample (Angulo 1996; Turekian and Wedepohl 1961). The mathematical expression of CF is shown in the following equation:

$$\mathrm{Cf} = C_{\mathrm{metal}}/C_{\mathrm{background}}, \quad (3)$$

where C_{metal} is the concentration of targeted metal. $C_{\mathrm{background}}$ is the concentration of uncontaminated local (background).

Pollution load index (PLI) concerns the number of times a metallic content in a sediment sample is in excesses against the background concentration value. Thus, it portrays the comprehensive toxicity of sample with respect to heavy metal. Tomilson et al. (1980) noted that in X sample, it is the nth root of n number multiplied by the

contamination factor. It is expressed as mathematically, as shown in the following equation:

$$\mathrm{PLI} = (\mathrm{CF1} \times \mathrm{CF2} \times \mathrm{CF3} \ldots \ldots \ldots \ldots \mathrm{CF}n)1/n. \quad (4)$$

The Cf and PLI of the PTMs were evaluated according to the standard outlined by Lacutusu (2000).

Results

Heavy metal concentrations within the basin are presented in Table 1. Virtually, all sediment samples from the Upstream (UpS) and downstream (DnS) sections of the sub-basins indicated the presence of some potential toxic metals (PTMs)—zinc (Zn), nickel (Ni), manganese (Mn), iron (Fe), chromium(Cr), lead (Pb), vanadium (V), molybdenum (Mo), scandium (Sc), and europium (Eu).

In rainy season, concentrations of Zn, Ni, Mn, Fe, Cr, Pb, V, Mo, Sc, and Eu range from below detection limit (BDL) − 8.7, 0.02–0.07, 1.1–9.1, 1.1–8.1, 0.01–0.04, 1.5–3.0, 0.09–0.13, 0.01–0.05, BDL − 0.01, and BDL − 0.03 mg/kg, respectively, while the dry season presented ranges between BDL − 9.6, 0.03–0.07, 1.0–7.9, 1.1–5.2, 0.01–0.04, 1.9–3.1, 0.1–0.13, 0.02–0.07, BDL − 0.01, and 0.01–0.05 mg/kg, respectively. The average concentrations in mg/kg for the potential toxic metals (PTMs) in rainy season are 1.4 (Zn), 0.04 (Ni), 3.52 (Mn), 4.74 (Fe), 0.03 (Cr), 1.91 (Pb), 0.1 (V), 0.02 (Mo), 0.003 (Sc), and 0.01 (Eu), while in the dry season, the values are 4.48 (Zn), 0.06 (Ni), 2.65 (Mn), 1.58 (Fe), 0.03 (Cr), 2.88 (Pb), 0.12 (V), 0.04 (Mo), 0.006 (Sc),

Table 1 Sediments' PTMs' concentrations in rainy a season

Seasons	River sediment	Location	Heavy metals (mg/kg)[a]									
			Cr	Eu	Fe	Mn	Mo	Ni	Sc	Pb	V	Zn
Rainy	Ankpa	Upstream	0.04	0.02	1.2	1.8	0.02	0.05	< 0.01	1.8	0.09	< 0.01
		Downstream	0.02	< 0.01	1.2	1.8	0.02	0.04	< 0.01	2.0	0.09	< 0.01
	Obele	Upstream	0.01	0.02	8.1	9.1	0.01	0.06	< 0.01	1.7	0.01	< 0.01
		Downstream	0.04	0.02	1.1	2.1	0.01	0.03	< 0.01	1.9	0.13	< 0.01
	Adada	Upstream	0.02	0.01	1.2	1.8	0.01	0.04	0.001	1.8	0.09	< 0.01
		Downstream	0.02	0.03	8.0	4.0	0.01	0.02	0.01	1.9	0.11	< 0.01
	Oji	Upstream	0.02	0.01	6.3	5.8	0.02	0.03	< 0.01	2.1	0.12	1.9
		Downstream	0.03	< 0.01	7.2	1.9	0.02	0.03	< 0.01	1.6	0.09	1.9
	Mamu	Upstream	0.01	0.01	5.9	1.1	0.01	0.07	< 0.01	1.5	0.1	2.0
		Downstream	0.02	< 0.01	7.6	1.2	0.03	0.04	0.01	1.9	0.12	< 0.01
	Ezu	Upstream	0.04	0.01	1.1	4.7	0.05	0.02	0.01	3.0	0.11	8.7
		Downstream	0.03	0.02	8.0	6.9	0.01	0.03	< 0.01	1.7	0.09	2.3
	Control	River source	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
	Average		0.03	0.01	4.74	3.52	0.02	0.04	0.003	1.91	0.10	1.40
	σ^b		0.01	0.01	3.23	2.60	0.01	0.02	0.00	0.38	0.01	2.50
Dry	Ankpa	Upstream	0.03	0.01	5.2	1.0	0.04	0.07	< 0.01	3.0	0.11	5.9
		Downstream	0.03	0.03	1.4	5.1	0.04	0.03	0.01	3.1	0.12	1.8
	Obele	Upstream	0.04	0.01	1.1	2.2	0.05	0.07	< 0.01	3.1	0.12	9.6
		Downstream	0.03	0.02	1.1	1.8	0.04	0.06	< 0.01	3.0	0.13	1.3
	Adada	Upstream	0.01	0.02	1.5	4.7	0.02	0.07	0.01	2.6	0.10	7.9
		Downstream	0.04	0.05	1.5	7.9	0.04	0.05	< 0.01	3.1	0.10	7.6
	Oji	Upstream	0.03	0.05	1.1	2.2	0.05	0.07	0.01	3.1	0.13	2.7
		Downstream	0.04	0.02	1.6	2.2	0.04	0.06	< 0.01	2.9	0.13	8.0
	Mamu	Upstream	0.04	0.03	1.1	< 0.01	0.07	0.06	0.01	3.0	0.12	5.9
		Downstream	0.03	0.06	1.1	1.3	0.04	0.06	0.01	2.8	0.13	1.6
	Ezu	Upstream	0.03	0.05	1.1	2.2	0.03	0.03	0.01	1.9	0.13	< 0.01
		Downstream	0.04	0.03	1.2	1.2	0.03	0.05	0.01	3.0	0.10	1.4
	Control	River source	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
	Average		0.03	0.03	1.58	2.65	0.04	0.06	0.006	2.88	0.12	4.48
	σ^b		0.01	0.02	1.16	2.19	0.01	0.01	0.01	0.34	0.01	3.34

[a]Maximum detection limit of the equipment used is 0.01 mg/kg

[b]Standard deviation

and 0.03 (Eu). Such results suggest an increase in the concentration of the PTMs in the dry season, expect for Fe and Mn that decreased in dry season. Weathering and erosion could be the reason for higher Fe and Mn in the rainy season, since most host rocks are rich in both elements. Therefore, the distribution of the heavy metals in the solid phase in various geologic formations within the basin must have influenced the general variability in concentrations of potential toxic metals in the sediments.

From the analyses, the results also showed that the average concentrations of Zn, Ni, Mn, Fe, Cr, Pb, V, Mo, Sc, and Eu at both upstream and downstream reaches of the basin are 3.71, 0.05, 3.05, 2.91, 0.03, 2.38, 0.11, 0.03, 0.005, and 0.02 mg/kg and 2.15, 0.04, 3.11, 3.42, 0.03, 2.41, 0.11, 0.03, 0.004, and 0.02 mg/kg, respectively. This suggests increase in PTMs concentrations from upstream to downstream reaches. However, the heavy metal concentrations in the sediments of the basin were high with respect to the sediments at the river source (background), where the PTMs were below detection limit of 0.01 mg/kg (Table 1). Though, there was no significant difference in composition of the background samples from both wet and dry seasons (Table 1).

In general, Table 1 indicates varied composition of PTMs in stream sediments of the basin. However, standard deviation of the various PTMs detected revealed a slight variation between the sampled sediments. The standard deviation ranged between 0.00 and 3.23 in the rainy season and 0.01–3.34 at the dry season (Table 1). These values were considered low (slight variation), and could be suggesting that similar sources (possibly the same sources) and processes are responsible for the accumulation of PTMs in sediments of the basin.

Discussions of results

From the results in Table 1, the concentrations of potential toxic metals (PTMs) at the source of the stream sediments were below instrument's detection limit of 0.01 mg/kg. Thus, in line with (Rzetala 2015; Pandey and Singh 2017), it was adjudged that existence of PTMs at the source (background) is attributed to geology due to surficial fluvio-geomorphic processes. Higher concentrations in PTMs at other locations than the source connotes substantial additions through local geology and anthropogenic activities.

In the drainage basin, heavy metal concentration shows Fe, Mn, Zn, and Pb as predominantly higher (most times more than triple) than the other metals (Ni, V, Mo, Eu, Cr, and Sc) (Fig. 5a–f). But generally, the order is thus: Fe > Mn > Zn > Pb >>> V > Cr > Ni > Mo > Eu > Sc (Fig. 5g). Scandium (Sc) has the least concentration and in most cases, below detection limits (Table 1). However, Fe and Mn which ranked high in the sediments were at a tolerable level for organisms (Edokpayi et al. 2016). Supporting the findings on Fe as the highest occurring PTM in most drainage basins in Nigeria, are Olowu et al. (2010), Akpan and Thompson (2013) and Bubu et al. (2017). The reason could be due to its prevalence in earth's rocks–cum-anthropogenic activities. Though Fe ranked higher than other heavy metal in concentration in the present study, it has been observed to be generally very low in sediments of the basin and its environs (Eddy and Ukpong 2005; Ujah et al. 2017; Okiotor et al. 2018). Occurrence of Zn and Pb could be direct consequence of Pb–Zn mineralization and mining at Enyigba, Ameri, and Ishiagu and other anthropogenic activities within the basin (Igwe et al. 2014; Makinde et al. 2016). Furthermore, average Zn content increased from 1.40 mg/kg in the rainy season to 4.48 mg/kg in the dry season, and this could be due to re-deposition and sorption by soils engendering zinc-laden sediments.

The trend of concentrations of heavy metals in the drainage basin is thus: Rivers Adada > oji > Ezu > Obele > Mamu > Ankpa (Fig. 6a). River Adada recorded the highest concentration of heavy metal within the basin with about 20% of the total concentration load, while River Ankpa has the least concentration with 13% (Fig. 6b). Table 1 illustrates in Fig. 6c showed that seasonality could have influenced the distribution of the heavy metals with the dry season having higher concentration than wet season. Wang et al. (2011) have shown that 30–98% of heavy metals in rivers are transported in sediment-mixed forms due to re-deposition and sedimentation of PTMs-laden sediments and reduced precipitation. The implication is that precipitation, erosion, runoff, and river discharge (volume and flow rate) reduce PTMs' levels in sediments during the rainy season (Pandey and Singh 2017).

The PTMs' concentrations were lower in the upstream sediments than the downstream except at Ankpa (rainy season), Obele (rainy and dry seasons), Oji (rainy season), and Mamu (dry season) (Fig. 6c). Such was attributed to high velocity runoff and the upstream serving as access for large amount of effluents, while high concentrations at downstream is expected, because they serve as reservoirs of PTMs.

Level of PTMs (Fe, Cr, Mn, Pb, Ni, and Zn) in the basin was significantly lower than the threshold values locally and internationally- USEPA (1999); WHO (2004), Consensus-based Sediment Quality Guidelines (CBSQGs), Burton Jr. (2002), Wisconsin Department of Natural Resources- (Wisconsin Department of Natural Resources (WDNR) 2003), and other major rivers' sediments (Table 2, Fig. 7).

Sediments' risk analysis

Local sediment quality guidelines (SQGs) are vital in identifying "contaminants of concern" and to rank "areas of

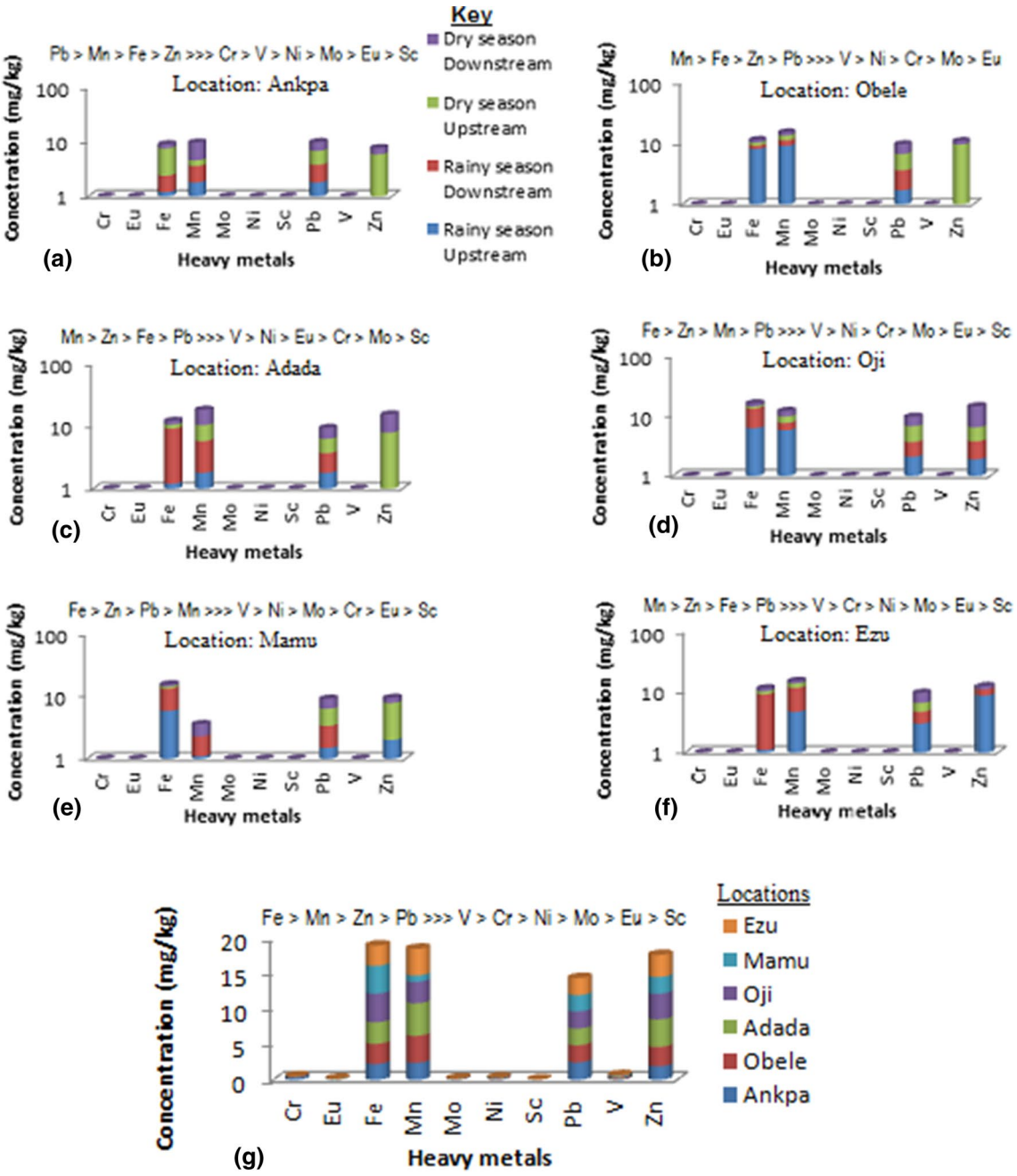

Fig. 5 General order of PTMs in Anambra drainage basin

concern" in an ecosystem. Due to the absence of domestic standard, Long and Morgan (1990) and Macdonald et al. (2000) suggested the use of consensus-based sediment quality guidelines (CBSQGs) in assessing the sediments' risk potentials in basins.

Thus, the effect range-low (ERL), effect range-medium (ERM), threshold effect concentration (TEC), and the probable effect concentration (PEC) or adverse biological effects on marine organisms indicates that Anambra drainage basin is relatively unpolluted between the seasons (Table 3). Consequently, this implies that no toxic effect on aquatic organisms is likely to occur within the basin. It is needful that protection and preservation of this relatively friendly aquatic environment is given priority.

Basin's heavy metals' spatial distribution

Spatial variation was noted in the distribution of heavy metals (Figs. 8, 9). Fe, Mn, Pb, and Zn had similar pattern in Obele, Oji, and Ezu at the south–western section (Fig. 8a–d),

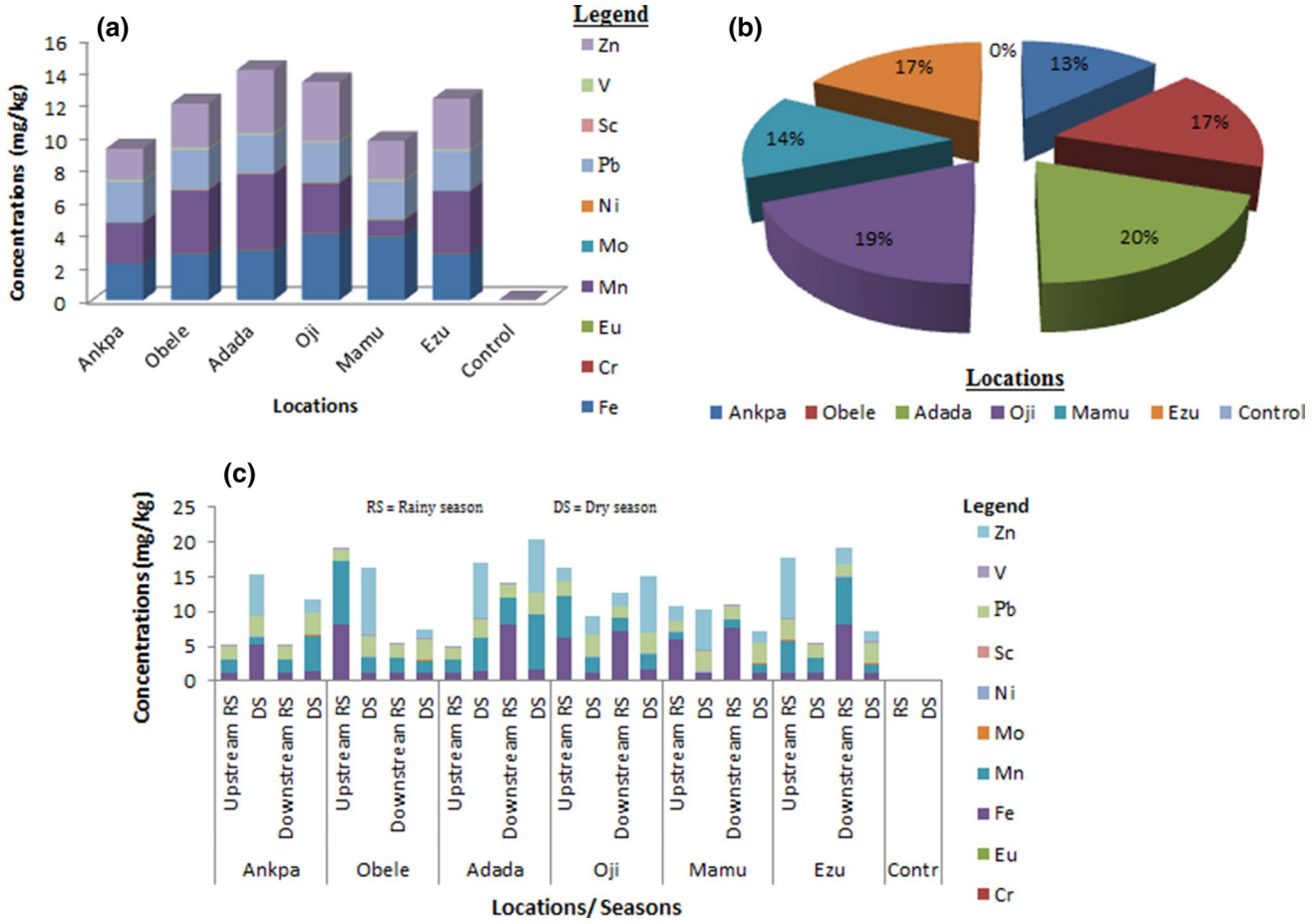

Fig. 6 Distribution and seasonal variation of PTMs in the basin's sediments

Table 2 Comparison of average concentration of PTMs in sediment

Drainage Basin	Fe	Zn	Ni	Mn	Cr	V	References
Anambra Basin, Southeast, Nigeria	3.16	2.94	0.05	3.08	0.03	0.11	Present study
Ganga River Basin, India	31,988.6	67.8	26.7	372	69.9	–	Pandey and Singh (2017)
Euphrates, Irag	2249.5	48.0	67.1	228.2	58.4	–	Salah et al. (2012)
Tapacura River Basin, Brazil	7470	18.9	1.1	53.8	1.70	–	Aprile and Bouvy (2008)
Saale River Basin, Germany	–	813	124	–	386	66.5	Moller and Einax (2013)
Morava River Basin, Czech	–	135.36	35.74	–	50.99	32.44	Bednarova et al. (2013)
Gan River Basin, China	–	139.44	25.43	–	59.94	78.54	Hua et al. (2016)
Ibeno Drainage Area, Niger Delta, Nigeria	23.06	0.05	2.06	9.56	–	3.31	Nwadinigwe et al. (2014)
Mvudi River Basin, South Africa	5244	26.56	–	887	97.76	–	Edokpayi et al. (2016)
Elemi River Basin, Southwest Nigeria	1.10	2.71	–	1.67	0.37	–	Ibigbami et al. (2017)
Tembi River Basin, Iran	235.5	38.0	101.4	423	48.75	–	Shabehzadeh et al. (2014)
Yauri River Basin, Northeast Nigeria	185.5	61.94	66.94	–	43.12	–	Yahaya et al. (2012)
World Average	57,405.9	303	102.1	975.3	126	–	Martin and Maybeck (1979)

– Denote data not available

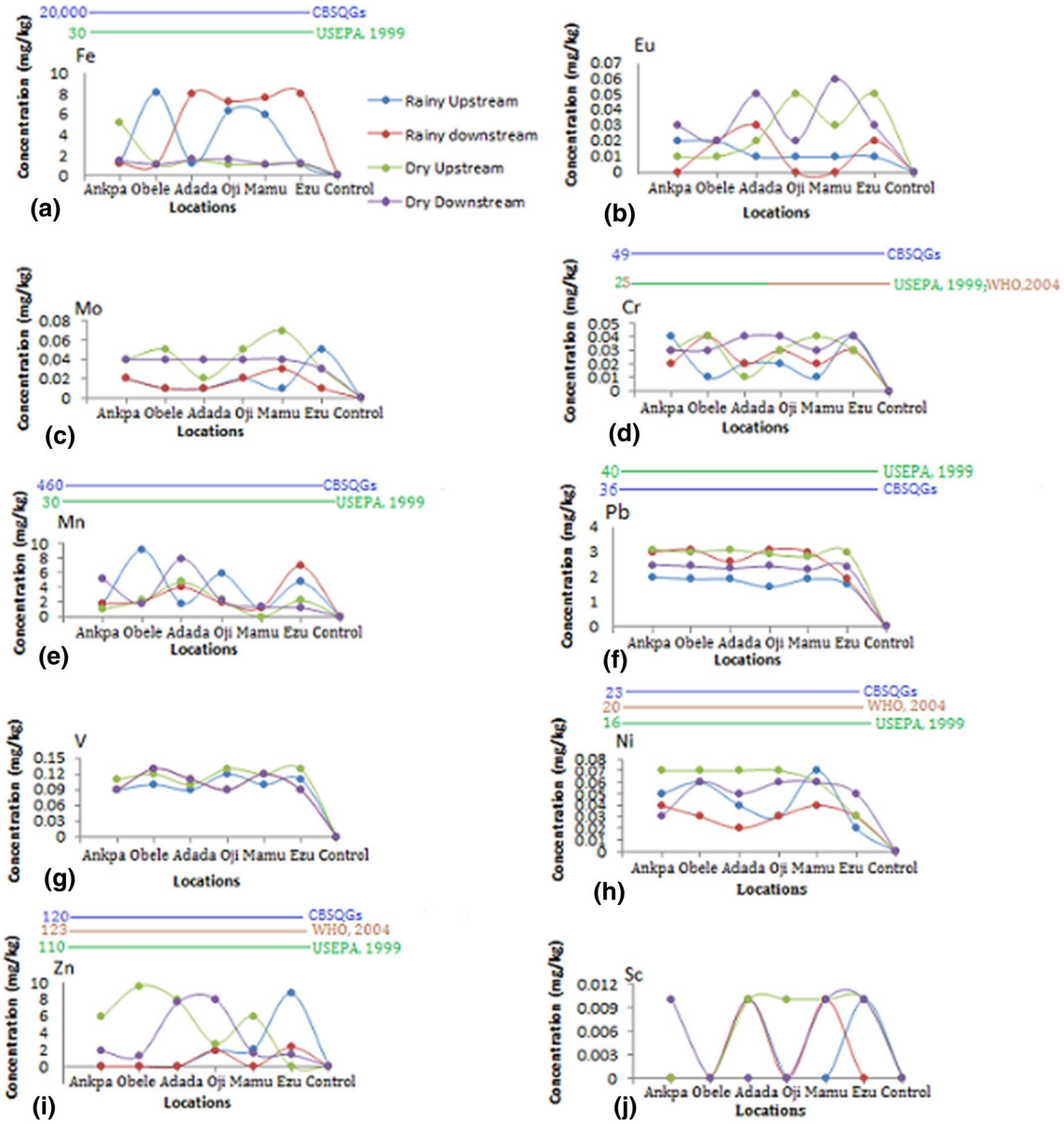

Fig. 7 Comparison of some PTMs with relevant standards

Table 3 Consensus-based sediment quality guideline

Heavy metal	ERL	ERM	TEC	PEC	RS	DS	UpS	DnS
Cr	80	145	43	110	0.03	0.03	0.03	0.03
Ni	30	50	23	49	0.04	0.06	0.05	0.04
Zn	120	270	120	460	1.4	4.48	3.72	2.16
Fe	–	–	20,000	40,000	4.74	1.58	2.91	3.42
Mn	–	–	460	1100	3.52	2.65	3.05	3.12
Pb	35	110	35.8	128	1.91	2.88	2.38	2.41

RS rainy season, *DS* dry season, *UpS* upstream, *DnS* downstream

– Connote data not available

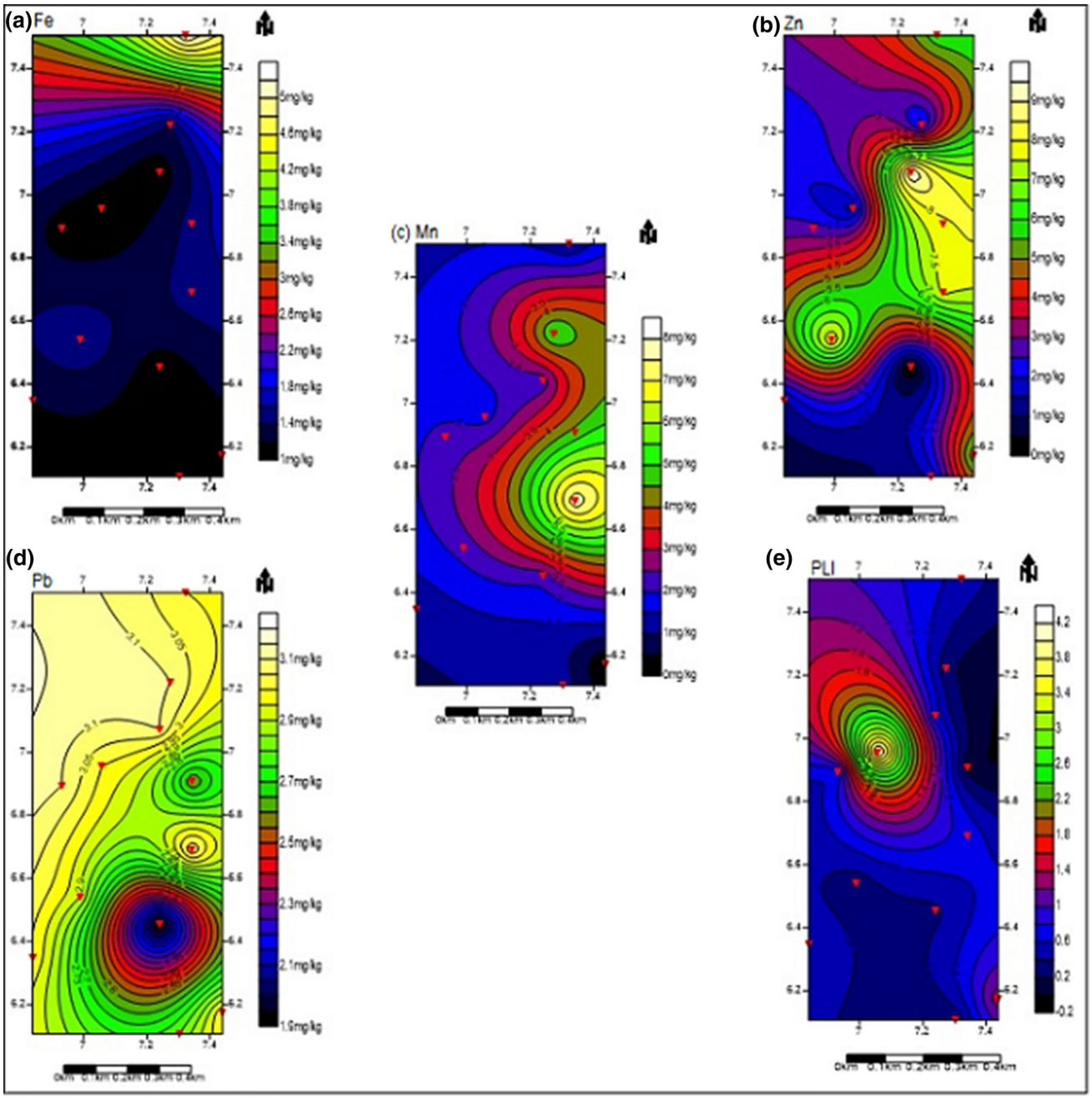

Fig. 8 Spatial distribution of major PTMs and PLI map of the basin

wherein the flood plain is underlain by alluvial plain and Imo shale (Figs. 1, 2, 3) which strengthens the stability index and humic composition. Furthermore, afore mentioned metals are mobile in rock minerals (Thomas 1974; Pedro 1968; Carrol 1970), implying that PTMs in the basin could be influenced by lithology, weathering, deposition, and sedimentation.

The high heavy metal concentration in Oji River could be an indirect impact of the Oji (regional) power distribution facility, thus suggesting anthropogenic influences. The sediments from Adada River showed higher accumulation of PTMs than other sediments (Fig. 6a). This is explained by anthropogenic activities such as agricultural inputs (agrochemicals) emanating from large-scale rice farming and production favored by water-logged clayey lithology. Eu, Sc, Mo, V, Cr, and Ni concentrations were highest at the northern and eastern regions of the basin (Fig. 9). Such places have higher elevation and steep slope being the head of the drainage basin (Figs. 1, 2, 3). Thus, these areas are prone to accelerated erosion.

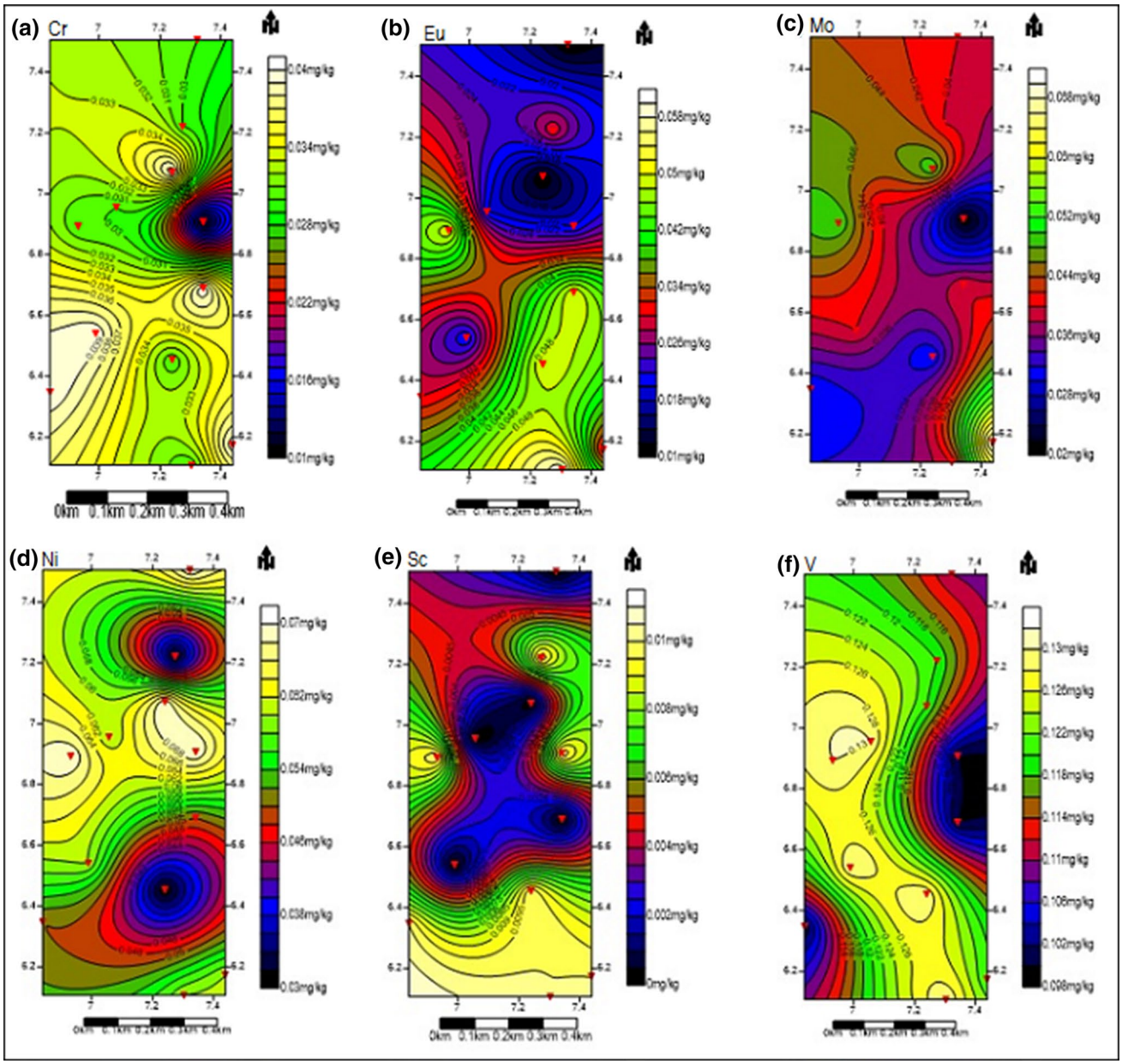

Fig. 9 Spatial distribution of other PTMs in basin's sediment

Figures 10, 11 show the variograms of the PTMs' distribution in relation to distance. The variogram shows that PTMs such as Cr, Eu, Mn, Ni, Pb, Zn, and others are unevenly distributed, as the concentration nuggets (variogram points) of the various PTMs are not equally apart (Fig. 10). Figure 11a shows that two sediments have abnormal enrichment of Fe when compared to other sediments of the basin. Scandium (Sc) showed an even distribution within the basin (Fig. 11b). From the variograms, it was observed that majority of the nuggets fall below the linear sill (Figs. 10, 11a), indicating a positive spatial correlation between various PTMs' concentrations from the different sediments of the basin. This suggests the same source(s) or geochemical processes for each of the heavy metals in the sediments. This agrees with the result of the standard deviation. However, the few that plotted above the sill (negative correlation) implies that same PTMs in sediments could be from a different source.

PTMs' accumulation and enrichment

The index of geo-accumulation (Igeo) of Zn, Ni, Mn, Fe, Cr, Pb, V, Mo, Sc, and Eu in the rainy season ranged from 0 to 3, −3 to 2, 0 to 3, 0 to 3, −4 to 0, 0 to 2, −2 to −1, −8 to

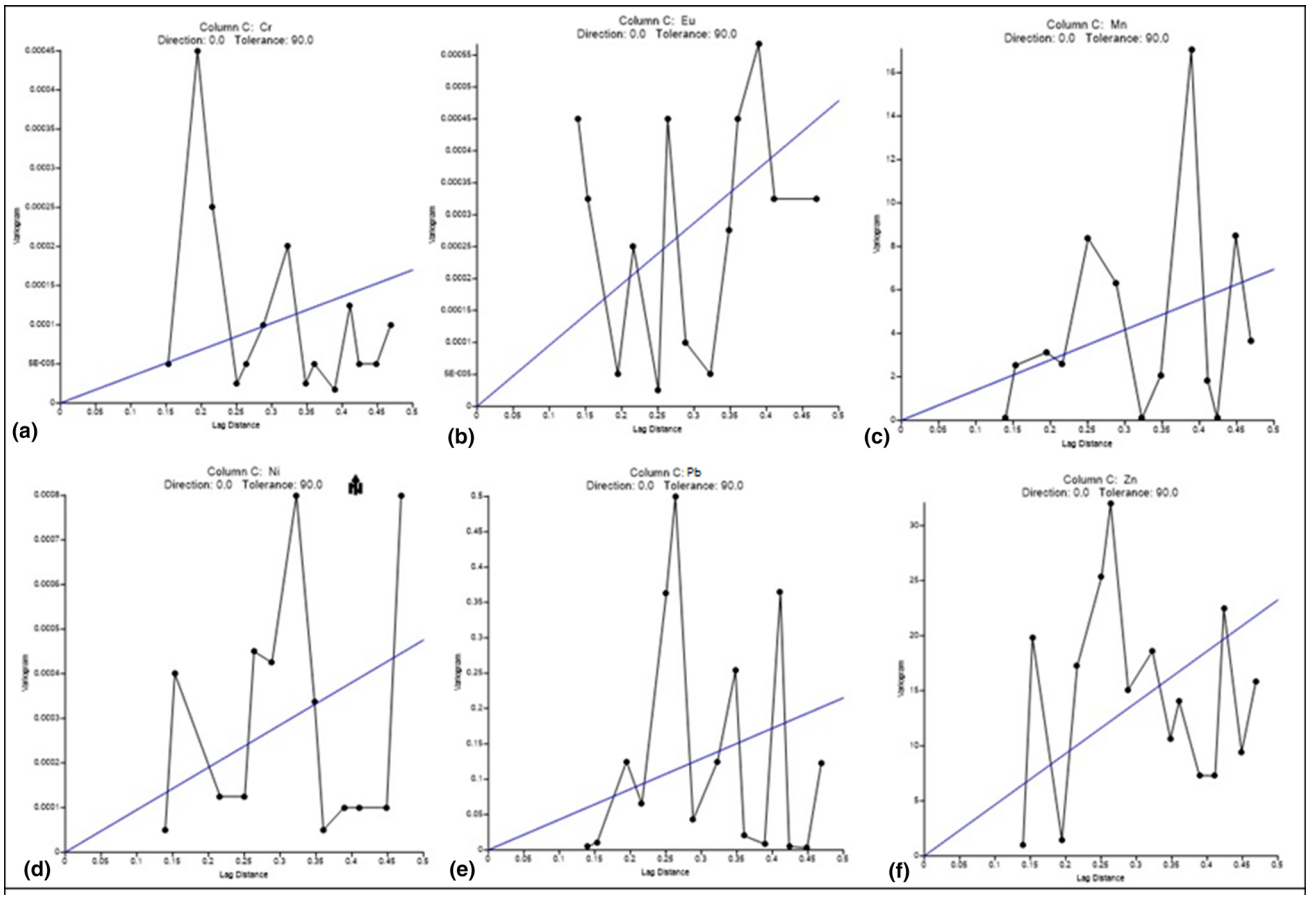

Fig. 10 Linear variogram of some PTMs' distribution in Anambra drainage sediments

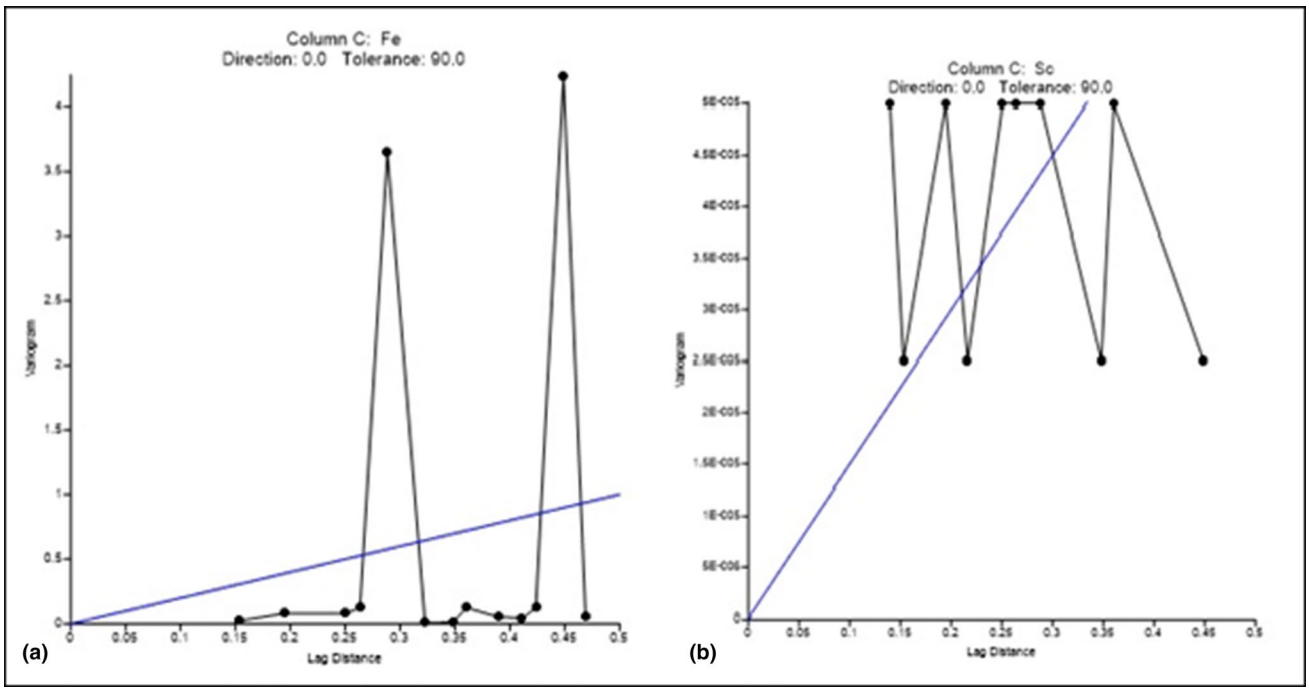

Fig. 11 Linear variogram of Fe and Sc in the drainage basin

Table 4 Sediment geo-accumulation of PTMs in both seasons

Seasons	River sediment	Location	Heavy metals_Igeo									
			Cr	Eu	Fe	Mn	Mo	Ni	Sc	Pb	V	Zn
Rainy	Ankpa	Upstream	−2.492	−5.468	0.567	1.074	−7.430	−2.511	0	0.953	−2.585	0
		Downstream	−3.492	0	0.567	1.074	−7.430	−2.833	0	1.105	−2.585	0
	Obele	Upstream	−4.492	−5.468	3.322	3.412	−8.430	−2.248	0	0.870	−2.433	0
		Downstream	−2.492	−5.468	0.442	1.296	−8.430	−3.248	0	1.031	−2.054	0
	Adada	Upstream	−3.492	−6.468	0.567	1.074	−8.430	−2.833	−5.392	0.953	−2.585	0
		Downstream	−3.492	−4.888	3.304	2.226	−8.430	−3.833	−5.392	1.031	−2.295	0
	Oji	Upstream	−3.492	−6.468	2.959	2.762	−7.430	−3.248	0	1.175	−2.170	0.940
		Downstream	−2.902	0	3.152	1.152	−7.430	−3.248	0	0.783	−2.585	0.940
	Mamu	Upstream	−4.492	−6.468	2.865	0.364	−8.430	−2.026	0	0.690	−2.433	1.015
		Downstream	−3.492	0	3.230	0.489	−6.845	−2.833	−5.392	1.031	−2.170	0
	Ezu	Upstream	−2.492	−6.468	0.442	2.459	−6.109	−3.833	−5.392	1.690	−2.295	3.136
		Downstream	−2.907	−5.468	3.304	3.012	−8.430	−3.248	0	0.870	−2.585	1.216
Dry	Ankpa	Upstream	−2.907	−6.468	2.683	0.226	−6.430	−2.026	0	1.690	−2.295	2.575
		Downstream	−2.907	−4.883	0.789	2.577	−6.430	−3.248	−5.392	1.737	−2.170	0.862
	Obele	Upstream	−2.492	−6.468	0.442	1.364	−6.109	−2.026	0	1.737	−2.170	3.278
		Downstream	−2.907	−5.468	0.442	1.074	−6.430	−2.248	0	1.690	−2.054	0.393
	Adada	Upstream	−4.492	−5.468	0.889	2.459	−7.430	−2.026	−5.392	1.483	−2.433	2.996
		Downstream	−2.492	−4.146	0.889	3.208	−6.430	−2.510	0	1.737	−2.433	2.940
	Oji	Upstream	−2.907	−4.146	0.442	1.364	−6.109	−2.026	−5.392	1.737	−2.054	1.447
		Downstream	−2.492	−5.468	0.982	1.364	−6.430	−2.248	0	1.641	−2.054	3.015
	Mamu	Upstream	−2.492	−4.883	0.442	0	−5.623	−2.248	−5.392	1.690	−2.170	2.575
		Downstream	−2.907	−3.883	0.442	0.605	−6.430	−2.248	−5.392	1.590	−2.054	0.693
	Ezu	Upstream	−2.907	−4.146	0.442	1.364	−6.845	−3.248	−5.392	1.031	−2.054	0
		Downstream	−2.492	−4.883	0.567	0.489	−6.845	−2.510	−5.392	1.690	−2.433	0.500

Table 5 Index of geo-accumulation classification

Igeo range	Significance
<0	Unpolluted
$0<\text{Igeo}<1$	Unpolluted to moderately polluted
$1<\text{Igeo}<2$	Moderately polluted
$2<\text{Igeo}<3$	Moderately to strongly polluted
$3<\text{Igeo}<4$	Strongly polluted
$4<\text{Igeo}<5$	Strongly to very strongly polluted
$\text{Igeo}>5$	Very strongly polluted

−5, −5 to 0, and −6 to 0, while the Igeo for the PTMs were 0–3, −2 to 3, 0–3, 0–3, −4 to −1, 1–2, −2 to 0, −7 to −5, −5 to 0, and −6 to −3 (Table 4). The Igeo grading of Lacutusu (2000) and Fagbote and Olanipekun (2010) in Table 5 analysis portrayed that except for Zn, Mn, and Fe, and geo-accumulation of PTMs in sediments in the basin was unpolluted during the rainy season. The drainage basin sediments were unpolluted with Cr, Eu, Mo, Ni, Sc, and V, with $\text{Igeo}\leq 0$ at the upstream and downstream sites (Table 5). Table 5 evidences that some sediments were moderately to strongly polluted by Zn, Mn, Pb, and Fe particularly at the downstream and Obele Upstream reaches, because $\text{Igeo}\leq 2$. In the dry season, sediments remained unpolluted with Cr, Eu, Mo, Ni, V, and Sc. Their Igeo values were less than 0 (Table 4). On the other hand, the pollution status of sediments (moderately to strongly polluted) with Zn, Pb, Fe, and Mn remained unchanged, since Igeo values spanned between 0 and 4 (Table 4). These observations might imply that the upstream pollution status could play an important role in determining heavy metal pollution downstream (Luo et al. 2013).

Enrichment factor (Ef) was used to find the extent of pollutants and its anthropogenic impacts on sediments. EF ranging above 1.5 connotes anthropogenic origin, while less denotes non-anthropogenic sources or crustal enrichment (Zhang and Liu (2002). The Ef values were below 1.5 with regard to Cr, Eu, Mn, Mo, Ni, Sc, Pb, and V, while Fe and Zn showed a higher enrichment at 3 (Adada Upstream, Mamu Up–cum-downstream) and 2 (Mamu and Ezu upstream) stations, respectively, in the rainy season (Table 6). In dry season, Cr, Eu, Mn, Mo, Ni, Sc, and V indicated values less than 1.5, but Fe showed a significant enrichment (5.49) at Ankpa upstream (Table 6). Pb showed an anomalous concentration at some sites such as Ankpa upstream and Obele,

Table 6 Wet and dry seasons' enrichment factor of sediments

Seasons	River sediment	Location	Heavy metals_EF									
			Cr	Eu	Fe	Mn	Mo	Ni	Sc	Pb	V	Zn
Rainy	Ankpa	Upstream	0.084	0.011	0.704	0	0.003	0.083	0	0.919	0.079	0
		Downstream	0.042	0	0.704	0	0.003	0.067	0	1.022	0.079	0
	Obele	Upstream	0.004	0.002	0.940	0	0.0002	0.020	0	0.172	0.017	0
		Downstream	0.072	0.009	0.553	0	0	0.043	0	0.832	0.098	0
	Adada	Upstream	0.042	0.005	0.704	0	0.001	0.067	0.011	0.919	0.079	0
		Downstream	0.019	0.007	2.111	0	0.001	0.015	0.005	0.437	0.044	0
	Oji	Upstream	0.013	0.002	1.147	0	0.001	0.016	0	0.333	0.033	0.283
		Downstream	0.06	0	4	0	0.003	0.047	0	0.774	0.075	0.864
	Mamu	Upstream	0.035	0.009	5.662	0	0.002	0.191	0	1.254	0.144	1.570
		Downstream	0.063	0	6.685	0	0.006	0.1	0.017	1.456	0.158	0
	Ezu	Upstream	0.032	0.002	0.247	0	0.003	0.013	0.004	0.587	0.037	1.599
		Downstream	0.017	0.003	1.223	0	0	0.013	0	0.227	0.021	0.288
Dry	Ankpa	Upstream	0.114	0.010	5.489	0	0.010	0.21	0	2.758	0.174	5.095
		Downstream	0.022	0.006	0.290	0	0.002	0.018	0.004	0.559	0.037	0.305
	Obele	Upstream	0.069	0.004	0.528	0	0.006	0.095	0	1.295	0.086	3.769
		Downstream	0.063	0.011	0.645	0	0.006	0.1	0	1.532	0.114	0.624
	Adada	Upstream	0.008	0.004	0.337	0	0.001	0.045	0.004	0.509	0.034	1.452
		Downstream	0.019	0.006	0.200	0	0.001	0.019	0	0.361	0.020	0.831
	Oji	Upstream	0.052	0.022	0.528	0	0.006	0.095	0.009	1.295	0.094	1.060
		Downstream	0.069	0.009	0.768	0	0.005	0.082	0	1.212	0.094	3.140
	Mamu	Upstream	0	0	0	0	0	0	0	0	0	0
		Downstream	0.088	0.045	0.893	0	0.008	0.139	0.016	1.980	0.158	1.063
	Ezu	Upstream	0.052	0.022	0.528	0	0.003	0.041	0.009	0.794	0.094	0
		Downstream	0.127	0.024	1.056	0	0.006	0.125	0.017	2.298	0.132	1.008

Mamu, and Ezu downstream, while Zn had such abnormal concentration at Ankpa and Obele upstream and Oji downstream (Table 6). Overall, Cr, Eu, Mn, Mo, Ni, Sc, and V remained at minimal enrichment, while Fe, Mn, Zn, and Pb revealed severe enrichment.

The contamination factor (Cf) of each detected PTMs in rainy and dry seasons' sediments is presented in Table 7. Lacutusu (2000) PTMs' classification (Table 8) shows that Mn, Pb, Zn, and Fe are slightly polluted to very severely polluted in rainy and dry seasons, with the Cf ranging between 1 and 15, 1–5; 2–14, and 2–15, respectively (Table 7). Other PTMs such as Cr, Eu, Mn, Mo, Sc, and V except Ni, when compared with Table 8, stand in the range of very slight contamination to moderate contamination. Thus, Cf is between 0 and 0.36 (Table 7). Nickel portrayed different ratings at different seasons—slight contamination to severe pollution (Table 7). Nickel in the rainy season's sediments is slight contaminated to moderately contaminated with Cf ranging from 0.10 to 0.36, while dry season showed very severe contamination to severe pollution with CF ranging between 0.9 and 7.1 (Table 7). These observations could be attributed to erosion and deposition of sediments in both seasons, respectively. The Ef and Cf values may be largely driven by human economic activities such as mining and agricultural inputs and crustal processes such as weathering and erosion of the basin rock materials and minerals' deposition at the different seasons.

From MCB (Modified Contamination Base) values in Table 7, all sampled station spanned from severely to excessively polluted (MCD ≥ 8) in the rainy season except at Ankpa upstream, where there was no contamination (MCD ≤ 0), as shown in Table 7. However, in dry season, all the sampled sites revealed cases of severe pollution, with MCD ≥ 9 (Table 7).

In the case of the PLI at both seasons of the year (Table 9), Obele downstream and Mamu upstream revealed evidence of pollution, with their PLI values > 1. However, sediments from Ankpa, Obele, and Oji (upstream) and Ezu (downstream) showed evidence of severe contamination with PLI values of 0.54, 0.67, 0.73, and 0.61, respectively (Table 9), and could become polluted if appropriate measures are not put in place. The PLI map is presented in Fig. 8e, with areas around Oji upstream and Obele downstream showing evidence of slight and severe pollution, respectively.

Table 7 Contamination factor of both wet and dry seasons' sediments

Seasons	River sediments	Location	Heavy metals_CF										MCD
			Cr	Eu	Fe	Mn	Mo	Ni	Sc	Pb	V	Zn	
Rainy	Ankpa	Upstream	0.267	0.034	3.158	0.009	0	2.903	0.25	0	2.222	0.263	0
		Downstream	0.133	0	3.158	0.009	0	3.226	0.25	0	2.222	0.211	9.019
	Obele	Upstream	0.067	0.034	15.965	0.004	0	2.742	0.278	0	15	0.316	34.121
		Downstream	0.267	0.034	3.684	0.004	0	3.065	0.361	0	2.037	0.158	9.468
	Adada	Upstream	0.133	0.017	3.158	0.004	0.036	2.903	0.25	0	2.222	0.211	8.745
		Downstream	0.133	0.051	7.018	0.004	0.036	3.065	0.306	0	14.815	0.105	25.437
	Oji	Upstream	0.133	0.017	10.175	0.009	0	3.387	0.333	2.879	11.667	0.158	28.616
		Downstream	0.2	0	3.333	0.009	0	2.581	0.25	2.879	13.333	0.158	22.601
	Mamu	Upstream	0.067	0.017	1.930	0.004	0	2.419	0.278	3.030	10.926	0.368	18.708
		Downstream	0.133	0	2.105	0.013	0.036	3.065	0.333	0	14.074	0.211	19.780
	Ezu	Upstream	0.267	0.017	8.246	0.022	0.036	4.839	0.306	13.182	2.037	0.105	28.960
		Downstream	0.2	0.034	12.105	0.004	0	2.742	0.25	3.485	14.815	0.158	33.651
Dry	Ankpa	Upstream	0.2	0.017	1.754	0.017	0	4.839	0.306	8.940	9.630	0.928	25.795
		Downstream	0.2	0.051	8.947	0.017	0.036	5.00	0.333	2.727	2.593	1.052	20.010
	Obele	Upstream	0.267	0.017	3.860	0.022	0	5.00	0.333	14.545	2.037	7.140	26.795
		Downstream	0.2	0.034	3.158	0.017	0	4.839	0.361	1.970	2.037	0.967	12.712
	Adada	Upstream	0.067	0.034	8.246	0.009	0.036	4.194	0.278	11.970	2.778	4.309	28.040
		Downstream	0.267	0.085	13.860	0.017	0	5.00	0.278	11.515	2.778	4.145	34.214
	Oji	Upstream	0.2	0.085	3.860	0.022	0.036	5.00	0.361	4.091	2.037	2.008	15.892
		Downstream	0.267	0.034	3.860	0.017	0	4.677	0.361	12.121	2.963	4.091	24.709
	Mamu	Upstream	0.267	0.051	0	0.030	0.036	4.839	0.333	8.939	2.037	4.388	16.971
		Downstream	0.2	0.102	2.281	0.017	0.036	4.516	0.361	2.424	2.037	1.190	12.093
	Ezu	Upstream	0.2	0.085	3.860	0.013	0.036	3.065	0.361	0	2.037	0	9.656
		Downstream	0.267	0.051	2.105	0.013	0.036	4.838	0.278	2.121	2.222	0.955	12.027

Table 8 Contamination and pollution standards

CF and PLI ranges	Significance
< 0.1	Very slight contamination
0.10–0.25	Slight contamination
0.26–0.5	Moderate contamination
0.51–0.75	Severe contamination
0.76–1.00	Very severe contamination
1.1–2.0	Slight pollution
2.1–4.0	Moderate pollution
4.1–8.0	severe pollution
8.1–16.0	Very severe pollution
> 16.0	Excessive pollution

Table 9 Pollution load index grading of the sediments

Location	Environment	PLI
Ankpa	Upstream	0.5376
	Downstream	0.2698
Obele	Upstream	0.6709
	Downstream	4.1485
Adada	Upstream	0.0642
	Downstream	0.7316
Oji	Upstream	0.6607
	Downstream	0.2889
Mamu	Upstream	1.3419
	Downstream	0.2437
Ezu	Upstream	0.3558
	Downstream	0.6052

Environmental implications of the basin's PTMs

Sediments are vital in the functioning of drainage basin and excessive accumulation of heavy metals in it causes pollution (Yu et al. 2010; Wang et al. 2011; Osakwe et al. 2014). Pollutants which accumulate in the stream sediments are transported into basins through high tides, runoff–cum discharge, and re-settlement of particles at downstream (Ezeh and Anike 2009; Gerhat and Blomquist 1992; Igwe et al. 2014).

Anambra drainage basin exists in a weakly consolidated sedimentary rock and supports a wide array of human economic activities—agricultural practice, water supply for irrigation, and municipal use. Engineering materials are

also sourced from the river sediments due its durability for construction purposes (Igwe et al. 2014, 2015). Thus, such exposes the basin to PTMs contamination risks and could lead to long term accumulation of PTMs which is considered unhealthy for humans and aquatics (McCluggage 1991; Duruibe et al. 2007; Fatoki et al. 2002; Alloway and Ayres 1993; USEPA 2007; Sakan et al. 2007; Harikumar et al. 2009; Ip et al. 2007; Igwe et al. 2014).

Although this study did not carry out an appraisal to ascertain the level of exposure to PTMs and possible resultant disorder, the risk prone to the residents cannot be overemphasized or ignored due to intensive utilization of the basin for livelihood. Thus, it was concluded that evaluation of the basin sediment should be not be relegated to the background, because the present PTMs concentration index can turn out to be "tomorrows poison". This is because even at very low concentrations, Pb can be harmful (Wendy 2005; Pehlivan et al. 2009), coupled with Pb–Zn mineralization obtainable in the drainage basin.

Conclusion

This study assessed the concentration and spatial distribution of potential toxic metals (heavy metal) in sediments within the Anambra drainage basin. Results indicated accumulation of heavy metals with the trend: Fe > Mn > Zn > Pb >> > V > Cr > Ni > Mo > Eu > Sc and Rivers Adada > oji > Ezu > Obele > Mamu > Ankpa (Figs. 5, 6a, b). The PTMs' concentrations were higher in the dry season and downstream sediments than in the rainy seasons and upstream, respectively, except on few instances (Fig. 6c). PTMs concentration values were also higher than background, implying possible accumulation and enrichment in sediments.

Heavy metal evidenced variation in space. It revealed that PTMs is highly concentrated in areas of high socio economic activities. From the spatial and pollution load index maps, River Obele, Adada, and Oji showed slight pollution than other sub-basins in close proximity within Enyigba, Ameri, and Ishiagu mines due to Pb–Zn mineralization. Therefore, sampling of sediments from these areas with high PTMs may require more attention in future researches.

Within the basin, PTMs' enrichment, accumulation, and contamination did not exceed relevant standards-USEPA (1999), WHO (2004) and CBSQGs criterion. Data analyses by Igeo, Ef, and Cf indicated moderate-to-severe accumulation and enrichment of PTMs. This poses a risk to the basin utilization in the future. Findings in this study are in agreement with Singh et al. (2005), Dhanakumar et al. (2011), Kumar et al. (2013) and Singh and Pandey (2014) observation that drainage basins are showing rising levels of heavy metals.

This study, therefore, provided sediment data which are important in many respects—designing and development of sustainable monitoring, control and management strategies for the basin protection. Conclusively, the drainage basins needs effective monitoring, since it supports a vast section of agrarian middle belt and part of south eastern Nigeria.

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