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Assessment of stream sediments pollution by potentially toxic elements in the active mining area of Okpella, Edo State, Nigeria

The Mining-Geology-Petroleum Engineering Bulletin
UDC: 504
DOI: 10.17794/rgn.2019.2.5

Professional paper

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Abstract

An active gold mining area in Okpella, Edo State, Nigeria was studied to assess the contribution of gold mining to the concentrations of potentially toxic elements (PTEs) in stream sediments. Standard geochemical sampling and sample treatment techniques were employed, and samples were analysed using the energy dispersive X-ray fluorescence (XRF) method. The concentrations of arsenic (As), cobalt (Co), chromium (Cr), copper (Cu), mercury (Hg), nickel (Ni), lead (Pb) and zinc (Zn) were determined in fifteen stream sediment samples from an active gold mining area, which also receives discharged marble mine water. The enrichment factor (EF) and geoaccumulation index (I_{geo}) were calculated using the XRF analysis results to assess the level of PTEs pollution in the area. The sediments showed a PTEs concentration trend of Cu > Zn > Pb > As > Cr > Hg > Ni > Co. The EF results revealed extremely severe enrichment of Hg, moderate enrichment of Cu, minor enrichment of As and Pb, and no enrichment of Co, Cr, Ni and Zn in the sediments. The I_{geo} also showed that the sediments were extremely polluted with Hg, moderately polluted with Cu but there was no evidence of pollution from other PTEs. Extreme pollution of the sediments by Hg and its enrichments in Cu, As and Pb are due to indiscriminate active artisanal gold mining in the area. It is recommended that immediate remediation measures should be enforced to mitigate the possible environmental health hazards to humans and livestock in the area.

Keywords:
enrichment factor, geoaccumulation index, mining activities, pollution, potentially toxic elements.

1. Introduction

The pollution of soils, sediments, plants and water by potentially toxic elements (PTEs) such as arsenic (As), cobalt (Co), chromium (Cr), copper (Cu), mercury (Hg), nickel (Ni), lead (Pb), zinc (Zn) and others is a critical environmental problem in the world, particularly in developing nations where indiscriminate and illegal mining and other industrial activities take place. These pollutants often have negative health effects such as damage of the kidney, lungs, brain and other internal organs, blindness, and even death to humans and livestock as they are exposed to PTEs through different pathways including direct ingestion of contaminated soils, plants and water as well as inhalation of dust (**Carla et al., 2014; Waziri, 2014; Tomašek et al., 2016; Odukoya et al., 2018**).

In recent times, the aquatic ecosystem is increasingly being polluted by PTEs via activities such as artisanal mining, industrial wastewater discharges, fossil fuel combustion, sewage wastewater and atmospheric deposition of toxic metals (**Hakanson, 1980; Tijani et al., 2005; Tijani and Onodera, 2009**). PTEs have a great ecological significance due to their toxicity, tendency to accumulate in both sediments and biota and non-biodegradable nature (**Ahmadipour et al., 2014**). Most of the PTEs, and particularly As, Pb and Cd are highly toxic to plants, livestock and humans; other metals such as Cu, Zn and Ni are important in biological systems, however, an excess of these metals in biological systems is dangerous (**Nowrouzi and Pourkhabbaz, 2014**). Hence, to avoid the poisoning of humans and livestock by PTEs, there is a need to frequently assess and monitor sediment and water quality in the aquatic ecosystem (**Sekabira et al., 2010**).

Determination of the concentrations of PTEs in stream sediments and the application of pollution indices such as the enrichment factor (EF), geoaccumulation index (I_{geo}), pollution load index (PLI), anthropogenic factor (AF), metal contamination index (MCI), contamination factor (CF), etc to the analytical data are a viable means of revealing/assessing the level of pollution and the possible ecological and health risks of an area (**Sutherland, 2000; Meybeck et al., 2004; Qingjie et al., 2008**). This approach has been successfully used by **Tijani et al. (2005), Tijani and Onodera (2009), Seka-**

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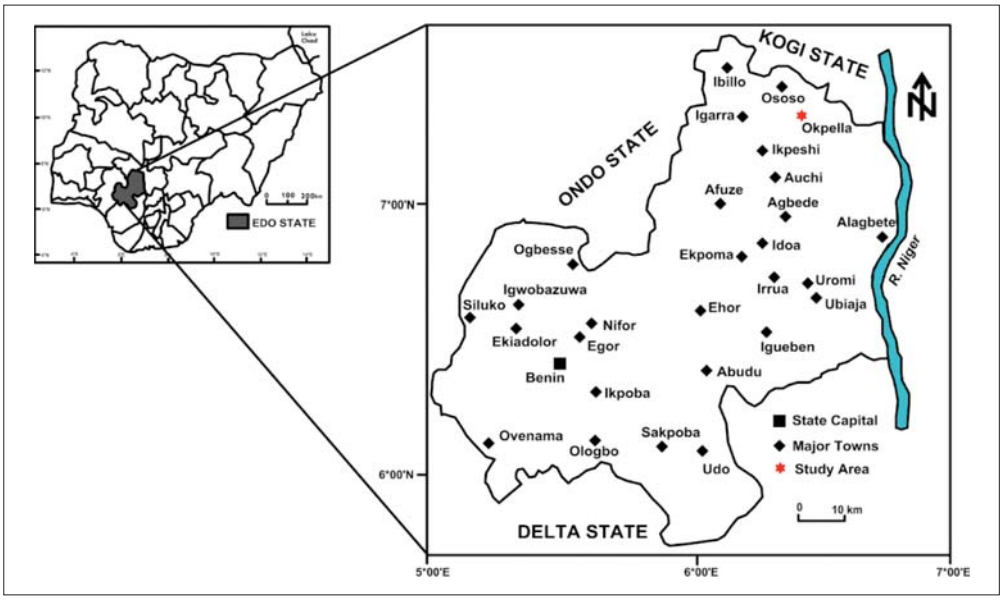

Figure 1: Location map of Edo State showing Okpella (after **Idu and Onyibe, 2007**)

bira et al. (2010), Nowrouzi and Pourkhabbaz (2014), Waziri (2014), Amadi et al. (2017), Odukoya et al. (2018) and others to assess the levels of PTEs pollution in different parts of the world. However, in Okpella where indiscriminate artisanal gold mining takes place, PTEs pollution assessment has not been done to date. This research, therefore, is aimed to assess the level of PTEs pollution of stream sediments collected from the active gold mining area in Okpella using the enrichment factor (EF) and the geoaccumulation index (I_{geo}) of the metals.

2. Methods

The study area, sampling site, sampling and analytical techniques, and data analyses are discussed below.

2.1. Study Area and Sampling Site

Okpella is located between latitude N07^{0}14$^{'}$ and N07^{0}22$^{'}$ and longitude E006^{0}15$^{'}$ and E006^{0}23$^{'}$ in the northeastern part of Edo State, Nigeria (see **Figure 1**). The area is the eastern extension of the Upper Proterozoic Igarra Schist Belt, Southwestern Nigerian Basement Complex. The lithologies in the area include granite gneiss, metasedimentary rocks and Pan-African intrusives. The metasedimentary rocks occurring in the area are comprised of garnet-biotite schist, marble and calc-silicate gneiss, quartzite and banded iron formation (BIF). The Pan-African intrusives include granite, charnockite, hybrid rocks, pegmatite, aplite and basic dykes (**Odeyemi, 1988; Ogunyele et al., 2018**) (see **Figure 2**).

In the northern part of the area (see **Figures 2 and 3**), indiscriminate artisanal mining of gold from sediments of the Uza River and its tributaries is ongoing. Exploitation is usually done during the dry season (October to March, sometimes up to June) when large amounts of sediments would have been deposited by water during the rainy season. These sediments are sourced from the surrounding gold-mineralised rocks through weathering and erosion. Large amounts of the stream sediments are collected by miners using shovels and head pans. The collected sediments are panned and washed with the stream water to separate the heavy minerals such as gold, pyrite, chalcopyrite and other sulphides from the light ones, e.g. quartz and feldspar. The gold grains and other heavy minerals being denser, separate from other minerals during panning. The heavy minerals are then mixed with mercury chemicals so as to separate gold from the other heavy minerals and gangue.

Large marble and calc-silicate gneiss deposits also occur in the area and are being exploited for the production of cement by the BUA Cement Company, Nigeria. A large marble quarry is located close to the Uza River (see **Figure 3**) and wastewater from the quarry is also discharged into the river. These industrial activities, use of Hg in gold extraction, tailings and gangue produced during artisanal gold mining, wastewater from marble quarrying as well as heavy vehicular emissions, possibly produce and release significant amounts of PTEs into the area causing various forms of pollution which require assessment and monitoring to mitigate environmental and health hazards.

The study was conducted along the Uza River and its tributaries in the central part of Okpella (see **Figure 3**) where the above highlighted activities take place. The river flows from the southwest to the northeast and has numerous tributaries which take their sources and derive sediments from the surrounding highlands.

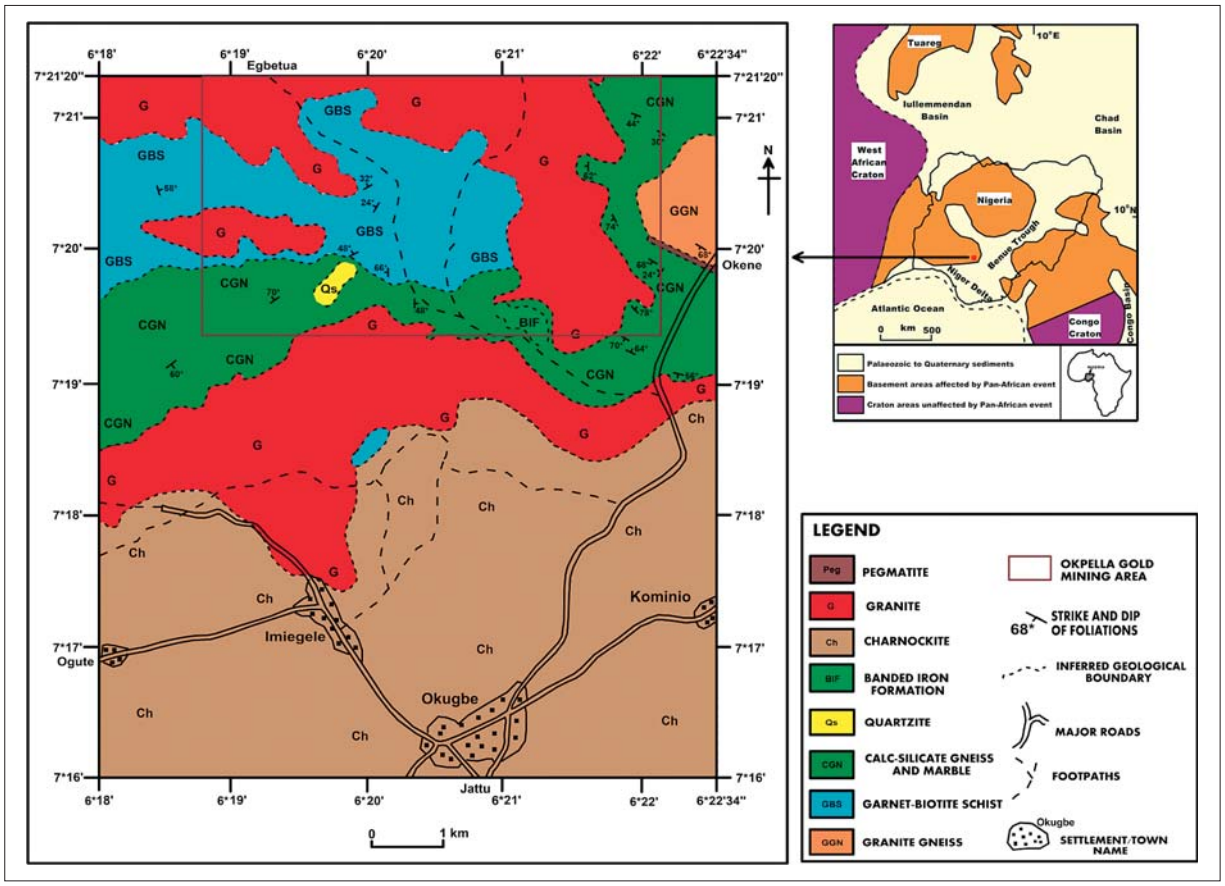

Figure 2: Geological map of Okpella showing the gold mining area (after **Ogunyele et al., 2018**) [inset: Regional geological setting of Nigeria (modified after **Woakes et al., 1987**)]

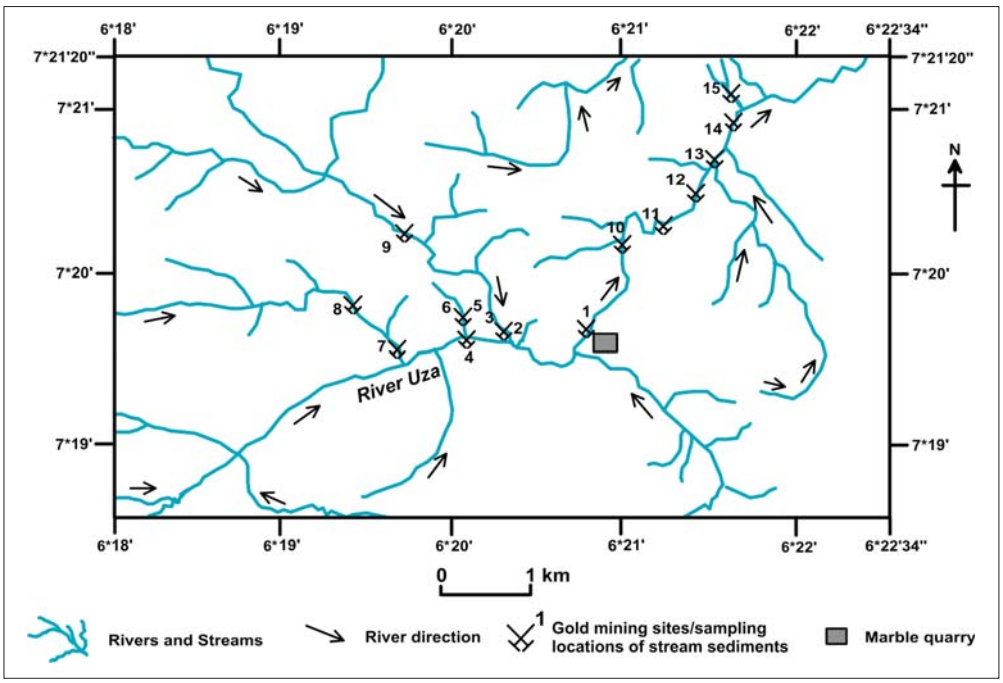

Figure 3: Drainage map of Okpella gold mining area showing the sampling locations of stream sediments

2.2. Sampling and Sample Analysis

Fifteen sediment samples weighing 100 g each were collected at depths between 0 – 20 cm from different gold mining sites along the Uza River in Okpella (see **Figure 3**) using a hand trowel and plastic sieve to drain off the water. The samples were kept in clean polythene bags and transported to the laboratory. The sampling was done at the end of the 2016-2017 mining period in the area (June, 2017).

The samples were air-dried at room temperature, lumpy samples were disaggregated using an agate mortar and pestle, and sieved using an electrical stainless sieve to < 90 microns (170 mesh) so as to get the silty to clayey fractions for analysis. The sieved samples were further reduced in grain size by pulverising to < 63 microns (230 mesh) using a pulveriser. All glassware and equipment used for this preparation were washed with nitric acid to avoid possible contamination. The pulverised samples were homogenised using a homogeniser, pelletised and analysed for PTEs (As, Co, Cr, Cu, Hg, Ni, Pb and Zn) using an energy dispersive X-ray fluorescence (ED-XRF) machine (pANalytical model) at the National Geosciences Research Laboratory, Kaduna, Nigeria. Fe was also analysed in the samples as an immobile element to calculate the enrichment factor (EF). The major limitation of the XRF method relating to this study is that it determines the total concentrations of the elements in the samples, and not only concentrations caused by pollution. However, this limitation is reduced by the use of pollution indices to assess the pollution level in the area.

2.3. Data Analyses

The level of pollution of the stream sediments by PTEs was determined using two pollution indices, namely: the enrichment factor (EF) and the geoaccumulation index (I_{geo}). Correlation analysis of the PTEs was also done to determine the inter-relationships among them.

The EF is a relatively simple and easy tool for assessing the enrichment degree of a metal and comparing the pollution of different environmental media (**Benhaddya and Hadjel, 2013**). The EF is based on standardisation of the analysed metals against a conservative reference element such as Fe, Al, Mn, Sc and Ti (**Sutherland, 2000**). In this study, Fe was used as a conservative reference element because it has a relatively higher precision of measurement as a major element and it has also been widely used as a normalising metal in geochemical studies (Sutherland, 2000). According to **Ergin et al. (1991)**, the EF is defined as follows:

$$EF = \frac{\left(C_n / C_{Fe}\right)_S}{\left(C_n / C_{Fe}\right)_B} \quad (1)$$

where:

$(C_n/C_{Fe})_S$ is the ratio of the concentration of a metal *n* and Fe in the sample; and

$(C_n/C_{Fe})_B$ is the ratio of the concentration of a metal *n* and Fe of the background.

In this study, the world average shale data (**Turekian and Wedepohl, 1961**) was used to provide the background metal levels: As (13 mg/kg), Co (19 mg/kg), Cr (90 mg/kg), Cu (45 mg/kg), Ni (68 mg/kg), Pb (20 mg/kg), Zn (95 mg/kg) and Fe (47,000 mg/kg). For Hg (0.18 mg/kg), **Marowsky and Wedepohl (1971)** data on shale was used. The world average shale data is used because it is the most abundant sediment in the Earth constituting about 82% of all sediments in the world **(Mead, 1907)**. According to **Zhang and Liu (2002)**, EF values between 0.5 and 1.5 indicate that the metal is entirely from crustal materials or natural processes, whereas EF values greater than 1.5 suggest that the sources are more likely to be anthropogenic.

I_{geo} is used to determine metal contamination in sediments by comparing current concentrations with pre-industrial levels (**Muller, 1969**). I_{geo} is calculated as follows:

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

where:

C_n is the measured concentration of metal *n* in the sediment; and

B_n is the background value for the metal *n* (global average shale data) according to **Turekian and Wedepohl**

Table 1: Pollution categories based on Enrichment Factor (EF) and Geoaccumulation Index (I_{geo}) **(Muller, 1969; Nowrouzi and Pourkhabbaz, 2014)**

Enrichment Factor			Geoaccumulation Index		
Level	**Value**	**Categorisation**	**Class**	**Value**	**Categorisation**
I	<1	No enrichment	0	<0	Unpolluted
II	1-3	Minor enrichment	1	0-1	Unpolluted to moderately polluted
III	3-5	Moderate enrichment	2	1-2	Moderately polluted
IV	5-10	Moderately severe enrichment	3	2-3	Moderately to strongly polluted
V	10-25	Severe enrichment	4	3-4	Strongly polluted
VI	25-50	Very severe enrichment	5	4-5	Strongly to extremely strongly polluted
VII	>50	Extremely severe enrichment	6	>5	Extremely polluted

(1961); and factor 1.5 is used because of possible variations of the background data due to lithological variations.

Interpretations of the results of the EF and I_{geo} according to **Muller (1969)** and **Nowrouzi and Pourkhabbaz (2014)** are given in **Table 1**.

3. Results and Discussion

The summary of PTEs' concentrations in the stream sediment samples of Okpella gold mining area is presented in **Table 2**. The average concentrations of PTEs in the sediments show a trend of Cu > Zn > Pb > As > Cr > Hg > Ni > Co. The ranges are as follows: Cu (57-112 mg/kg); Zn (10-50 mg/kg); Pb (4-36 mg/kg); As (2.8-25 mg/kg); Cr (9-18 mg/kg); Hg (6-25 mg/kg); Ni (3-11 mg/kg); Co (2-9 mg/kg); and Fe (13566-25524 mg/kg).

The weighted mean and median of Cu, As and Hg in the stream sediments are significantly higher than that of the average shale and continental crust. Pb concentration in the stream sediments is close to that of the average continental crust but lower than that of the average shale. These higher concentrations imply contributions from anthropogenic sources and possible pollution of the environment. The other PTEs, that is, Co, Cr, Ni and Zn are lower in concentrations than the average shale and continental crust suggesting natural sources (**Turekian and Wedepohl, 1961**).

The EF values show extremely severe enrichment of Hg (151.60), moderate enrichment of Cu (4.48) and minor enrichments of As (2.46) and Pb (2.02) in the stream sediments (see **Table 3**). The EF values of the PTEs which are greater than 1.5 indicate anthropogenic contribution to the enrichment of the stream sediments. The other PTEs (Co, Cr, Ni and Zn), however, show no enrichment. Au is often associated with the analysed PTEs (as pathfinders); hence Cu, As and Pb have been released into the stream sediments as a result of mining as well as weathering of the gold-mineralised rocks in the area causing enrichment. Waste water from the marble quarry may have also contributed to the enrichment, although in a minute amount compared to gold mining. High Hg concentration and enrichment in the sediments is mainly caused by the use of Hg in gold extraction in the area.

Table 2: Summary of potentially toxic elements (PTEs) concentrations in the stream sediment samples of Okpella mining area (n=15)

Element (mg/kg)	Minimum	Maximum	Weighted Mean	Median	Average Shale*	Average Continental Crust +
As	2.8	25	14.09 ± 6.31	13	13	0.055
Co	2	9	6.00 ± 2.45	7	19	11.6
Cr	9	18	12.19 ± 2.47	11	90	69
Cu	57	112	88.56 ± 17.23	92	45	14.3
Hg	6	25	12.00 ± 5.40	10	0.18**	0.056
Ni	3	11	6.50 ± 2.65	7	68	18.6
Pb	4	36	17.78 ± 9.64	16	20	17
Zn	10	50	30.61 ± 14.35	32	95	52
Fe	13566	25524	20668 ± 3692	21097	47000	30890

***** after **Turekian and Wedepohl (1961)**. Concentration of the average sediment is taken as the global average shale data as shales constitute about 82% of all sediments in the Earth.
****** after **Marowsky and Wedepohl (1971)**
+ after **Wedepohl (1995)**

Table 3: Enrichment factor, geoaccumulation index and pollution level in the stream sediments of Okpella mining area

Element	Enrichment Factor (EF)	Pollution level	Geoaccumulation Index (I_{geo})	Pollution level
As	2.46	Minor enrichment	< 0	Unpolluted
Co	0.72	No enrichment	< 0	Unpolluted
Cr	0.31	No enrichment	< 0	Unpolluted
Cu	4.48	Moderate enrichment	0.39	Unpolluted to moderately polluted
Hg	151.60	Extremely severe enrichment	5.47	Extremely polluted
Ni	0.22	No enrichment	< 0	Unpolluted
Pb	2.02	Minor enrichment	< 0	Unpolluted
Zn	0.73	No enrichment	< 0	Unpolluted

Table 4: Correlation of PTEs in stream sediment samples of the Okpella mining area

Elements	As	Co	Cr	Cu	Hg	Ni	Pb	Zn
As	1							
Co	-0.152	1						
Cr	**0.986**	0.234	1					
Cu	0.242	**0.960**	0.245	1				
Hg	0.126	**0.955**	-0.272	-0.098	1			
Ni	**0.976**	0.002	-0.358	0.199	-0.377	1		
Pb	0.235	-0.113	-0.215	-0.221	-0.443	0.546	1	
Zn	0.115	-0.342	-0.246	-0.356	0.453	0.334	0.007	1

The I_{geo} also reveals that the sediment samples are extremely polluted with Hg, unpolluted to moderately polluted with Cu but unpolluted with all the other PTEs (see **Table 3**). The level of pollution of sediments in the Okpella mining area by Hg is too high and warrants that remediation measures are taken quickly as this may pose serious environmental hazards. Water from the Uza River and its tributaries are used for drinking and other domestic purposes by people in the area. The river also flows into other rivers in the area. This may cause serious health challenges to the miners and community at large as pollutants in the sediments are released into water and taken up by plants, both of which are consumed by humans and livestock.

There is a need to sensitise the miners in the area on the best practices to be adopted in mining operations. On the other hand, continuous assessment and monitoring of the levels of PTEs in soils, sediments, water and plants in the area should be done so as to engage the necessary remediation and/or control measures to constrain the input of PTEs as well as the potential environmental health impacts.

3.1. Correlation analysis of the potentially toxic elements

Correlation analysis was done to determine the interrelationships among the analysed PTEs. The correlation coefficients (R^2) of PTEs in the sediments are shown in **Table 4**. The results indicate that As-Cr, Co-Cu, Hg-Co, As-Ni have significant correlations of 0.986, 0.960, 0.955, 0.976 in the level of P = 0.01, respectively. This suggests that the elements in association simultaneously increase or decrease in concentrations in the sediments, and the release of a particular element in the association may also cause the release of the other. For example, as As is released into the environment, Cr is also likely to be released (**Lapworth et al., 2012**). The remaining elements, either show no correlation or negative correlation.

4. Conclusions

Stream sediments collected from an active mining area in Okpella, Edo State, Nigeria showed a PTE concentration trend of Cu > Zn > Pb > As > Cr > Hg > Ni > Co. The pollution indices (EF and I_{geo}) used in assessing the level of pollution in the area revealed that Hg is a major pollutant of the sediments in the area. Minor enrichment of Cu, As and Pb are also present. As-Cr, Co-Cu, Hg-Co, and As-Ni tend to form elemental associations in the area. The observed PTEs' enrichments and pollution of the sediments, particularly by Hg, are mainly due to indiscriminate artisanal gold mining in the area. This may pose serious health hazards to humans and livestock in the area due to ingestion from its release into water and plants. These findings, therefore, call for the urgent need to remedy and/or control the level of pollution in the study area.

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