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ENVIRONMENTAL GEOCHEMICAL STUDIES ON THE EFFECTS OF COAL MINING IN AKWUKE- AWKANAWNAW, ENUGU, SOUTHEASTERN NIGERIA

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ABSTRACT: *Geochemical media such as water, soil, blackshales and plants were collected around Akwuke community in Awkanawnaw in Enugu area of southwestern Nigeria, and analysed for physicochemical parameters, inorganic ions /salts and heavy metal abundance. The ultimate goal was to investigate the geochemical environment and ascertain if the abandoned Okpara coal mine has any contamination effect on geoenvironment. The measured pH range of 3.98-4.42 renders the water as acidic to moderately acidic and consequently unsuitable drinking purposes, vegetation and aquatic life and wild life. Other physical and inorganic /organic parameters in water such as TDS, EC, Turbidity, TOC, total harness, Cl-, NO_3, PO_4, F, CN, Ca, Mg, Na and K all fall below recommended standard for potable water guidelines by WHO and EU and they do not portend any health threat to the end-users. Heavy metals results indicated that Fe comprise the most abundant metal in all the media except in plants where Zinc top the list. This is evidence that Fe is of main interest in all the media. It is only in soil sample s that the elements: Fe, Zn, Cr, Cd, Pb, Mn, Cu and Ni exceed standards by US EPA for agricultural soils. This high concentration of potentially toxic metals in soils and acidic water condition constitute a threat to the ecosystem. Specifically, acidic and Fe polluted waters are not benign for fish growth and survival of aquatic biota. Also, acidic and ferruginous waters corrode borehole installation materials and produce iron stained water with characteristic reddish colour and offensive odour. Assessment of the comparative heavy metal abundance in water plants, soil and black shale revealed that there is more heavy metal enrichment loading in soil than other media. The hazard potential is that soils serve as a source that can release heavy metals into other media by various processes of remobilization.Therefore, phytoremediation can be adopted in the for heavy metal attenuation in soils.*

KEY WORDS: geoenvironment, ecosystem, potentially toxic, phytoremediation

INTRODUCTION

Coal exploration activities started in Nigeria near Udi in 1909 by the mineral Survey of southern Nigeria. Also, between 1909 and 1913 more coal outcrops were located outcropping at intervals along the Enugu escarpment (Famuboni, 1996). Coal is a major by products in the chemical industry. Environmental geochemical studies encompasses the diverse factors that control the sources, dispersion and distribution of elements in the environment their pathways into soils, foodstuffs and water supplies and their influence on plant and animal health (Thornton, 1996).
Both the quality of coal and the effects of land disturbance caused by surface and underground

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coal mining differs from region to region (Turbak, et al 1979). Most of the coal mines which were actively developed in Enugu area from the early twentieth century were closed due to economic conditions or exhaustion of the ore resources and became important source of heavy metal contamination to the neighboring environment. Many mine were abandoned without any management of the waste materials and tailings. Environmental investigation and remediation of those areas is therefore urgently needed. The nearby Okpara coal mine to Akwuke community is an abandoned coal mine. Akwuke village is selected in this study for geochemical investigation of the extent of contamination by heavy metals in plants, soil, and water sources. The mine along with tailings and waste rock piles has been abandoned for upwards of twenty years without any remediation and the nearby village Akwuke has been used for cultivation of crops. Akwuke village is the immediate community around Okpara coal mine in Enugu. The source of drinking water is from hand dug wells and boreholes drilled within the community and from stream channels that run through the mine site Fig 1. Water drains the coal dump sites located along stream banks. Coal contains heavy metals which dissolved in acidic water with low pH values. Low pH values are due to the oxidation of pyrite (Adaikpo et al (2005) and Todd and Fall, (1997). The severity of the influx of untreated mine drainage on streams is based on factors such as frequency, volume and chemistry of the drainage and size of the buffering capacity of the receiving stream (Todd and Fall, 1997).

The ultimate aim of this study is to investigate the impact of coal mining activity on the environment and suggest remedial measures. Previous works by various workers such as Eziegbo and Ezeanyim, (1993), Onuoha, et al (2004), Sikakwe, et al (2015), Sikakwe, et al (2016) and Famuboni, (1996) among others discussed groundwater around Enugu Municipality and other parts of parts of Enugu area due to coal mining and mine drainage contamination in Okpara coal mine.

Study area description

Akwuke village is located within latitudes 6^0 24’ N and 6^0 22’N and longitude 7^0 26’E and 7^0 29’ (Fig, 1). Akwuke village is found in Awkananaw in Enugu which is at the eastern foot of a North-south trending cuesta that constitute a major surface and subsurface water divide for two hydro geologic basins; the Cross River and the Anambra basins toile to the east and the town respectively. The western edge is dominated by the Enugu escarpment. The escarpment is deeply indented by deep valleys and have been cut by headwaters of the Ekulu, Nyaba and Atafu streams near the sources of some tributaries (Adaikpo, et al 2005).

Akwuke village extends from Okpara coal mine site at an elevation of 234m drain by Orob and Nyaba stream at the mine site. The streams flow down gradient to Akwuke village. Akwuke village border with Gariki along Enugu/ PortHarcourt expressway at an elevation of 204m. Akwuke village is part of Awkanawnaw. There is a confluence of Nyaba and Orob Rivers at an elevation of 199m. There is Anyanaba and Ayo streams draining Akwuke village. The highest elevation was recorded at Okpara coal mine site and the lowest elevation at the village main square. The soil is lateritic. The topography of characterized by undulations with topographic lows and highs and traversed by deep gulley.

The study area has a warm climatic condition and experience dry and wet seasons. The wet season starts in April and terminate in October, while the wet dry season commence in

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November and end in March. The area is characterized by heavy rainfall in the wet season (Inyang, 1974). There is a mean annual rainfall of value over 1500mmm (Onwuka et al 2005).

Geology and hydrogeology

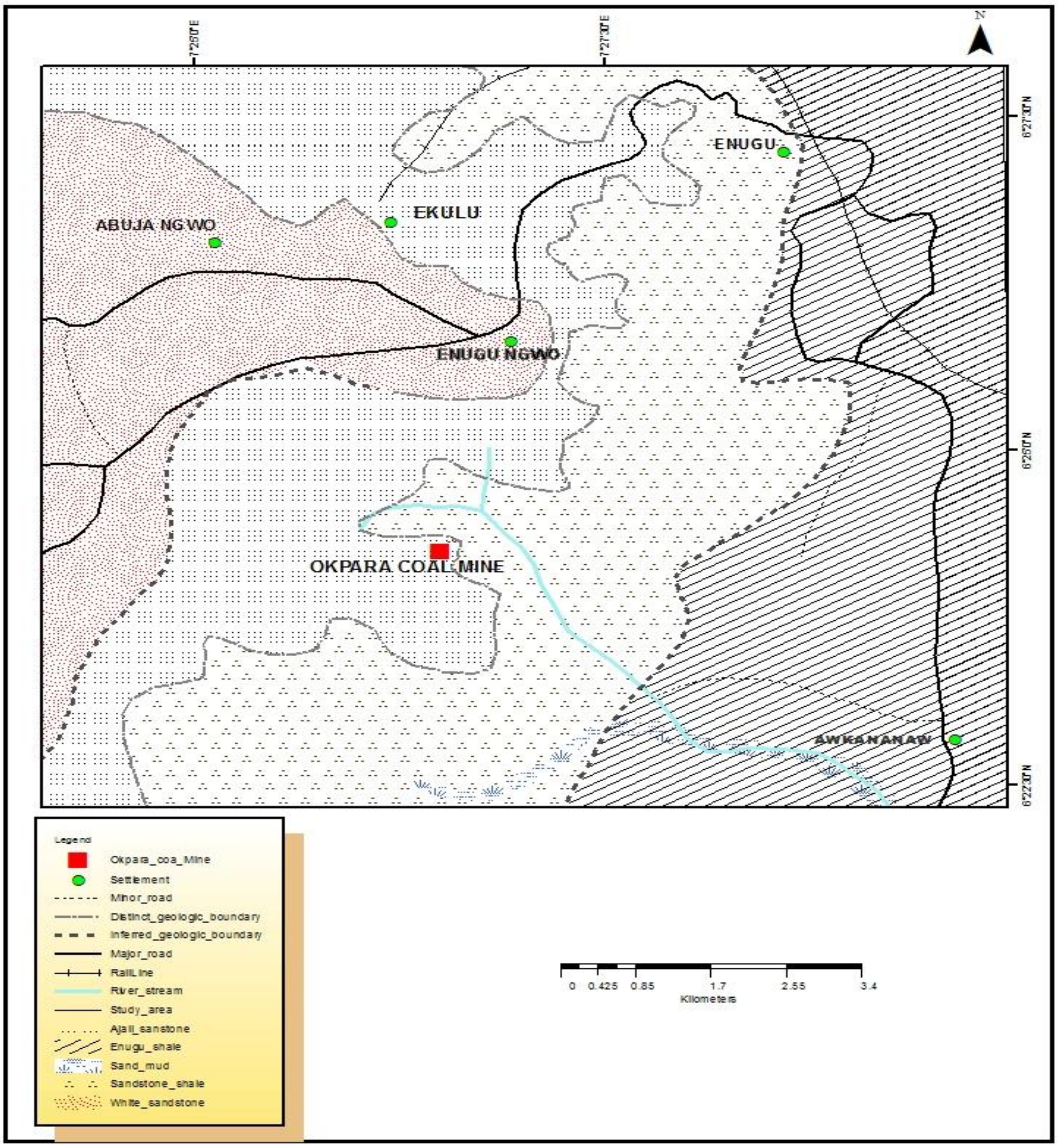

FIG. 1 Geologic map of the study area

Enugu urban is underlain by Enugu shales and mudstones. Intercalations of sandstones and sandy shales are reported by Reijers (1996) in the formation. The shales weathered rapidly to red clay soil which forms lateritic capping of considerable thickness (Ezeigbo and Ezeanyim, 2006). The two geologic formations underlying the Enugu area coal fields are the Mamu Formation and the Ajali Formation. The Mamu is the oldest formation in the coal fields with a maximum thickness of about 370m, which consist of sandstones, shales and mudstones. The

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Ajali Formation is the main aquifer in the area and contributes nearly all the groundwater entering the coal mines. It consist of unconsolidated poorly sorted, friable, white to grey sand stones exhibiting pronounced current bedding (Offodile, 2002).

The laterised overburden is porous and permeable and varies in thickness up to a maximum of about 20m depending on topography (Onwuka et al 2004). The overburden constitute the only known aquifer directly beneath the city of Enugu and has become an important source of water supply, the source of recharge is by rainfall. The depth to the water table is influenced by topography and seasons. Observation at the well construction site shows that the saturated thickness varies between 0-7m.

MATERIALS AND METHODS

Sample collection

Seven water samples, five shale samples, five soil samples, three types of plants species were collected from different locations across the study area. The water samples were collected from mine ponds stream channels, springs, boreholes and hand dug wells across the study area. Water samples were collected in clean plastic bottles. Two water samples were collected from each location, one acidified with three drops of concentrated HNO_3 to a ph of about 2 for analysis of cations. The unacidified was used for the analysis of anions. Physical parameters such as such as pH, turbidity, electrical conductivity, temperature and total dissolved solids were measured insitu using digital redox pH meter, spectrophotometer, conductivity, TDS meter and mercury in glass thermometer respectively.

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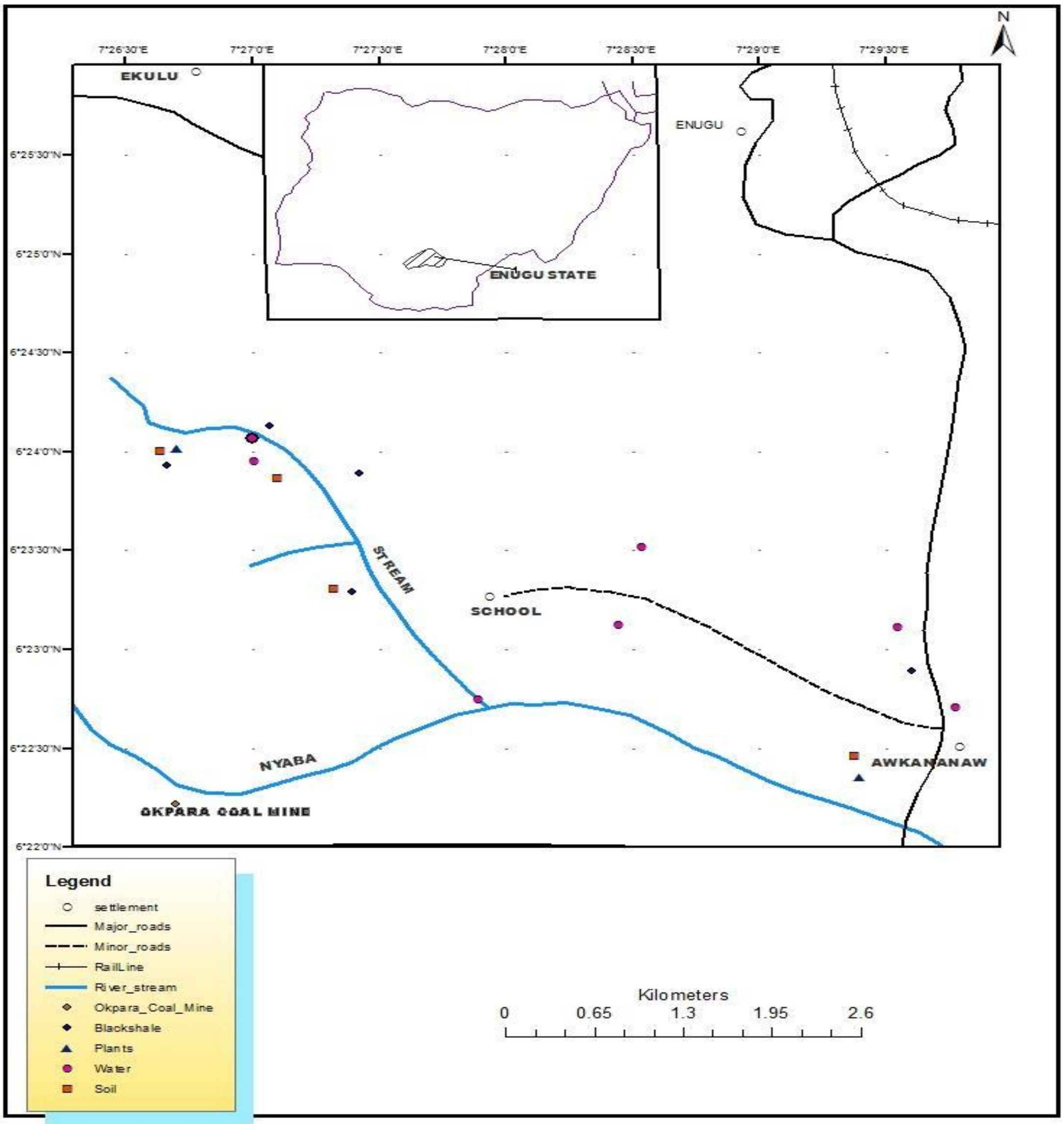

Fig. 2 Sample location map of the study area

Shale samples were collected using a geological hammer, soil samples were collected using a hand trowel. Three species of plants; kyllinga pumula, pteridium aquilinium and paspalu conjugatum were collected in six different locations.

Sample preparation

Water samples were stored in a cold refrigerator till the following day before being transported to a reputable laboratory for analysis. The shale samples were disaggregated with an agate motar and pistle after being sundried and the sieved with a 80 mesh sieve. The sieved samples were put in well labelled envelops for analysis in the laboratory.

A mass of 0.5g of powdered soil and shale were carefully labelled appropriately. The samples were moistened with few drops of deionized water and 10ml of concentrated 4m HNO3added

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into each beaker. Beakers were then with glass tubes and place in a sand bath covered with a hot plate into a fume cupboard. The mixtures were refluxed at moderate temperature (<100^0) for one hour and then evaporated at a temperature ranging between 180^0-190^0C into dryness forming a white cake. The white cake residue was leached with 5ml of 5m HCl into already calibrated labelled test tubes and made up to 10mlwith deionized water. The test tubes were then were then allowed to stand for a clear aliquot to separate out. The test tubes were then sealed with plastic stoppers. The digested samples were then analysed for anions and cations using equipment such as AAS for heavy metal analysis in soil black shale and plants. Anions and cations were analysed by titration and chromatography.

Laboratory analysis

Physical parameters in water such as pH, EC, turbidity, total dissolved solids and temperature were measured insitu using digital pH meter, conductivity meter, and mercury in glass thermometer respectively. Anions and cations were measured using titration, ion chromatography. Heavy metals in shales, soils and plants were measured using AAS. Sulphate was analysed using using turbidimeter method sodium and potassium were determine by flame photometric method. Chloride nitrate and hardness of water inform of calcium carbonate were determined by simple titration using the Merk field chemical kits.

RESULTS AND DISCUSSION

Hydrogeochemistry and water quality

Results of physicochemical parameters in water samples are presented in table 1 and hydrochemical facies of water samples in fig. 2. Levels of physical parameters shows that the temperature is almost constant ranging from 27^0-28.8^0C with a mean and standard deviation of 28.03+0.77. Location 1 sample point is located at Okpara mine site. The pH ranged from 3.98 to 4.50 with a mean and standard deviation of 4.28+0.17. Temperature and pH affects solubility of heavy metals and hence their mobility and dispersion (Udom, et al 1996). The pH values can be classified as acidic. This may be due to the oxidation of pyrite from coal mine dumps (Cathles, 1982). This is also evidence of little or no dissolved carbonate and hydroxide ions in the samples Malamo, et al 1990). Electrical conductivity values ranged from 503-2850us/cm, with a mean and standard deviation of 1334+882. Turbidity ranged from 0.04-0.40, with a mean and standard deviation of 0.23+0.34. In comparison, TDS had a mean value of 106.24+13.85 and ranged from 20-440mg/l.

Low values EC (503-2850us/cm) with a mean of 1334us/cm as opposed to WHO standard of 2500us/cm is indicative of low dissolution of heavy metals in the study area (Siegel, 2002). Ezeigbo and Ezeanyim, (1993) reported EC value of 1550us/cm in surface water in Okpara coal mine. Low TDS can be explained by low dissolution of sulphates, calcium and bicarbonates (Keating, 2001). Low turbidity values in the area is due to low amount of suspended iron tailings caused by stream sediments. All the mean value of the physical parameters were below permissible limits set by WHO, USEPA, EU for potable water, with the exception of pH which exceeded permissible limits set by World guidelines for potable water ((Table 1).

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Table 1 physicochemical parameters of water samples from the study area

Parameter	1	2	3	4	5	6	7
Temperature (^0C)	27.3	28.8	28.7	27.0	28.5	28.0	28.3
pH	4.31	4.50	4.35	4.27	4.42	3.98	4.11
EC (Mv)	974	503	779	1180	916	2850	2140
Turbidity (NTU)	0.08	0.40	1.00	0.04	0.04	0.04	0.040
TDS (mg/l)	24.0	40.0	440	60	20	100	60
NO_3^- (mg/l)	11.47	9.18	11.03	10.15	11.47	14.12	12.35
SO_4^{2-} (mg/l)	1.38	6.20	10.30	11.20	1.38	296.20	158.45
PO_4^- (mg/l)	0.041	0.05	0.099	0.12	0.083	0.083	0.091
Cl^- (mg/l)	100	40	250	150	530	100	60
CN (mg/l)	0.08	0.12	0.16	0.12	0.04	0.08	0.12
F “	0.08	0.04	0.12	0.06	0.04	0.08	0.04
TOC “	0.00036	0.0019	0.0014	0.0014	0.0016	0.0014	0.00096
Na^+ “	1.16	1.04	2.09	1.19	1.02	1.21	1.16
Ca^{2+} “	20.02	14.01	6.01	10.01	16.02	12.02	20.02
K^+ “	0.803	0.692	0.914	0.813	0.785	0.884	0.826
Mg^{2+} “	6.032	6.026	4.014	16.04	26.07	16.04	6.03
Total hardness “	65.07	50.05	25.02	65.06	105.10	70.07	70.70
Fe “	0.092	0.106	0.483	0.148	0.257	0.316	0.094
Zn “	0.045	0.062	0.128	0.088	0.093	0.104	0.042
Cr “	0.000	0.006	0.019	0.011	0.005	0.010	0.042
Se “	0.010	0.002	0.012	0.004	0.002	0.008	0.00
Cd “	0.000	0.000	0.002	0.000	0.000	0.002	0.000
Ba “	0.000	0.000	0.004	0.002	0.000	0.003	0.000
Mo “	0.004	0.002	0.008	0.005	0.004	0.003	0.000
Pb “	0.000	0.000	0.008	0.000	0.002	0.003	0.000

Mean values of anionic chemical parameters such as sulphates (69.30+0.6, phosphate (0.07+0.04), Chloride (175+84.3, cyanide (0.10+0.004), fluoride (0.07+0.03 (Table 2) were below world standards for potable water except cyanide. The major cations recorded concentrations of Na (1.27+0.30, Ca (14.0+4.78), K (0.82+0.07) and Mg (11.46+7.6). all the mean cation values are below world standards for potable water. Total hardness recorded a mean and standard deviation of 64+22.30 and ranged from 25.02-105.10 it is below the standard of 200mg/l prescribed by EU for potable water. Low sulpahate values recorded in the study can be attributed to insufficient pyritization and also due to its relative mobility in water (Siegel, 2002). Turbak and MC Fetters (1979) reported a sulphate value of 6.79mg/L in a sedimentation pond in Montana coal mine while Eziegbo and Ezeanyim and Ezeanyim (19930 obtained a value of 420mg/l in Okpara mine compared to a mean value of 69.3mg/l recorded in this study. Phosphate is a natural constituent of water but usually very low. The low level of phosphate in the area can be explained by the absence of phosphate fertilizers (Udom et al 1996). Source of nitrate are legumes and nitrogenous fertilizers. Nitrate in excess of 50mg/l is

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hazardous to health. Low chloride mean value of 175.71mg/l in the area is explained by it low mobility in water. The sources of chloride are probably coal vitrains (Zielinski, 2001). Onwuka, et al (2004) reported a value of 230mg/l of chloride in Enugu town relative to the value of 175.7mg/l obtained in this study.

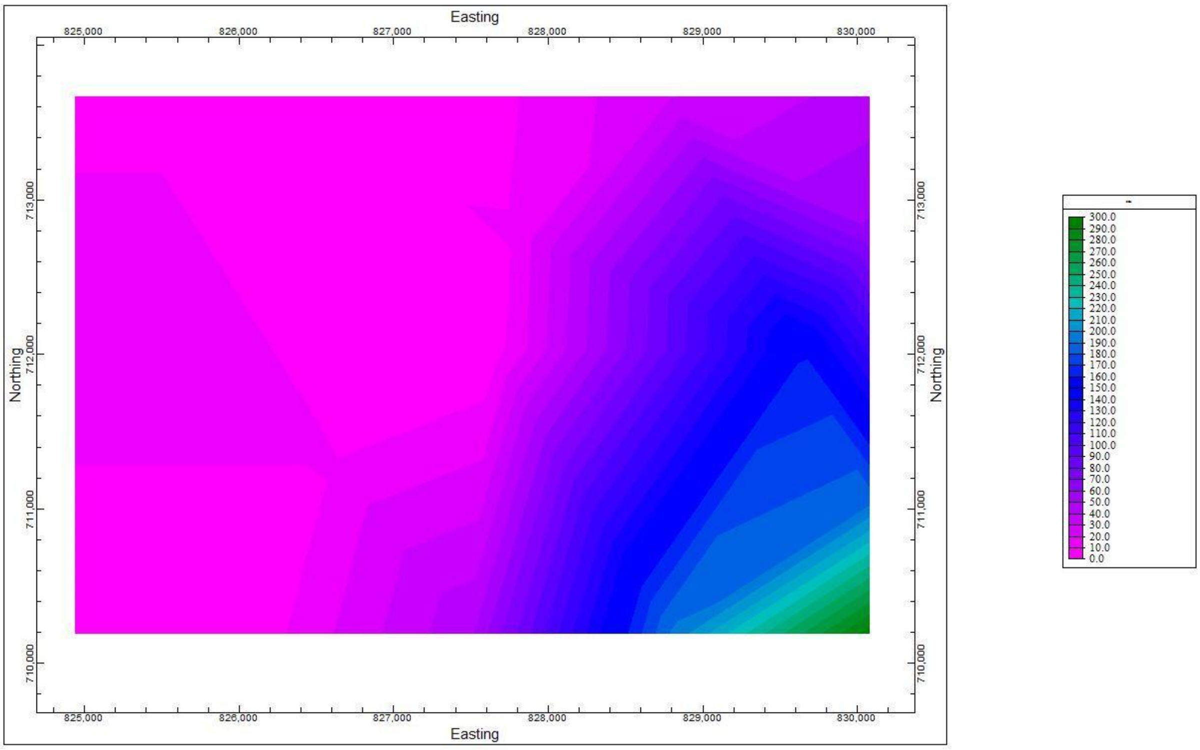

Fig 3 spatial distribution of sulphate in water samples of the study area

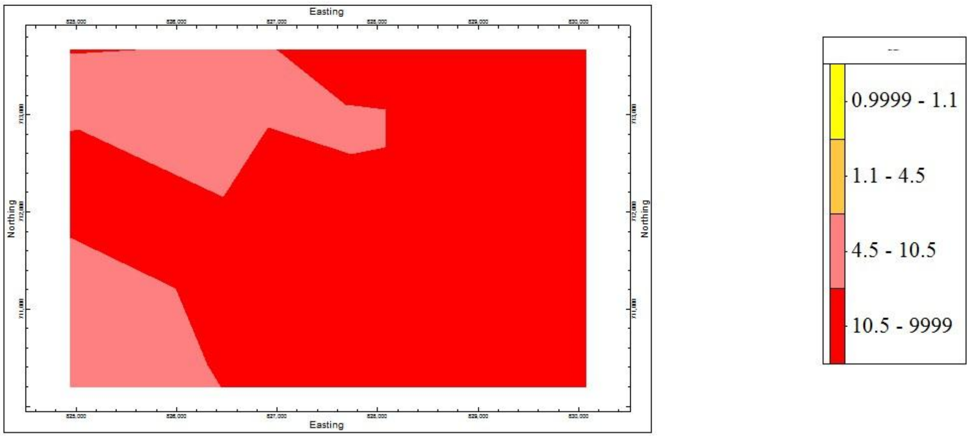

Fig. 4 Distribution of NO_3 concentration in the study area

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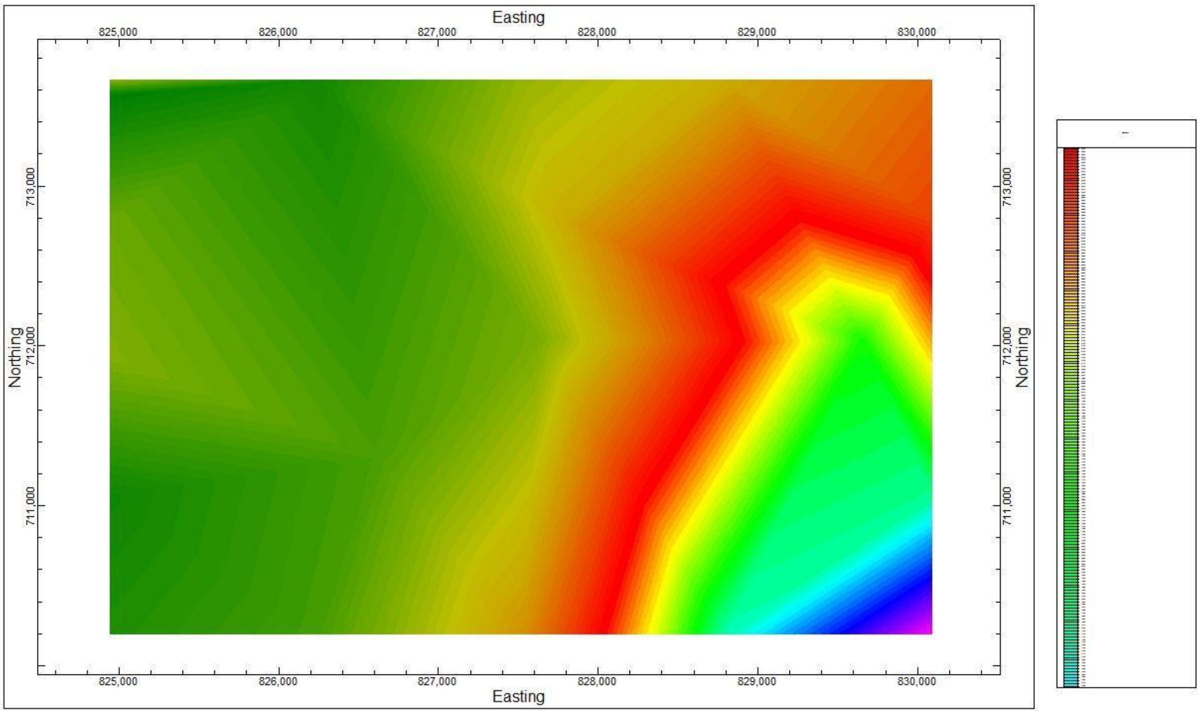

Fig. 5 Distribution of EC in the study area

Statistical summary of physicochemical parameters in water

Table 2 statistical values of physicochemical parameters of water samples

parameters			Range	Mean	WHO	EU
Physicochemical Parameters	Temp ^{0}C	7	27-28.8	28.03		
	pH	7	3.98-4.42	4.28	65.05	
	EC (us/cm	7	779-2850	1335	1400	
	TDS (mg/l)	7	20-440	106.3		250
	Turbidity (NTU)	7	0.04-1.00	0.23		
	TOC	7	0.0036-0.0019	0.001		
	Total Hardness(Mg/l)	7	25.2-105.1	64.44		
Major inorganic /salts (Mg/L)	Cl^-	7	40-250	175.71	250	250
	SO_4^{2-}	7	1.38-158.45	69.30		250
	NO^{3-}	7	9.18-14.12	11.40	50	50
	PO_4^{3-}	7	0.041-0.12	0.07	1.00	
	CN	7	0.04-0.16	0.10	0.07	
	F^-	7	0.04-0.12	0.07	1.5	
	Ca	7	6.01-20.02	14.01	75	
	Mg	7	4.014-26.07	11.46		
	Na	7	1.02-1.16	1.27		200
	K	7	0.692-0.914	0.82		

This disparity may be explained by seasonal variation. Fluoride occurs in industrial fumes. Excess fluoride causes teeth mottling. Above 4-6mg/l it reduces the prevalence of osteoporosis and collapse vertebrae. Deficiency causes pain and tenderness of bones (Keller, 1976).

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Cyanide concentration had a mean and standard deviation of 0.10+0.04. Cyanide values in all locations exceeded permissible value of 0.07mg/L for potable water by WHO 2006, except in location 5 where it recorded a value of 0.04mg/L. the source of cyanide could be from natural sources. It can be secreted by bacteria, algae, fungi, plants and insects. Therefore, low levels of cyanide can appear in naturally occurring surface and groundwater samples which would not be expected to contain it. Species of plants such as cassava, corn, beans and potatoes are cyanogenic. Cyanide is not persistent in soil and water. Cyanide volatilizes by oxidation precipitation effects of sunlight causes cyanide degradation (Siegler, 1976). Total organic carbon is low in the study area. Only TOC levels >4mg/l call for remediation. TOC, pH and alkalinity levels are the controlling factors in determining the effectiveness of enhanced coagulation for a particular water source (WHO 2007). At TOC >4 mg/l it is likely that total halo methane levels exceed 100ug/l in water (GCDWQ 2015).

Cations

Major cations such as Na, Ca, K and Mg ranged very low in water samples (Table 2). The values fall below permissible standards for potable water (Table 1). Sodium had a mean of 1.27mg/l. the highest value was obtaine in location 3 (Akwuke Village). Calcium (14.01+4.78), Mg (11.46+7.60) recorded higher levels than other cations. The mean level of K in the area was 0.82+0.07 potassium ranged from 0.692-0.914. calcium is a biophile, the low value can be explained by low dissolution of feldspathic minerals with which the surface water comes in contact with (Udom et al 1996). Magnesium is probably from magnesium carbonate. Calcium and magnesium are responsible for temporary and permanent hardness of water. Pagenkopt and Whiteworth (1977) reported values of 53 and 28mg/l of calcium and magnesium respectively in the Tongue River near Decker coal mine. The highest concentration of magnesium was obtained at location 5 (borehole) at Christian Nwoye's compound and the least value (6.03mg/l) at location 7 (hand dug well) at Gariki Akwuke road Awkanawnaw near menax meat shop. Calcium recorded the highest concentration of 20.02mg/l in location 7 (Menax meat shop) and a least value of 6.01mg/l in location 3 (Nyaba Orob Rivers confluence). Next on the line is Sodium with a highest value of 2.09mg/l in location3 and least value of 1.02mg/l in location 5 (borehole at Christian Nwoye compound. Also K had the highest concentration of 0.914mg/l in location 3 (Orob/Nyaba Rivers confluence and least value of 0.692mg/l in location 2 (Okpara mine pond). Calcium and magnesium ae the dominant cations recorded in the study area which squares with the findings of Ezeigbo and Ezeanyim (1993) in the study area. From Table 2 it is evident that the major cation trend is in the order: Ca>Mg>Na>K in this study and this is consistent with the findings of Rose and Cravotta (1998) in Pennsylvania coal mine water.

Anions

Nitrate recorded a highest value of 14.12mg/l in location 6 (spring water near Enugu Port Harcourt expressway). And the least concentration of 9.18mg/l in location 2 (Okpara mine pond the highest concentration of sulphate (158.45mg/l) was obtained at location 7 (Gariki Akwuke road near Menax meat market and the lowest value of 1.378mg/l at location 1 (Okpara coal mine pond). Phosphate concentration recorded maximum value (0.124mg/l) at location 4 (Anyenaba spring) and least value of 0.041mg/l at location 1. Chloride maximum concentration of 530mg/l was recorded at location 5 (borehole at Christian Nwoye's compound) and the lowest value of 60mg/l at location 7 (Gariki Akwuke road). Moreover, the highest value of

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cyanide was recorded at 3 and the lowest value at location of 0.04mg/l at location 5. Furthermore, fluoride maximum concentration (0.12mg/l) was obtained at location 3 and lowest value of (0.04mg/l) at locations 2, 5 aand 7. The TOC of water samples recorded a maximum value of 0.044mg/l at location 4 (Anyenaba spring) and the lowest value of 0.00036mg/l at location 1.

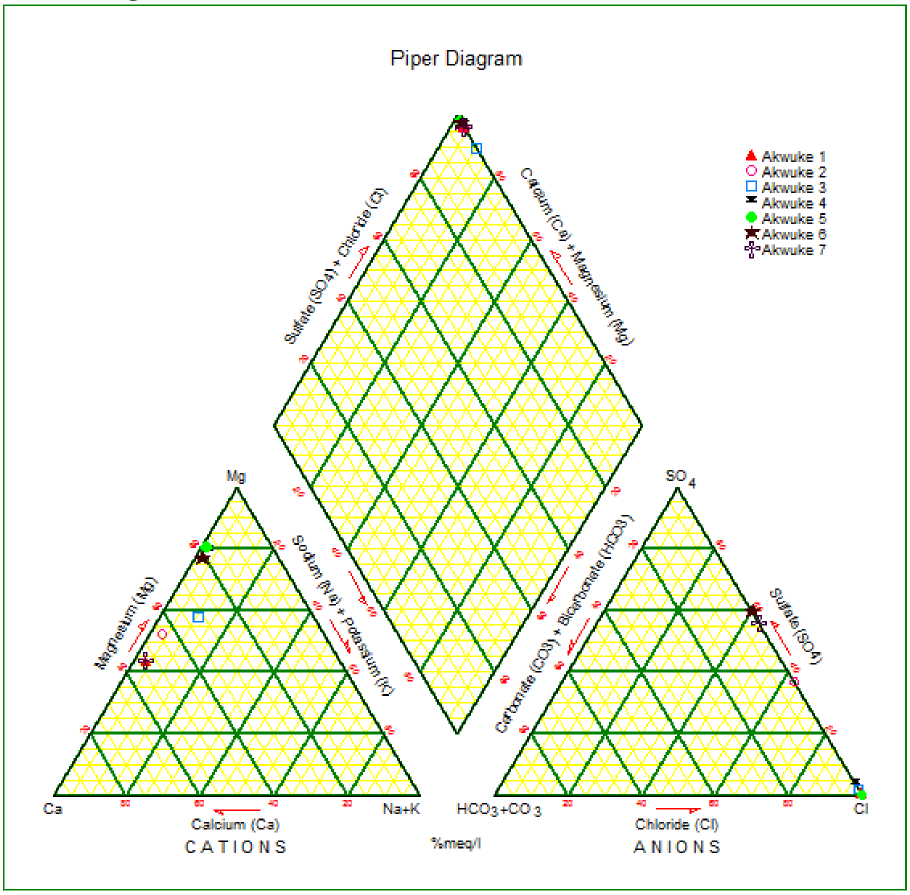

FIG. 5 Piper diagram showing hydrochemical facies of water samples from the study area

To further evaluate and interpret the shallow water composition in the study area major ions were expressed in units of mill equivalent per litre (Meq/L) and plotted on Piper diagram (Fig. 2). Details on the geochemical interpretation of water samples on the Piper diagram can be found in Piper (1944) and Hem, (1985). As indicated in fig.2 the hydrochemical facie of the study area displayed high Mg+SO4. Some of the locations displayed high concentration of Cl and SO4 anion. In the cation region displayed higher concentration of Ca+Mg. this shows that the study area is predominantly Ca+Mg-Cl+SO4 hydrochemical facie. The mineral water is dominated by Mg, Cl and SO4 ions. These squares with findings of Ezeigbo and Ezeanyim (1993) in Okpara coal mine and Woo, et al (2002) who reported Ca+Mg, SO4 water types near a coal mine.

The mean value of total hardness (64.44mg/l) recorded in water samples in this study is below WHO 2007standard of 200mg/l for potable domestic and irrigation purposes. Total hardness in all the locations also fall below this value of 200mg/l.

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Heavy metals concentration in water, plants and soil samples (mg/kg)

Table 3 Statistical values of heavy metals in water, soil, p;ants and blackshales from the study area

	Water			Plants			Soil			WHO	EU	Black shale			
Parameter Mg/l	N	Range	Mean	N	Range	Mean	N	Range	Mean			N	Range	Mean	Background value
Fe	7	0.092-0.483	0.214	6	0.27-0.63	0.442	4	1.52-8.56	7.177	-	0.2	5	4.94-5.50	4.61	4.72
Zn	7	0.045-0.128	0.080	6	1.4-1.85	1.638	4	4.85-6.10	5.292	-	-	5	3.15-3.66	3.43	95
Cr	7	0-0.019	0.013	6	0.01-0.06	0.03	4	1.08-1.21	1.140	0.05	0.05	5	0.60-0.75	0.40	90
Se	7	0.002-0.012	0.005	6	0.01-0.02	0.013	-	-	-	0.01	0.01	-	-	-	-
Cd	7	0-0.002	0.001	6	0.02-0.04	0.028	4	1.22-1.57	1.370	0.003	0.005	5	0.69-1.13	0.95	0.3
Ba	7	0-0.004	0.001	-	-	-	-	-	--	0.07	-		-	-	-
Mo	7	0.003-0.008	0.004	-	-	-	-	-	-	0.07	-		-	-	-
Pb	7	0-0.008	0.002	6	0.02-0.43	0.097	4	4.11-5.33	4.602	0.01	0.01	5	2.20-3.70	2.94	20
Ni	-	-	-	6	0.01-0.09	0.038	4	0.76-1.05	0.712	0.07	0.02	5	0.33-0.67	0.34	50
Cu	-	-	-	6	0.45-0.67	0.573	4	1.10-1.23	1.150	2.0	2.0	5	0.70-1.00	0.30	45
Mn	-	-	-	6	0.33-0.53	0.457	4	2.61-3.30	2.950	0.4	0.05	5	0.90-1.75	1.32	850

The distribution of heavy metals in the sampled media (water, plants, soil and baclshales are summarized in table 3 and compared with maximum permissible levels for potable water by WHO 2006 and EU (2004) and average values of uncontaminated shales (Turekian and Wedepohl (1961). As presented in table 3 heavy metal analysis in water samples show a trend of Fe>Zn>Cr>Se>Mo>Pb>Cd>Ba. In this light Fe is depicted as the most abundant heavy

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metal in water and Ba are the least (Table 3). none of heavy metal in water exhibited mean concentrations above levels prescribed both WHO and EU for potable water with exception of Fe that possess mean concentration slightly above permissible levels by those world guidelines. Naturally, heavy metals should be dissolved in acidic waters, but processes such as co precipitation, and desorption could lead to attenuation of heavy metals concentration in acidic waters (Sikakwe, et al 2015). The findings in this study that Fe is the most abunce elements in water could be explain as the proximity of the area to Okpara coal mine. Research on the dominance of iron in water is also supported be the findings of Rose and Cravotta, (1998) and Adaikpo, et al 2003). The acidic nature of the mine waters and Fe content can cause corrosion to borehole installation materials also acidic water can impact on aquatic biota (Baller and Schofield 1982, Atkins and Singh 1982). Ferruginous waters are responsible for the formation of scales in the delivery pipes as well as pollution of surface environments.

The mean levels of Fe and Zn in plants (Table 3) which are respectively given as 0.442mg/l and 1.638mg/l are lower by 10.68 and 58 times the background values of (Turekian and Wedepohl, 1961). Similarly, the respective mean levels of Fe, Cd, given as 7.275mg/kg and 1.345mg/kg are higher by 1.52 and 4.57 times the respective background values. In blackshales the mean value of Fe (4.61mg/kg), Cd (0.95mg/kg) shows that Fe is almost equal to the background value while Cadmium is 3.17 times higher than the background value. Apart from these specified chemical species the values of all other chemical constituents in soils plants and blackshales are within permissible limits of the relevant guidelines standards. Heavy metal concentration in mg/kg in plants are in the following order: Zn>CU>Mn>Fe>Pb>Ni>Cd>Se, while those in soil are in this order: Fe>Zn>Pb>Mn>Cd>Cu>Cr>Ni. In blackshales the trend is in the order of Fe>Zn>Pb>Mn>Cd>Cr>Ni>Cu (Table 3).

Chemical analysis shows that Fe is the most abundant in chemical specie in soil and blackshales while Zn took the lead in plant. Se, Ni and Cu are the least in plants, soil and blackshales respectively. The predominance of Fe in most media is in consonance with the views that Fe is common in coal mine drainage, since flowing streams in the area drain Okpara coal mine which is away from the study area. The implication in having high Fe content of soils and blackshales portends that the precipitation of ferric hydroxide may result in Fe contaminated water in borehole and streams. Also of particular interest is the enrichment loading of various magnitude of heavy metals (Zn, Cr, Cd, Se, Mo, Ni, Cu and Mn) in plants soil and blackshales samples compared to their corresponding levels in water. The relative enrichment of heavy metals in soils than water and plant is evidence that sorption of heavy metals in soils and blackshales is higher than in plants and water (Sigel, 1974).

The higher mean values of Zn and Cu in soil than in plants: paspalu conjugatum, kyllinga pumula and pteridium aquilinium shows that the plant species are not good accumulators of these elements but are sorbed in soil. Fe, Zn, Mn and Mo levels exhibited higher concentrations in the plant species around the Port Harcourt expressway than at the mine site. This may be due to oxidizing environment, and relative mobility and anthropogenic input. On the contrary Pb, Cr, Ni, Cu and Cd possess higher concentrations in plants at the upstream part of the study area than the downstream. This could be explained by the presence of coal mine dumps in the upstream part (Salami, et al 2007). Values of potentially toxic metals Fe, Cr, Cd, Pb, Cu, Ni and Mn established in this study are within the normal range for plants (Chon et al 1999).

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Kyllinga Pumula plant species had higher heavy metal levels than the paspalu conjugatum and pteridium aquilinium in this study.

Trace elements bioavailability in soils is influenced by pH, redox condition, organic matter and the presence of competing elements such as Ca, Mg and P and in low pH <3 soils the bioavailability of Cd, Co, Cu, Ni and Zn is high (Bhattacarya et al (2006). Low pH are recorde in this study that explains the high levels of Zn, Cu and Ni in soils. The presence of blackshales in the study which contain oxidation of sulphate minerals in blackshales could generate acids and consequently lower the pH of groundwater (Woo, et al 2002). This is the probable reason why low values are recorded in the study area. Blackshales have strong environmental geochemical effects on soils and water, plants readily take up trace elements from these soils and water where they grow (Fang, et al 2001). The trace element enrichment loading in plants in the area must have been largely contributed by this means.

CONCLUSION

From the foregoing it is obvious that minor effects of acid mine drainage from Okpara coal mine and environmental geochemical effect of blackshales underlain in the study area has effect on water quality in the study area by low pH values. The low pH values makes the water to fall below the world standard guidelines for potable water. Low pH value affect vegetation and aquatic life. The concentration of other ionic species such as sulphate, phosphate, nitrate and chloride fall within acceptable limits for potable water. The excess Fe and acidic nature of sampled water is not conducive for to fish growth and sustenance of the aquatic biota among other deleterious effects. Ferruginous and low pH waters are also susceptible to corrosion of borehole installation materials and the production of Fe water with characteristic colouration and offensive odour. Mean values of heavy metals in water, plants, soil and blackshales shows that low concentration of heavy metals were obtained in water, but the values of heavy metals in in plants surpass those recorded in plants. The plant species; Kyllinga Pumula, paspalu conjugatum and pteridium aquinalium show low heavy metal accumulation ability. Analysis also shows that heavy metals are sorbed in soils showing a higher concentration of this potentially toxic metals in soils than in water and plants.

Heavy metals obtained in blacshales are were lower than those recorded in soils. Generally, soils exhibited the highest heavy metal concentrations than other sampled media. It is evidenced that the black shales are weathered and this weathering caused an enrichment loading of heavy metals in soils. Potentially toxic heavy metals such as Mo, Mn, Pb, Fe, Cd, Cu and Cr attained mean concentrations exceeding the permissible levels for suitable soils for cultivation purposes (USEPA 2006). This is evident that the source of heavy metal release into water and absorption by plants is from the soil. For the reduction of potentially toxic elements in in the study area in soil, phytoremediation can be adopted for attenuation of the heavy metal species in soils for cultivation purposes.

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