

THE PRELIMINARY ASSESSMENT OF THE POLLUTION STATUS OF STREAMS AND ARTIFICIAL LAKES CREATED BY MINING IN THE MINING DISTRICT OF ENYIGBA, SOUTH EASTERN NIGERIA, AND THEIR CONSEQUENCES

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ABSTRACT

The distribution of Pb, Zn, Cu, Cd, Ni and As in waters and sediments in streams and entrapped water bodies around the mining district of Enyigba was evaluated. The result of analyses show that the concentration of Cu varies from 0.006 to 0.100 mg/l in waters in streams and mine pits (surface water), with a mean of 0.02 mg/l; Zn from 0.008 to 0.023 mg/l with a mean of 0.01 mg/l. The concentration of Pb, Ni, Cd and As in all samples of surface water is lower than 0.001 mg/l. The concentration of Pb in sediments vary from 54 mg/kg to 63356 mg/kg with a mean of 4245 mg/kg; Zn from 72mg/kg to 1386.5 mg/kg with a mean of 349.68 mg/kg; Cu from 11.5 mg/kg to 808.5 mg/kg with a mean of 84.48 mg/kg; Cd from 0.5 mg/kg to 5.5 mg/kg with a mean of 3.35 mg/kg; Ni from 0.5 mg/kg to 1197 mg/kg with a mean of 282.66 mg/kg and As from 0.05 mg/kg to 1.5 mg/kg. It is established that there is no significant pollution of surface water by heavy metals analysed, based on WHO Standard of 1993. There is however significant pollution of sediments by Pb, Zn and Ni and to a smaller extent Cu. The consequences of the observed pollution include the introduction of pollutants in the downstream reaches of the streams and the Ebonyi River during the periods of high flow, the accumulation of the pollutants in the tissues of organisms that live in the sediments which may get passed to higher organisms that prey on these organisms and the eventual effect on humans, through the food chain.

KEYWORDS: Lead-zinc mineralisation, hydro-geochemical survey, sediment survey, pollution status, enrichment index and food chain.

INTRODUCTION

Background to the Study

The inhabitants of Enyigba are historically farmers. Pb – Zn mining have however become important as well as salt making because of existence of Pb - Zn mineralization and salt springs in the area. Activities of small scale miners have left behind numerous artificial ponds and pits, which form sources of drinking water for the inhabitants, especially during the periods of water scarcity. Traditionally, Pb, Zn, Cu, Cd, Ni and As are associated with Pb – Zn mineralisation. These activities are capable of mobilising these elements, polluting soils, stream

waters and stream sediments. It is therefore necessary to assess the level of these metals in the stream networks in the area. The case of pollution of soils in Enyigba by Pb, Zn, Cd and to lesser extent Cu, is well established (Chukuma, 1994; Ezeh *et al.*, 2007). In terrestrial ecosystem, soils are the major recipient of heavy metals; while in aquatic systems, sediments are the major sink for metals (Sparks, 2005). From these, the metals can impact fresh water and groundwater systems. Fresh water systems are impacted due to runoff and drainage via sediments. In these systems they may change form or speciation and become available to the food chain, thereby affecting life, by causing

chronic and acute disorders. The sources, fluxes and pathways of these metals are important to assess pollution and appraise the possible health impacts of concentrations of these metals in this area.

Objectives of the study: The objectives of the study are as follows:

1. To establish the distribution patterns of Pb, Zn, Cu, Cd, As and Ni in surface waters especially in streams, ponds, artificial lakes left behind by the activities of small scale miners and stream sediments, in the area.
2. Assess the pollution status of stream waters by comparing their metal concentration with the WHO standards of 1993.
3. Assess the pollution status of stream sediments by use of sediment quality guideline established by Long *et al.* 1995.
4. Appraise the consequences of any established pollution

Study Area

Location

the study area is the mining district of Enyigba. Enyigba is 14 km south East of Abakaliki in South East Nigeria. The area of study lies between latitude 6° 07" N and 6° 12" N and longitude 8° 05" E and 8° 10" E.

Physiography

The relief of the area is undulating but with isolated hillocks that rise up to 200 m above sea level. There are two marked seasons in the study area, the dry and wet seasons. The wet season begins in March and ends in October. The dry season begins in October and ends in February. These two seasons are dependent on the two prevailing winds blowing over the country

at different times of the year. The dry hammattan wind from Sahara Desert prevails in the dry season. In the rainy season, the significant wind is the marine wind from the Atlantic Ocean. Temperature in the dry season ranges from 20°C to 38°C and during the rainy season 16° to 28°C. The average monthly rainfall ranges from 31mm in January and 270mm in July. The average annual rainfall varies from 1750mm to 2250mm. The vegetation of the area is Parkland, which is derived savannah. This is characterised by stunted trees and pockets of derelict woodland and secondary forests consisting of few shrubs with dispersed large trees and climbers. The major rivers in the area are the Akpara Izzi, Nwonyi Offia, Iyinu, Ikpete and Akpara Ezza. These are secondary tributaries of the Eastern Ebonyi Rivers which is located east of the area (Fig. 1). Akpara Izzi and Akpara Ezza are perennial streams, while the others are seasonal streams. They form the major sources of water for drinking, agriculture and other municipal purposes.

Geology

The lithology of the area comprises rocks of the Albian Asu River Group (Fig. 1). This consists of dark sandy shales, with fine grained micaceous sandstone and mudstone. The shales are often calcareous and pyritic. The Group is known to be associated with Pb – Zn mineralization. The rocks are extensively fractured, folded and faulted. There are known in Enyiba, eight Pb – Zn lodes which make up a part of the Abakaliki Pb – Zn deposits (Fig. 1). Apart from the main Enyigba lode, others are at Ameri, Ameka, Ikwo, Palmwine, Nine pence and Portuguese lodes (Orajaka, 1965).

METHODS

Hydro-geochemical survey: Water surveys were carried out in the following streams: Ameri, Nwansa, Akpara Ezza, Akpara Izzi and Amoji

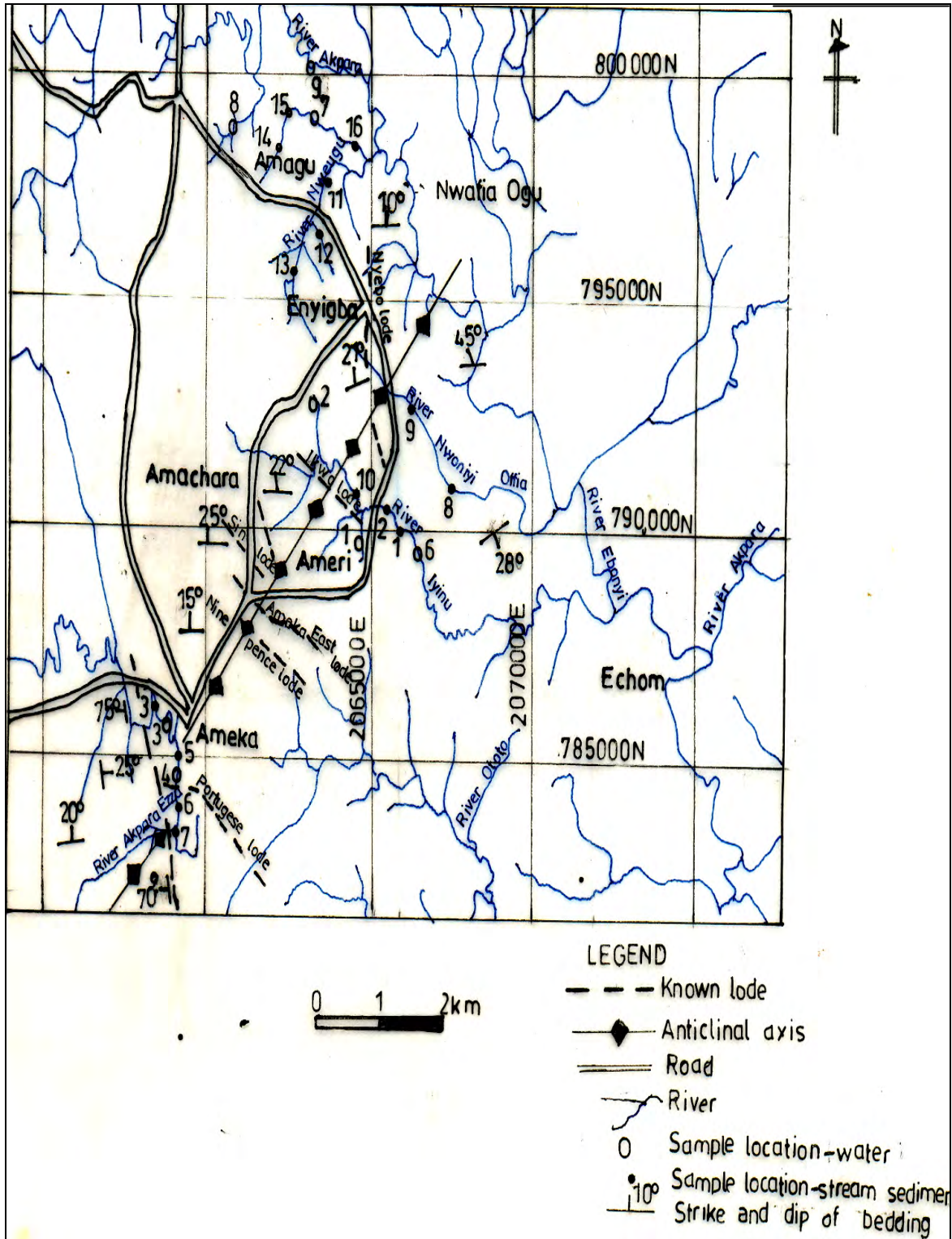


Fig. 1: The geology of Enyigba Pb – Zn Province (modified from Orajaka, 1965), with the location of sample points.

streams; ponds: Nwerugvu pond and artificial lakes left behind by the activities of small scale miners: Ameri Mining pits 1 and 2 in rainy season, 2005. 20 mls of water was collected at each point in hard polyethylene bottles. The bottles were cleaned by rinsing with strong metal-free 0.1M, HNO_3 before taking them to the field. At the point of collection the temperature and pH of the water was measured. The bottles were rinsed three times with the water being sampled before the samples were taken. The samples were acidified with few drops of metal-free 0.1M, HNO_3 upon collection to prevent metals loss through their adhesion to bottle surfaces. Acidification also releases into solution metal ions adsorbed onto suspended clays (Levinson, 1974), possibly by replacing the metal ions with H^+ from the acid. It also dissolves some metal containing colloids and soluble minerals. In this way some of the elements, which might have been lost or discarded, are available in true solution for analyses (Levinson, 1974). These samples were stored in the refrigerator and analysed within four days of collection by use of Buck Scientific Atomic Absorption Spectrometer 205 for Pb, Zn, Cu, Cd, Ni and As in the laboratories of Ideyi Consults in Port Harcourt, Nigeria.

Stream sediment surveys

Stream sediment sampling of these rivers was carried out in December 2005. A hand auger was used to scoop fine sediments from the stream beds. A handful of these fine sediments were put in polyethylene bags and labelled. A total of 23 samples were collected from all the streams. In both surveys, samples were picked in areas around the known Pb – Zn lodes.

Preparation of stream sediment samples

To dry the samples, they were laid out in pre-numbered evaporating dishes and placed in low temperature oven and maintained at 105°C for 12 hours. Each sample was disaggregated and homogenized by use of agate pestle and mortar. Ukpong, (1981) demonstrated that for sediments from the Benue Trough, the optimum grain size to achieve best geochemical contrast is the 120 mesh. That level of geochemical contrast is needed in exploration for mineral deposits. In environmental research with the purpose of assessment of total elements concentration, it is necessary to use a broader screen value (Mendham, 2000; Okoronkwo *et al.* 2005, 2006). The homogenised samples were passed through

a 100 mesh nylon screen. This will help extract metals from the <100 mesh fractions which is considered highly adsorptive fraction. The nylon screen was used to avoid contamination. The samples were digested by use of aqua regia based on standard methods described in Mendham, (2000). 0.5g of the screened samples was weighed out and placed in 20 ml beaker. 10 ml of aqua regia was added and steered. This was gently boiled on hot plate to a volume of 2.5ml. 10ml of deionised water was added and gently boiled to the volume of 5ml. This was kept to cool and thereafter filtered into 50ml measuring cylinder. Beaker and filter paper was washed into the cylinder to a level of 12.5ml. Deionised water was added to make up to 25ml. The aliquot was also analysed by use of Buck Scientific Atomic Absorption Spectrometer 205 for Pb, Zn, Cu, Cd, Ni and As in the laboratories of Ideyi Consults in Port Harcourt, Nigeria. The result of the analyses of the digests which was given in mg/l was converted to concentration of the metals in mg/kg of dry sediment.

RESULTS

The result of analyses for Cu, Zn, Pb, Cd, Ni and As in the surface waters and sediments are presented in Tables 1 and 2 respectively.

Surface water

Copper was present in all the samples of surface water from Enyigba. The range of concentration in surface water is from 0.004 – 0.026 mg/l with mean concentration of 0.02 mg/l. The concentration of Pb in all the samples of surface water in Enyigba is below the detection limit of the instruments. The range of concentration of Zn in samples of surface water is from 0.006 – 0.023 mg/l with mean concentration of 0.01mg/l. The concentration of As in 80% of all samples, Ni and Cd in all samples of surface water are below the detection limit of the analysing instrument.

Stream sediments

The range of concentration of Cu in sediments is from 11.5 – 808.50 mg/kg with mean concentration of 84.46 mg/kg. Lead in stream sediments varies from 54 mg/kg – 63356 mg/kg, with a mean concentration of 4245.09 mg/kg. The range of concentration of Zn in stream sediments is from 72.00 – 1386.50 mg/kg with the mean of 349.68 mg/kg. Cd concentration in stream sediments, range from 0.05mg/kg – 5.50mg/kg, with a mean of 3.35mg/kg. The concentration of

Ni in sediments varies from 0.01 – 1197.00mg/kg, with a mean concentration of 282.66 mg/kg and As from 0.01mg/kg to 1.5 mg/kg. The concentration of metals is observed to be more in sediments than in surface water.

Table 1: The concentration of Cu, Zn, Pb, Cd, As and Ni in surface water in Enyigba

Sample Location	pH	Metal concentration in mg/l					
		Cu	Zn	Pb	Cd	As	Ni
Ameri stream	7.0	0.010	0.016	<0.001	<0.001	<0.001	<0.001
Nwansa stream	5.4	0.010	0.011	<0.001	<0.001	<0.001	<0.001
Akpara Ezza 1	6.1	0.026	0.023	<0.001	<0.001	<0.001	<0.001
Akpara Ezza 2	6.1	0.008	0.010	<0.001	<0.001	<0.001	<0.001
Iyina stream	5.8	0.006	0.008	<0.001	<0.001	<0.001	<0.001
Nwerugvu pond	5.5	0.016	0.008	<0.001	<0.001	<0.001	<0.001
Iyina stream 2	6.1	0.004	0.006	<0.001	<0.001	<0.001	<0.001
Akpara Izzi	6.5	0.024	0.010	<0.001	<0.001	<0.001	<0.001
Amaoji stream	6.6	0.006	0.006	<0.001	<0.001	<0.001	<0.001
Ameri mining pit 1	6.8	0.100	0.016	<0.001	<0.001	<0.001	<0.001
Ameri mining pit 2	6.5	0.014	0.014	<0.001	<0.001	<0.001	<0.001

Table 2: The concentration of Cu, Pb, Zn, Cd, Ni and As in stream sediments in Enyigba

Sample Location	Metal concentration in stream sediments in mg/kg of dry sample					
	Cu	Pb	Zn	Cd	Ni	As
Iyinu 1	30.00	68.00	145.00	1.00	497.00	0.01
Iyinu 2	33.00	155.50	216.00	2.00	482.00	0.01
Akpara Ezza 1	91.00	8625.00	799.50	1.00	366.50	0.01
Akpara Ezza 2	11.50	67.50	72.00	1.00	0.01	0.05
Akpara Ezza 3	246.50	14345.00	993.00	0.50	22.50	1.00
Akpara Ezza 4	130.50	4339.00	462.00	2.50	25.50	0.01
Akpara Ezza 5	808.50	63356.00	1386.50	5.50	12.50	1.50
Nwoniyo Offia 1	24.00	182.00	138.00	3.50	250.50	0.01
Nwoniyi Offia 2	44.50	73.50	150.50	3.00	839.50	1.00
Iyinu 3	38.00	77.50	15.50	1.50	970.50	0.01
Nwerugvu 1	39.00	450.50	160.00	2.50	614.50	1.00
Nwerugvo 2	53.50	120.50	144.50	3.00	1197.00	1.00
Nwerugvu 3	50.50	102.50	170.00	3.00	687.50	0.01
Akpara izi 1	22.00	60.50	138.00	2.50	25.00	0.01
Akpara Izi 2	37.00	54.00	160.00	2.00	27.00	0.01
Akpara Izi 3	46.00	89.50	189.50	3.00	63.50	0.01

DISCUSSION

Pollution Status of Surface Waters in the Area

The concentration of Pb, Zn and Cu, Cd, As and Ni in surface waters are below toxic level in all the sampled streams based on WHO, 1993 Standards for drinking water. This is explained by the chemical speciation of the metals and the environmental factors like the availability of aqueous species that favours precipitation in sediments, as well as the sorption properties of the sediments. These, thus exercise control on the amount of metals that are in solution i.e. solution/solid state partitioning of the metals.

Pollution status of stream sediments

In characterising the contaminant level in stream sediments in Enyigba, the approach described in the United States' Environmental Protection Agency (USEPA) Mid-Atlantic Integrated Assessment (MAIA), for estuaries 1997-1998 Summary Report and the United States Geological Survey Water Resources Investigation Report 95-4267, was adopted. This was line with the sediment quality guideline established by Long *et al.* (1995). After reviewing nine elements that were observed to have ecological and biological effects on organisms, effect range low, (ERL) was defined as the lowest concentration of a metal that produced adverse

effect in 10% of organisms reviewed in the MAIA project. The effect range median, (ERM) designates the level at which 50% of the organisms studied reported harmful effects. Metal concentrations in sediments below ERL values are not expected to illicit adverse effects. Metal concentrations in sediments above ERM are likely to be very toxic. Table 3 shows the ERL and ERM limits for metal contaminants in sediments.

There are three assessment categories of sediments. They are good, when metal values

are below the ERL values, intermediate when above the ERL values but below the ERM values and poor when the metal values are above the ERM values. Table 4 shows the comparison of metal concentrations in sediments from Enyigba and the ERM values. With the ERM values as standards, it is possible to consider the pollution levels in terms of 'pollution indices' (PI). PI is the ratio of concentration of individual metal in sediment and ERM for that metal. PI expresses how many times the concentration of the individual metal is higher than the ERM for that metal in stream sediments. PI is designated as € (see Table 4).

Table 3: The ERL and ERM limits for metals (US –EPA – MAIA 1998)

Metal	ERL values in mg/kg	ERM values in mg/kg
Arsenic (As)	8.2	70
Cadmium (Cd)	1.2	9.6
Copper (Cu)	34	270
Lead (Pb)	47	220
Zinc (Zn)	150	410
Nickel (Ni)	21	52
Chromium (Cr)	81	370
Mecury (Hg)	0.15	0.71
Silver (Ag)	1	3.7

Table 4: Pollution index for stream sediments in Enyigba

Sample location	Metal concentration in mg/kg in stream sediment and their enrichment ratios €										Pollution index
	Cu	Cu €	Pb	Pb €	Zn	Zn €	Cd	Cd €	Ni	Ni €	
Iy1	30	0.11	68.0	0.31	145	0.35	1	0.00	497	9.56	2.07
Iy 2	33	0.12	155.5	0.71	216	0.53	2	0.21	482	9.27	2.17
Ake 1	91	0.34	8625.0	39.20	799.5	1.95	1	0.10	366.5	5.91	9.50
Ake 2	11.5	0.04	67.5	0.31	72	0.18	1	0.21	<0.001	0.00	0.15
Ake 3	246.5	0.91	14345	65.20	993	2.42	0.5	0.05	22.5	0.13	13.75
Ake 4	130.5	0.48	4339	19.72	462	1.13	2.5	0.26	25.5	0.48	4.41
Ake 5	808.5	2.99	63356	287.98	1386.5	3.38	5.5	0.57	12.5	0.24	59.03
Nwo1	24	0.09	182	0.83	138	0.34	3.5	0.36	250.5	4.82	1.29
Nwo2	44.5	0.16	73.5	0.33	150.5	0.37	3	0.31	839.5	16.14	3.46
Iy 3	38	0.14	77.5	0.35	15.5	0.04	1.5	0.16	970.5	18.66	3.87
Nwe1	39	0.14	450.5	2.05	160	0.39	2.5	0.26	614.5	11.82	2.93
Nwe 2	53.5	0.20	120.5	0.55	144.5	0.35	3	0.31	1197	23.02	4.89
Nwe3	50.5	0.19	102.5	0.45	170	0.41	3	0.31	687.5	13.22	2.92
Aki 1	22	0.08	60.5	0.275	138	0.34	2.5	0.26	25	0.48	0.29
Aki 2	37	0.14	54	0.25	160	0.39	2	0.21	27	0.52	0.30
Aki 3	46	0.17	89.5	0.41	189.5	0.46	3	0.31	63.5	1.22	0.51

It was calculated by use of the formula:

$\epsilon = C/ERM$, Where C is concentration of individual metal in stream sediments.

The ERM value for Cu is 270mg/kg. Copper attains toxic levels in sediments in action of Akpara Ezza stream with values of up to 808.5mg/kg i.e. above the ERL values and enrichment index (ϵ) of 2.99. In other sampled streams, the copper concentration is below toxic level i.e. below ERL values or lies between the ERL and ERM values. The ERM value for Pb is 220 mg/kg. The average enrichment index (ϵ), of Pb in stream sediments in the area is 18.51. The enrichment index of Pb attains toxic levels in Nwerugvu Streams 2.05 and sections of Akpara Ezza Stream ranging from 19.72 to 287.98. The lowest levels were recorded at Akpara Izi and Nwoniya Offia. The ERM value for Zn is 410mg/kg. The average enrichment index (ϵ) of Zn in samples of stream sediments in the area is 0.83. The values attain toxic levels in Akpara Ezza stream where the values range from 1.1 – 3.38. The ERM value of Cd is 9.6mg/kg. The enrichment index (ϵ) maintain values below toxic level in the samples of stream sediments. The ERM value for Ni is 52mg/kg. The average enrichment index (ϵ) of Ni in the area is 5.15. Nickel toxicity appears to be the most widespread in stream sediments in the area. The concentrations attains toxicity levels in the stream sediments samples from Iyinu, Nwoniya Offia, Nwerugvu and sections of Akpara Izzi Streams where the Nickel enrichment index range from 9.27 – 18.66, 4.82 – 16.14, 11.82 – 23.02 and <1.00 – 1.22 respectively. Arsenic contamination practically does not exist in the stream sediments in the area. The concentration levels of As in the samples of stream sediments range from <0.5 to 1.50 which is below the ERL for As in stream sediments. In Table 4, a case in which enrichment/pollution index is higher than 1 is highlighted in red. These represent cases of pollution of stream sediments by at least one metal. In summary as shown in Table 5, Iyinu stream has Ni pollution; Akpara Akpara Ezza Cu, Pb, and Zn; Nwerugvu Pb and Akpara Izzi Ni pollutions.

Consequences of the established metal distribution in stream sediments

The pollution of stream bed sediments has several consequences for stream ecosystem and human health. According to Gerhat *et al.*, 1992, during high stream flow, stream sediments are

mobilised and transported downstream, resulting to transportation and re-deposition in downstream reaches, of contaminants stored in them. Through this, contaminants are introduced into new areas of the stream ecosystem, thereby becoming available for ingestion by greater numbers of aquatic organisms. In the area of study, this is of serious concern because the streams constitutes the tributaries of the Ebonyi River, which is significant regionally as source of water for irrigation, municipal water supply and major source of fish, crustaceans and molluscs which are extensively used as food in the area. Organisms that live in the sediments can ingest the contaminants and accumulate them in their tissues (Gerhart, 1992; Montgommery, 2000). This may cause various physiological problems, even death of the organisms when pollutant concentrations exceed ERL and ERM values (Gerhart et al. 1992, and Long et al., 1995). This possibly explains the low fish population, as reported by inhabitants, in Akpara Ezza and Nwerugvu streams, compared to Akpara Izzi stream with lower level of pollution. These possible accumulated concentrations in these organisms can be passed on to higher organisms in the food chain as a result of the higher organisms ingesting contaminated organisms that live in the sediments (Gerhart et al., 1992 and Montgommery, 2000). Thus humans can be exposed to the contaminants through to the food chain. The human consumption of fish, crustaceans and molluscs from these streams with contaminated sediments and the human consumption of terrestrial animals that prey on contaminated fish can lead to bioaccumulation of the pollutants in humans.

CONCLUSION

The concentration of Pb, Zn, Cu, Cd, As and Ni in the samples of surface water in Enyigba, are below toxic level based on WHO standard of 1993 for drinking water. Based on ERL and ERM limits, there is significant pollution of sediments. The polluting metals are Cu, Pb, Zn and Ni. This may result to the transportation and deposition of contaminants in the lower reaches of the streams and the Ebonyi River which is significant regionally. Through this, pollutants can become available to more aqueous and higher organisms in the food chain and may bioaccumulate in them. Humans can thus become exposed to the contaminants.

Table 5: Summary of pollution assessment in stream sediments in Enyigba

Name of stream	Status	Polluting Metals						Cumulative Pollution
		Cu	Pb	Zn	Cd	Ni	As	
Iyinu	Polluted	-	-	-	-	√	-	Polluted
Akpara Ezza	Polluted	√	√	√	-	-	-	Highly Polluted
Nwonyi Offia	Clean	-	-	-	-	-	-	Clean
Nwerugvu	Polluted	√	-	-	-	√	-	Polluted
Akpara Izzi	Polluted	-	-	-	-	√	-	Polluted

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