Assessment Of Heavy Metal Contamination Of Water Sources From Enyigba Pb-Zn District, South Eastern Nigeria

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Abstract : A total of thirty (30) water samples were collected from the Enyigba Pb/Zn mining district to assess the contamination of the water sources as a result of mining of lead and zinc minerals in the area. This comprises of 12 samples of surface water, 14 from mine ponds and 4 from underground (borehole) water. The samples were acidified to stabilize the metals for periods more than four days without the use of refrigeration. The acidified water samples were analysed by a commercial laboratory at Projects Development Institute (PRODA), Enugu using Atomic Absorption Spectroscopy (AAS). The elements determined by this method are lead (Pb), zinc (Zn), copper (Cu), arsenic (As), cadmium (Cd), nickel (Ni), manganese (Mn) and cobalt (Co). The result and analysis of contamination factor showed that in surface water, Cd had the highest concentration followed by As and Pb, while Ni had the lowest. In mine ponds, Cd also had the highest concentration and followed by Pb and As and Ni the lowest. In borehole water, Cd has the highest concentration followed by Pb and As, while Ni had the lowest concentration. Compared to WHO permissible limits, the contamination of the heavy metals in all water sources are in order Cd>>>As>>Pb>Ni>Zn>Cu. In surface water, the order is Cd>>>As>>Pb>Ni>Zn>Cu; in mine ponds, it is Cd>>>Pb>>As>Ni>Zn>Cu, and in borehole water, the order is Cd>>>As>>Pb>Zn>Ni>Cu. The calculated contamination factors show very high contamination status for Cd, Pb and As. These levels of contamination and values indicate that under the prevailing conditions and environmental regulations in Nigeria, the mining district would face major and hazardous discharges of these metals to the water sources.

Keywords: Mineralization, Conmination Factor, Enyigba and Groundwater

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1. INTRODUCTION

The study area (Figure 1), 14 km southeast of Abakaliki, covered the Pb-Zn mining district of Enyigba and its surrounding villages of Ameka, Ameri and Ohankwu all in Ebonyi State, southeastern Nigeria. The deposit of Pb-Zn sulphides (galena and sphalerite) in Nigeria have been known for a long time but have only been exploited in the past on a very small scale. The lead-zinc field covers over 48,000 sq km in extent with lead-zinc mineralization at many centres. The deposits are localized in the Cretaceous sediments along 600 km long belt within the Benue Trough, a sediment filled intracratonic basin extending from Ishiagu (South of Abakaliki) north-eastwards to Gombe (Farrington 1952, Orazulike 1994). The occurrence of lead–zinc in the Benue valley has attracted a lot of attention. Mining of the ore has been carried out for a long time by both the natives, for local uses as cosmetics, and foreign companies, for export. Production of the ore started in the year 1925 (Offodile, 1989) but commercial production started in 1947 (Kogbe, 1989). Since the discovery of and mining of Pb-Zn deposits in Abakaliki and its environs in the early 1900s, data existing on the impact of their mining on the environment are very rare. Metal contamination that occurs as a result of mining characterized by elevated toxic metal concentrations and acid rock and mine drainage, continue several years after the cessation of mining activities. Heavy metal effluents from the weathering of the mineral deposits and mine dumps affect both the surface and underground water quality and soil. These levels of contamination in the area lead to low agricultural production, and adversely affect the ecosystem if present at anomalously high level. This study is to assess the levels of heavy metals contamination of the surface and underground water as may have resulted from the lead-zinc mining in the area.

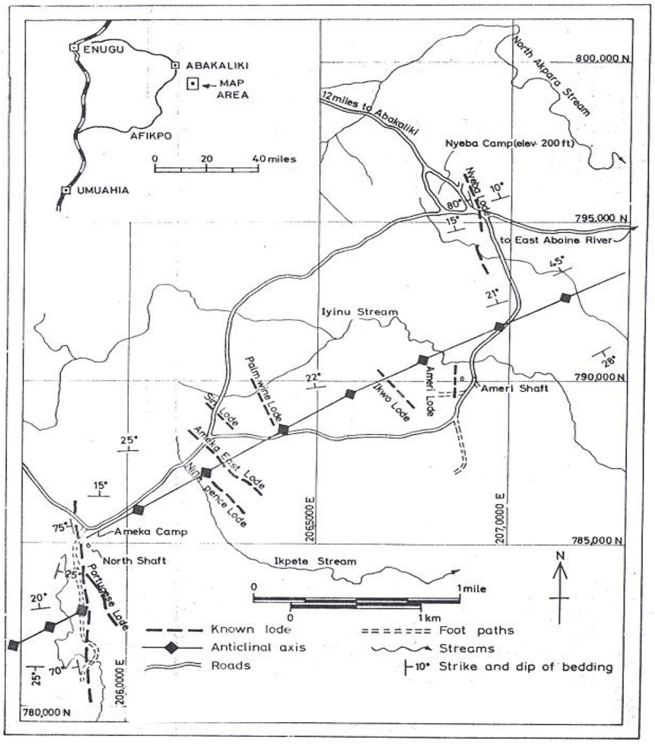

Figure 1. *Geological map of lead-zinc deposits of Enyigba district, near Abakaliki, Lower Benue Trough. The area is underlain by Abakaliki shales (Modified from Orajaka, 1965).*

2: THE STUDY AREA

In the study area, the topography is undulating plain alternating with running of ridges and hills from east to west. The plains are underlain by shale and some mudstones. The Enyigba, Ameri and Ameka are marked by

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undulating range of shale outcrops, which serve as the host for Pb-Zn mineral ore bodies. The whole area formed the “Abakaliki anticlinorium” and generally underlain by shales. The area had about 60m as its highest elevation and 30m as its lowest elevation above sea level. The area falls within the tropical rainforest belt of South East Nigeria, and characterized by an average rainfall of 1750-2000 mm per annum. The highlands are characterized by drought resistance grasses, along stream and rivers. Among the vegetation includes economic mangoes trees, orange trees, and palm and coconut trees. The drainage system of the area is dendritic in pattern, which is a function of the lithology. The area is majorly drained by Ebonyi River. All the drainage systems flow eastward to join the Cross River somewhere outside the area. The Abakaliki shale of lower Cretaceous age is exposed in the area. The sedimentary rocks are predominantly black calcareous (calcite-cemented) shale with occasional intercalation of siltstone (Figure 2). The shale formation belongs to the Asu-River Group of the Albian Cretaceous sediments. The Asu River group which consists of alternating sequence of shales, mudstone and siltstone with some occurrence of sandstone and limestone lenses in some places and attains an estimated thickness of 1500 meters (Agumanu 1989, Farrington, 1952). Kogbe (1989) described the sediments as consisting of rather poorly-bedded sandy limestone lenses. The shales in some places are highly weathered and ferrugenized. The rocks are extensively fractured folded and faulted. From field observations, the rocks of the area consist of variably coloured shale and mudstone that has been imbedded by lead – zinc vein mineralization, baked intrusive shale as well as ironstone along veins. The ironstone occur as inter-beds within the shale and as vein filling. The vein mineralization is hosted within the dark shale (Nnabo et al. 2011). The geology and mineral resources are the major factors responsible for availability of the heavy metals in the area. While the sulphide mineralization have high concentration of these metals, the shale host are capable of retaining them from ancient sea (Nnabo et al. 2011).

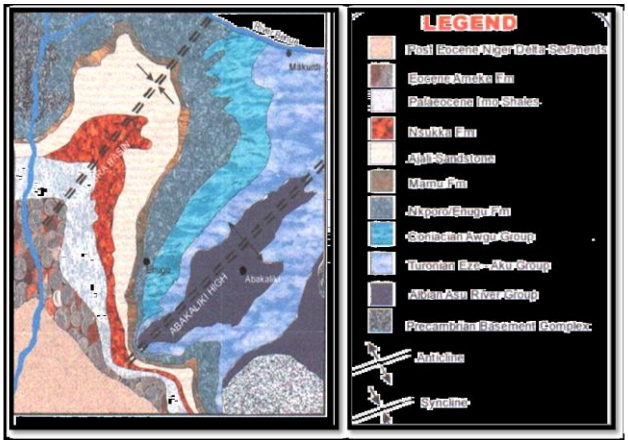

Fig. 2: *General geologic map of Southeastern Nigeria showing Abakaliki basin in the Lower Benue Trough (Modified after Hoque, 1977).*

3. METHODOLOGY

Water sampling was carried out in the months of August and September. Sample locations **(Figure 3)** were located on 1:90,000 scale topographic map and recorded on site with a conventional global positioning system (GPS) instrument. Water samples for analyses were collected from surface (stagnant) and ground sources including mine ponds, mine pits, seeping from mine dumps, boreholes, and streams found in and around the area of mining activities. Notes were taken on the nature of any mineral coatings related to the water, if any, because these are often indicators of degraded water quality. Water samples were collected from sources where the water was deemed to be representative of a geological or mine setting and would yield information on the mobility of metals in that environment. Flow rate (for moving sources) and water characteristics (colour, suspended material, bed colours or mineralogy) are recorded and pH was measured using portable pH metre– HANNA pHep Hi 98127. The pH measurement is as plotted on Figure 4. The pH meter (HANNA pHep Hi 98127) with built–in temperature electrode was a calibrated based on standards solution. The field standards were buffered solutions of pH 4.0, 7.0 and 10.0. The measurement of pH carries an uncertainty of about ±0.05 standard unit. The water sample for analyses was collected with disposable 60 ml bottles. The disposable polyethylene bottle was rinsed three times in the sampled water prior to collection. The sample was acidified at the site with three drops of ultrapure 1:1 HNO_3. The acid stabilized metals for periods more than four days without the use of refrigeration. Laboratory and field blank tests were carried out using deionized water. The acidified water samples were analysed by a commercial laboratory at Projects Development Institute (PRODA), Enugu using Atomic Absorption Spectroscopy (AAS). The elements determined by this method are lead (Pb), zinc (Zn), copper (Cu), arsenic (As), cadmium (Cd), nickel (Ni), manganese (Mn) and cobalt (Co).

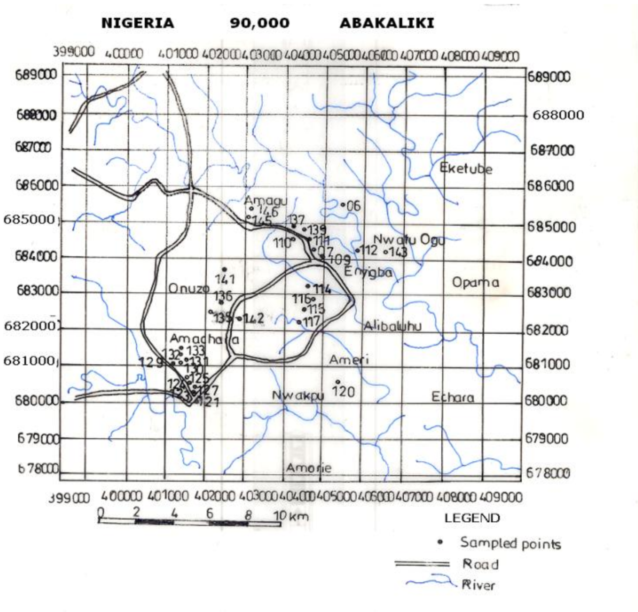

Figure 3. *Figure 19. Location of Water Samples collected from Enyigba and its Environs.*

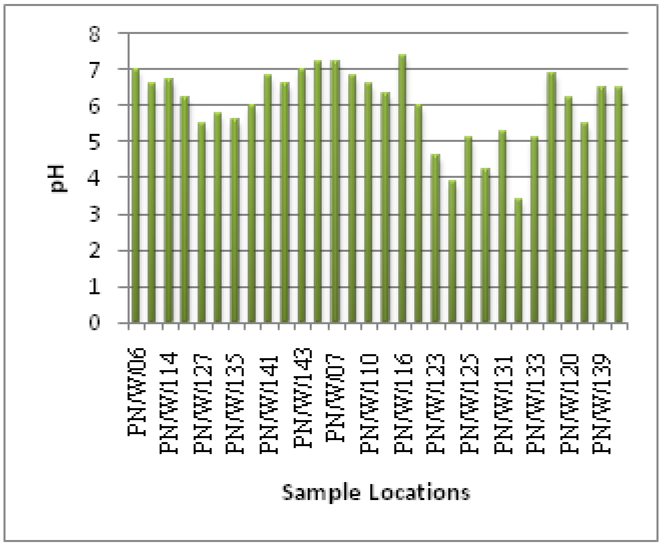

Figure 4. *The plot of field measurement of pH of the water samples from Enyigba mining district.*

4. RESULTS OF HEAVY METAL ANALYSIS IN WATER.

The results of the analysis of water samples for their contamination by heavy metals are shown in Tables 1 to 4. The tables also contain the statistical data for each metal. The concentrations of each metal that are above the World Health Organization (WHO, 2011) established maximum limits of heavy metals permissible in water (Table 5) are highlighted.. The content of As, Cd, Ni and Pb in many of the samples are above the WHO maximum permissible limits for drinking water. The distributions of As, Cd and Pb in all the sampled sites are plotted in Figures 5 to 7..

Table 1: *Concentration of heavy metals in water (in mg/l) and its assessment with the maximum limits established by the World Health Organization (WHO, 2011). (NL = No limit).*

Sample No	**Location**	**Sample type**	**pH**	**As**	**Cd**	**Co**	**Cu**	**Mn**	**Ni**	**Pb**	**Zn**
PN/W/06	Enyigba Stream 1	Surface	7.0	Nil	**3.2**	4.2	0.17	**0.42**	**1.49**	**0.7**	0.56
PN/W/112	Enyigba stream 2	Surface	6.6	**0.3**	**6.0**	1.26	0.08	0.06	**1.43**	Nil	0.54
PN/W/114	Ameri stream	Surface	6.7	Nil	**1.40**	1.71	0.06	0.11	Nil	**0.20**	0.09
PN/W/121	Ohankwu stream 1	Surface	6.2	Nil	**1.30**	0.60	0.05	0.02	**0.88**	**0.20**	0.01
PN/W/127	Ohankwu stream 2	Surface	5.5	**2.50**	**13.5**	Nil	0.02	0.21	**0.97**	Nil	Nil
PN/W/130	Ameka stream 1	Surface	5.8	**0.20**	**12.3**	Nil	Nil	0.07	**0.42**	**0.30**	0.15
PN/W/135	Ameka stream 2	Surface	5.6	Nil	Nil	0.97	0.02	0.04	Nil	**0.20**	0.27
PN/W/137	Enyigba villa pond	Surface	6.0	**0.30**	Nil	4.60	0.06	0.20	**2.07**	**0.20**	Nil
PN/W/141	Enyigba villa stream 1	Surface	6.8	**0.20**	Nil	2.39	0.03	0.26	**1.58**	**0.10**	**9.70**
PN/W/142	Ameka villa stream	Surface	6.6	**0.25**	Nil	5.06	0.08	0.01	**0.52**	**0.20**	**6.40**
PN/W/143	Ebonyi River, Enyigba	Surface	7.0	**0.65**	Nil	3.90	0.04	0.197	Nil	**0.10**	**10.1**
PN/W/146	Enyigba villa stream 2	Surface	7.2	**0.13**	Nil	1.0	0.01	0.07	**0.63**	**0.10**	**7.50**
PN/W/07	Enyigba Shale quarry pond	Surface	7.2	Nil	**4.20**	3.65	0.13	0.07	Nil	Nil	**0.06**
PN/W/109	Enyigba Mine pond 1	Surface	6.8	**0.70**	**0.90**	2.35	0.06	0.07	Nil	**0.40**	0.23
PN/W/110	Mine dump drain, Enyigba	Surface	6.6	Nil	**3.70**	1.10	0.09	0.02	**0.08**	**0.04**	0.06
PN/W/111	Enyigba Mine pond 2	Surface	6.3	**0.40**	**1.10**	0.20	Nil	0.05	**3.63**	**0.10**	0.16
PN/W/116	Ameri Mine pond 1	Surface	7.4	**1.10**	**0.52**	0.03	0.01	0.12	Nil	**0.20**	0.05
PN/W/117	Ameri Mine pond 2	Surface	6.0	Nil	**3.00**	0.00	0.14	**3.46**	**0.57**	Nil	0.74
PN/W/123	Ohankwu Mine pond 1	Surface	4.6	Nil	Nil	Nil	1.02	**3.24**	Nil	**9.00**	0.42
PN/W/124	Ohankwu Mine pond 2	Surface	3.9	**1.40**	**11.00**	2.90	0.91	**1.80**	**1.89**	**5.70**	0.95
PN/W/125	Ohankwu Mine pond 3	Surface	5.1	**2.20**	**3.00**	4.19	0.04	0.18	**2.23**	**7.50**	0.32
PN/W/129	Ameka Mine pond 1	Surface	4.2	**0.30**	Nil	1.20	1.22	0.06	Nil	**1.40**	1.66
PN/W/131	Ameka Mine pond 2	Surface	5.3	Nil	**0.70**	Nil	0.10	**0.70**	**0.80**	**7.40**	0.13
PN/W/132	Ameka Mine pond 3	Surface	3.4	**2.40**	**9.10**	0.19	0.06	**1.28**	**0.38**	**5.00**	0.32
PN/W/133	Ameka Mine pond 4	Surface	5.1	Nil	**0.80**	Nil	0.05	0.17	Nil	**1.50**	0.11
PN/W/115	Ameri Mine shaft	U/ground	6.9	**0.44**	**0.20**	0.50	0.05	**0.54**	**0.24**	**0.30**	2.60
PN/W/120	F. T. C. Nwakpu, BH	U/ground	6.2	0.01	Nil	2.40	0.16	0.08	**0.31**	Nil	**7.50**
PN/W/136	Ameka village BH	U/ground	5.5	Nil	Nil	0.97	0.13	0.08	Nil	**0.10**	0.27
PN/W/139	Enyigba Prim. Sch. BH	U/ground	6.5	**0.09**	**0.50**	5.44	0.10	0.26	Nil	Nil	**6.60**
PN/W/145	Mine road, Enyigba BH	U/ground	6.5	**0.13**	Nil	2.40	0.09	**0.41**	Nil	Nil	Nil
TOTAL			**180.50**	13.7	76.42	53.21	4.98	14.26	20.12	40.94	57.50
MEAN			**6.02**	0.72	4.02	2.22	0.18	0.48	1.12	1.78	2.13
MAX			**7.40**	2.50	13.50	5.44	1.22	3.46	3.63	9.00	10.10
MIN			**3.40**	0.01	0.20	0.03	0.01	0.01	0.08	0.04	0.01
ST. DEV			**1.01**	0.79	4.19	1.63	0.31	0.86	0.89	2.81	3.24

WHO (2011) Max. Limit (mg/l)			.01	.003	NL	2	0.4	0.07	0.01	3

🟧	Exceeds the World Health Organization (WHO, 2011) Limit for Human Consumption

***Table 2.** Concentration of heavy metals in surface water (in mg/l) and its assessment with the maximum limits established by the World Health Organization (WHO, 2011) (NL = No limit)*

Sample No	**Location**	**pH**	**As**	**Cd**	**Co**	**Cu**	**Mn**	**Ni**	**Pb**	**Zn**
PN/W/06	Enyigba Stream 1	7.0	Nil	**3.20**	4.20	0.17	**0.42**	**1.49**	**0.70**	0.56
PN/W/112	Enyigba stream 2	6.6	**0.30**	**6.00**	1.26	0.08	0.06	**1.43**	Nil	0.54
PN/W/114	Ameri stream	6.7	Nil	**1.40**	1.71	0.06	0.11	Nil	**0.20**	0.09
PN/W/121	Ohankwu stream 1	6.2	Nil	**1.30**	0.60	0.05	0.02	**0.88**	**0.20**	0.01
PN/W/127	Ohankwu stream 2	5.5	**2.50**	**13.50**	Nil	0.02	0.21	**0.97**	Nil	Nil
PN/W/130	Ameka stream 1	5.8	**0.20**	**12.30**	Nil	Nil	0.07	**0.42**	**0.30**	0.15
PN/W/135	Ameka stream 2	5.6	Nil	Nil	0.97	0.02	0.04	Nil	**0.20**	0.27
PN/W/137	Enyigba villa pond	6.0	**0.30**	Nil	4.60	0.06	0.20	**2.07**	**0.20**	Nil
PN/W/141	Enyigba villa stream 1	6.8	**0.20**	Nil	2.39	0.03	0.26	**1.58**	**0.10**	**9.70**
PN/W/142	Ameka villa stream	6.6	**0.25**	Nil	5.06	0.08	0.01	**0.52**	**0.20**	**6.40**
PN/W/143	Ebonyi River, Enyigba	7.0	**0.65**	Nil	3.90	0.04	0.20	Nil	**0.10**	**10.1**
PN/W/146	Enyigba villa stream 2	7.2	**0.13**	Nil	1.00	0.01	0.07	**0.63**	**0.10**	**7.50**
TOTAL		77	**4.53**	37.70	25.69	0.62	1.67	**9.99**	**2.30**	**35.32**
MEAN		6.42	**0.57**	6.28	2.57	0.06	0.14	**1.11**	**0.23**	**3.53**
MAX		7.20	**2.50**	13.50	5.06	0.17	0.42	**2.07**	**0.70**	**10.10**
MIN		5.50	**0.13**	1.30	0.60	0.01	0.01	**0.42**	**0.10**	**0.01**
STD. DEV		0.56	**0.75**	4.94	1.62	0.04	0.12	**0.53**	**0.17**	**4.11**
WHO (2011) Max. Limit (mg/l)			.01	.003	NL	2	0.4	0.07	0.01	3

***TABLE 3.** CONCENTRATION OF HEAVY METALS IN MINE PONDS AND ITS ASSESSMENT WITH THE MAXIMUM LIMITS ESTABLISHED BY THE WORLD HEALTH ORGANIZATION (WHO, 2011). (NL = NO LIMIT).*

Sample No	**Location**	**pH**	**As**	**Cd**	**Co**	**Cu**	**Mn**	**Ni**	**Pb**	**Zn**
PN/W/07	Enyigba Shale quarry pond	7.2	Nil	**4.20**	3.65	0.13	0.07	Nil	Nil	**0.06**
PN/W/109	Enyigba Mine pond 1	6.8	**0.70**	**0.90**	2.35	0.06	0.07	Nil	**0.40**	0.23
PN/W/110	Mine dump drain, Enyigba	6.6	Nil	**3.70**	1.10	0.09	0.02	**0.08**	**0.04**	0.06
PN/W/111	Enyigba Mine pond 2	6.3	**0.40**	**1.10**	0.20	Nil	0.05	**3.63**	**0.10**	0.16
PN/W/116	Ameri Mine pond 1	7.4	**1.10**	**0.52**	0.03	0.01	0.12	Nil	**0.20**	0.05
PN/W/117	Ameri Mine pond 2	6.0	Nil	**3.00**	Nil	0.14	**3.46**	**0.57**	Nil	0.74
PN/W/123	Ohankwu Mine pond 1	4.6	Nil	Nil	Nil	1.02	**3.24**	Nil	**9.00**	0.42
PN/W/124	Ohankwu Mine pond 2	3.9	**1.40**	**11.00**	2.90	0.91	**1.80**	**1.89**	**5.70**	0.95
PN/W/125	Ohankwu Mine pond 3	5.1	**2.20**	**3.00**	4.19	0.04	0.18	**2.23**	**7.50**	0.32
PN/W/129	Ameka Mine pond 1	4.2	**0.30**	Nil	1.20	1.22	0.06	Nil	**1.40**	1.66
PN/W/131	Ameka Mine pond 2	5.3	Nil	**0.70**	Nil	0.10	**0.70**	**0.80**	**7.40**	0.13
PN/W/132	Ameka Mine pond 3	3.4	**2.40**	**9.10**	0.19	0.06	**1.28**	**0.38**	**5.00**	0.32
PN/W/133	Ameka Mine pond 4	5.1	Nil	**0.80**	Nil	0.05	0.17	Nil	**1.50**	0.11
PN/W/115	Ameri Mine shaft	6.9	**0.44**	**0.20**	0.50	0.05	**0.54**	**0.24**	**0.30**	2.60
TOTAL		78.80	**8.94**	**38.22**	16.31	3.88	**11.76**	**9.82**	**38.54**	7.81
MEAN		5.63	**1.12**	**3.19**	1.63	0.30	**0.84**	**1.23**	**3.21**	0.56
MAX		7.40	**2.40**	**11.00**	4.19	1.22	**3.46**	**3.63**	**9.00**	2.60
MIN		3.40	**0.30**	**0.20**	0.03	0.01	**0.02**	**0.08**	**0.04**	0.05
STD. DEV		1.25	**0.77**	**3.35**	1.46	0.42	**1.14**	**1.16**	**3.29**	0.71
WHO (2011) Max. Limit (mg/l)			.01	.003	NL	2	0.4	0.07	0.01	3

***TABLE 4.** CONCENTRATION OF HEAVY METALS IN UNDERGROUND WATER AND ITS ASSESSMENT WITH THE MAXIMUM LIMITS OF WORLD HEALTH ORGANIZATION (WHO, 2011). (NO LIMIT).*

Sample No	**Location**	**pH**	**As**	**Cd**	**Co**	**Cu**	**Mn**	**Ni**	**Pb**	**Zn**
PN/W/120	F. T. C. Nwakpu, BH	6.2	0.01	Nil	2.40	0.16	0.08	**0.31**	Nil	**7.50**

PN/W/136	Ameka village BH	5.5	Nil	Nil	0.97	0.13	0.08	Nil	**0.10**	0.27
PN/W/139	Enyigba Prim. Sch. BH	6.5	**0.09**	**0.50**	5.44	0.10	0.26	Nil	Nil	**6.60**
PN/W/145	Mine road, Enyigba BH	6.5	**0.13**	Nil	2.40	0.09	**0.41**	Nil	Nil	Nil
TOTAL		24.70	**0.23**	0.50	11.21	0.48	0.83	0.31	0.10	14.37
MEAN		6.18	0.08	0.50	2.80	0.12	0.21	0.31	0.10	4.79
MAX		6.50	0.13	0.50	5.44	0.16	0.41	0.31	0.10	7.50
MIN		5.50	0.01	0.50	0.97	0.09	0.08	0.31	0.10	0.27
STD. DEV		0.41	0.05	0.05	1.63	0.03	0.14	0.31	0.10	3.22
WHO (2011) Max. Limit (mg/l)			.01	.003	NL	2	0.4	0.07	0.01	3

🟧	Exceeds the limits established by the World Health Organization (WHO, 2011)

TABLE 5. *MAXIMUM LIMITS OF METALS PERMISSIBLE IN WATER ESTABLISHED BY THE WORLD HEALTH ORGANIZATION (WHO, 2011).*

Parameter	Limits (mg/l)
Arsenic	0.01
Cadmium	0.003
Copper	2
Manganese	0.4
Nickel	0.07
Lead	0.01
Zinc	3
Cobalt	No limit established.

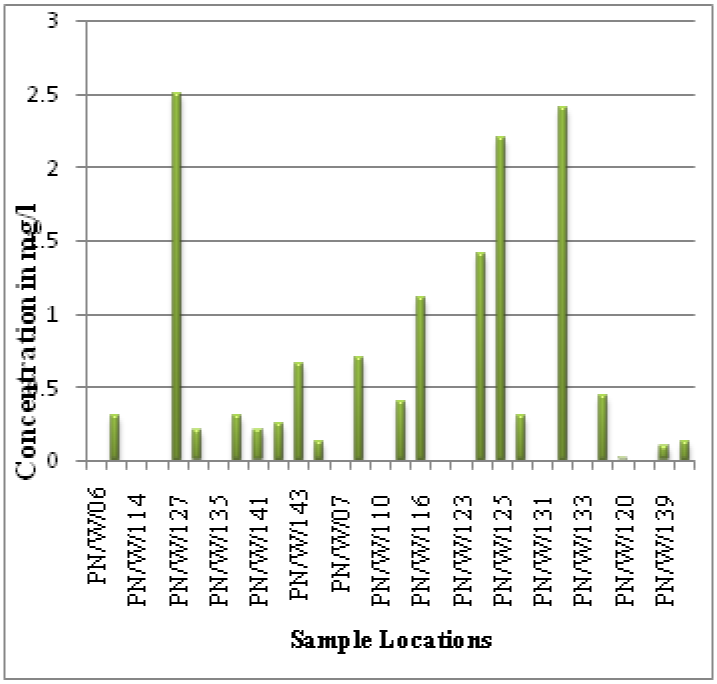

Fig. 5. *Concentration of arsenic in water from Enyigba and Environs.*

High contents of As in water were recorded in a stream from Ohankwu area (PN/W/127) and one mine pond from Ameka (PN/W/132) and two mine ponds from Ohankwu (PN/W/125 and 124) areas with values of 2.5, 2.4, 2.2 and 1.4 mg/l respectively (Tables 6 to 9; Figure 5). PN/W/127 is a stream that took its source from a mining hill at Ohankwu while PN/W/132, 125 and 124 are mine ponds where active local mining activities were taking place at the time the sampling took place. The content of *As* in the underground water was very low with a maximum value of 0.13 mg/l obtained from a borehole at Enyigba and environs.

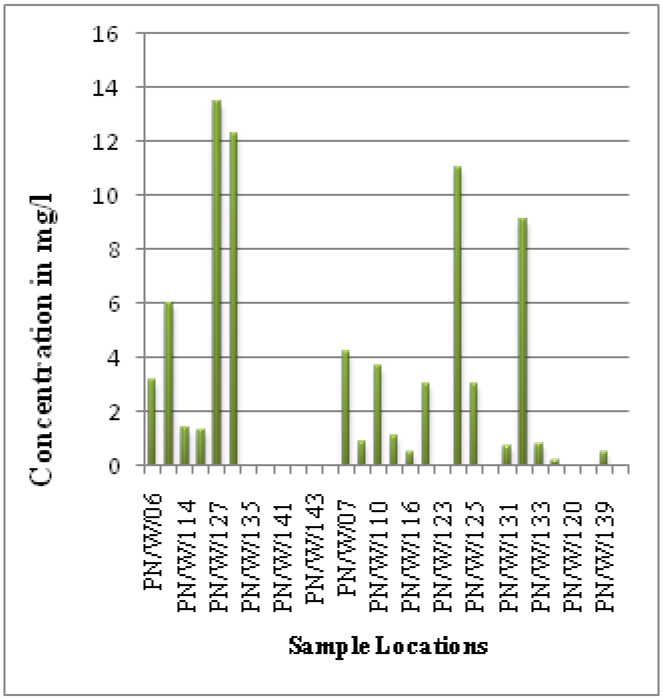

Fig. 6. *Concentration of cadmium in water from Enyigba and Environs.*

Very high concentration of Cd in water samples were recorded in two streams from Ohankwu (PN/W/127) and Ameka (PN/W/130) areas and two mine ponds from Ohankwu (PN/W/124) and Ameka (PN/W/132) areas with values of 13.5, 12.3, 11 and 9.1 mg/l respectively (Tables 6 to 9; Figure 6). PN/W/127 and PN/W/130 are streams that drain the mining areas at Ohankwu and Ameka while PN/W/124 and PN/W/132 are mine ponds where active local mining activities were taking place at the time the sampling took place. The content of *Cd* in the underground water was very low with a maximum value of 0.5 mg/l obtained from a borehole at Enyigba Primary School (PN/W/139).

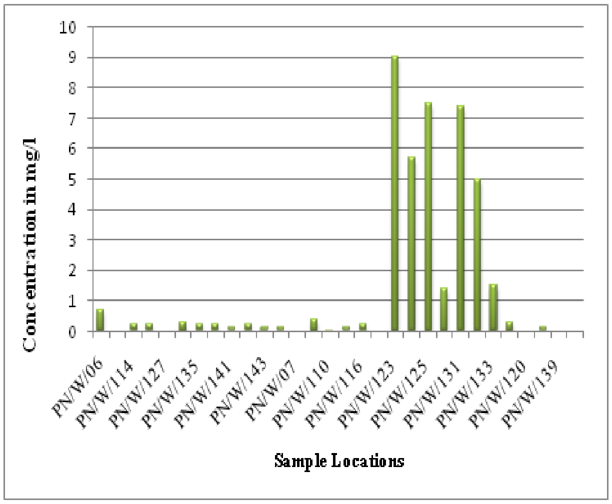

Fig. 7. *Concentration of lead in water from Enyigba and Environs.*

High values of Pb in water were concentrated in mine ponds from Ohankwu and Ameka areas (Tables 6 to 9; Figure 7). High concentrations of lead were recorded from samples PN/W/123, PN/W/125, PN/W/131, PN/W/124 and PN/W/132 with values of 9, 7.5, 7.4, 5.7 and 5 mg/l respectively which are located within the Pb-Zn mining areas. The contents of *Pb* in the surface and underground water samples were very low with a maximum value of 0.7 mg/l obtained from one stream at Enyigba and environs (PN/W/06).

Contamination Factor (*CF*).

The assessment of contamination of the water resources of Enyigba and Environs was also done using the calculation of contamination factors of the heavy metals in the water samples. This calculation was used to evaluate the potential risk of the heavy metals to the environment using the formula below (Kumar and Edward, 2009):

$$C_f^i = \frac{C_{0-1}^i}{C_n^i}$$

where C_{0-1}^i is the mean concentration of metal from the water sampling sites of the Enyigba and Environs (at least five) and was taken as the WHO maximum permissible limits of heavy metals in water as reference values (**see Table 5**). Four categories of contamination factor have been distinguished (Kumar and Edward, 2009, Tables 6 to 9 and Figures 8 to 11 showthecontamination factors of heavy metals in water samples from the Enyigba and Environs.

TABLE 6: *CONTAMINATION FACTOR OF HEAVY METALS IN WATER FROM ENYIGBA AND ENVIRONS*

As	CF	Cd	CF	Cu	CF	Mn	CF	Ni	CF	Pb	CF	Zn	CF	*DC*
0.72	**72**	4.02	**1340**	0.18	0.09	0.48	**1.20**	1.12	**16**	1.78	**178**	2.13	0.71	1590.80

TABLE 7: *CONTAMINATION FACTOR OF HEAVY METALS IN SURFACE WATER FROM ENYIGBA AND ENVIRONS.*

As	CF	Cd	CF	Cu	CF	Mn	CF	Ni	CF	Pb	CF	Zn	CF	*DC*
0.57	**57**	6.28	**2093.33**	0.06	0.03	0.14	**0.35**	1.11	**15.86**	0.23	**23**	3.53	1.18	2174.54

TABLE 8: *CONTAMINATION FACTOR OF HEAVY METALS IN MINE PONDS FROM ENYIGBA AND ENVIRONS.*

As	CF	Cd	CF	Cu	CF	Mn	CF	Ni	CF	Pb	CF	Zn	CF	*DC*
1.12	**112**	3.19	**1063.33**	0.30	0.15	0.84	**2.10**	1.23	**17.57**	3.21	**321**	0.56	0.19	1496.67

TABLE 9: *CONTAMINATION FACTOR OF HEAVY METALS IN UNDERGROUND WATER FROM ENYIGBA AND ENVIRONS.*

As	CF	Cd	CF	Cu	CF	Mn	CF	Ni	CF	Pb	CF	Zn	CF	*DC*
0.08	**8**	0.50	**166.67**	0.12	0.06	0.21	**0.53**	0.31	**4.43**	0.10	**10**	4.79	1.60	186.33

< 1	**1 – 3**	**3 – 6**	**➢ 6**
Low contamination factor	Moderate contamination factor	Considerable contamination factor	Very high contamination factor

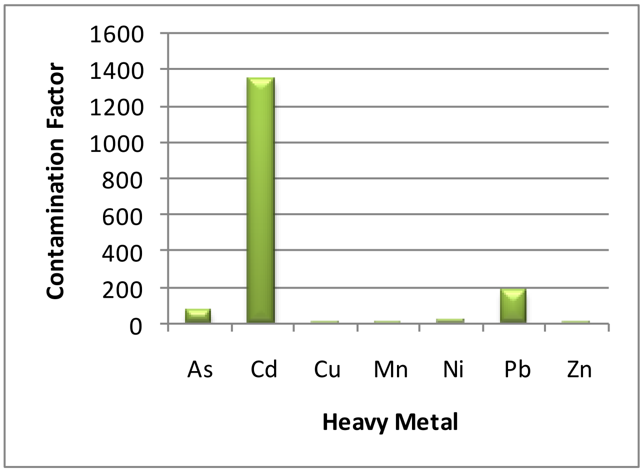

Fig. 8. *Contamination Factor of Heavy Metals in Water from Enyigba and Environs.*

Cadmium had the highest contamination factor in the entire water samples with a value of 1340, followed by *Pb* with a much lower value of 178 and *As* with a value of 72 (Table 6; Figure 8). The values for the other metals are very low.

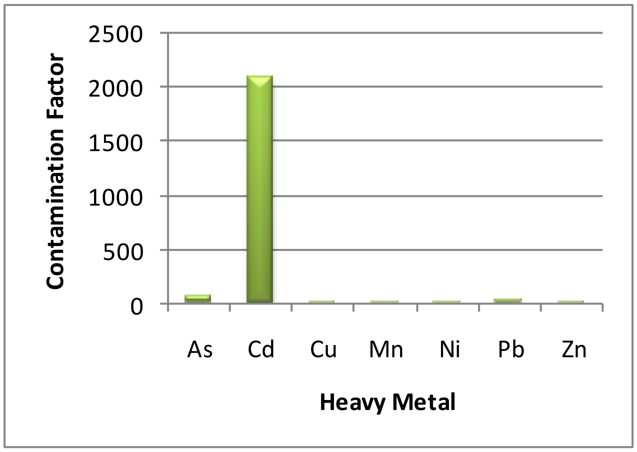

Fig. 9. *Contamination factor of heavy metals in surface water from Enyigba and Environs.*

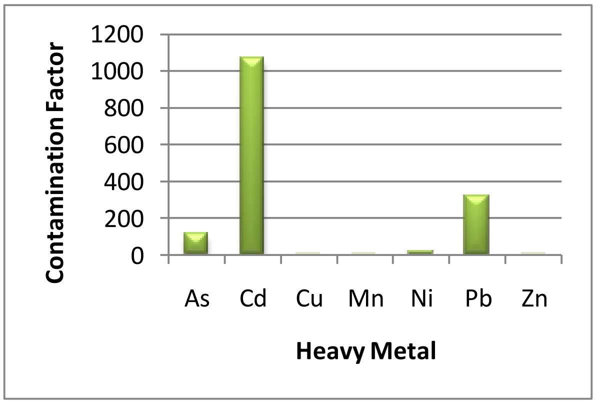

Fig. 10. *Contamination factor of heavy metals in mine ponds from Enyigba.*

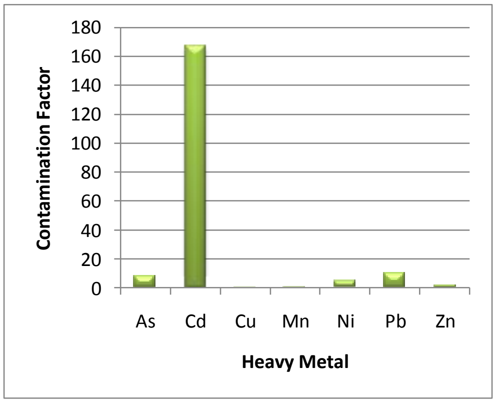

Fig. 11. *Contamination factor of heavy metals in underground water from Enyigba and Environs.*

Cadmium had the highest contamination factor in the surface water samples with a value of 2093.33, followed by *As* with a much lower value of 57 and *Ni* with a value of 15.86 (Table 7; Figure 9). *Cd* also had the highest contamination factor in mine ponds with a value of 1063.33, followed by *Pb* with a much lower value of 321, *As* with a value of 112 and *Ni* with a value of 17.57 (Table 8; Figure 10). In the borehole water samples, *Cd* again had the highest contamination factor with a value of 166.67, followed by *Pb* with a much lower value of 10 and *As* with a value of 8 (Table 47; Figure 65).

5. DISCUSSION

5.1. Surface Water

The concentration of arsenic in water from the Enyigba and Environs varied from 0.01 to 2.5 mg/l with an average value of 0.72 ± 0.79 mg/l with very high contents in water recorded in stream from Ohankwu area and mine ponds from Ameka and Ohankwu areas with values of 2.5, 2.4 and 2.2 mg/l respectively (Tables 6 to 9; Figure 5). These samples were collected at sites where active local mining of Pb/Zn are still taking place. Uncontrolled local mining activities has led to generation of heavy metal pollutants with negative influences on the nearby environment (Onyedika and Nwosu, 2008; Johnston et al. 2008; Antunes et al. 2008). Mining and related operations are the most important anthropogenic sources of heavy metals to the environment (Boussen et al. 2008). Waters nearby the mine wastes generated from mining of Ba-Pb-Zn quartz veins at Segura area, central Portugal, was reported to have high contents of As and Mn (Antunes et al. 2008). The content of *As* in the underground water was very low with a maximum value of 0.13 mg/l obtained from a borehole at Enyigba village. The concentration of *As* in many locations (eight each from surface and mine pond water, and two from underground water) were above the WHO (2011) maximum permissible limit for water quality (Tables 6 to 9). These high values may have been the consequence of Pb-Zn mining activities in Enyigba area. In Simav area (Turkey), As-rich mine wastes of an abandoned Cu-Pb-Zn mine have been the potential sources of As in the aquifer (Gunduz and Simsek, 2008). High As in surface and subsurface water was mainly related to the occurrence of arsenopyrite in the area. In surface water, high concentration of As was recorded from Ohankwu Stream, Ebonyi River at Enyigba, Enyigba Stream and Village pond with concentrations of 2.5, 0.65, 0.3 and 0.3 mg/l respectively. These values are 250, 65, 30 and 30 times above the WHO (2011) maximum permissible limit of 0.01 mg/l for water quality (Table 2, Figure 5). The total concentration of As in surface water (4.53 mg/l) is 453 times the WHO standard and contributed significantly to the pollution index of heavy metals in surface water. The average content of 0.57 mg/l of As in surface water is 57 times above the WHO (2011) limit for water quality (Table 5). These may have been associated with the Pb/Zn veins and mining activities in the area. The dissolved concentrations of As persist at relatively high levels in the area due to additional inputs contributed by contaminated waters that drain the old mine workings and mine dumps. This is supported by the As contents of the rocks, mine dumps and the soils, and moderately mobility of As in neutral to alkaline conditions (Plant and Raiswell, 1983). It is difficult to pinpoint the exact concentration of As in drinking water that can lead to a particular health problems as the effects from exposure to As in drinking water typically takes many years to develop. The best way to find out if one is being exposed to excessive amount of As is to test the source of water one drinks from. The majority of exposure to environmental As occurs by taking As that is present in water, soil, dust and food. Drinking water that contains As at high concentrations for many years may be linked to a variety of health problems. In surface water, elevated concentration of Cd was recorded from Ohankwu, Ameka and Enyigba streams with concentrations of 13.5, 12.3 and 6 mg/l respectively. These values are 4500, 4100 and 2000 times the WHO (2011) maximum permissible limit of 0.003 mg/l for water quality (Table 2, Figure 6). The total concentration of Cd in surface water (37.7 mg/l) is 12567 times the WHO standard and contributed very significantly to the pollution index of heavy metals in surface water. The average content of 4.02 mg/l of Cd in surface water is 1340 times above the WHO (2011) limit for water quality (Table 5). Cadmium is a natural, usually minor constituent of surface and groundwater. It enters aquatic systems through weathering and erosion of bedrocks and soils. Much of the cadmium entering fresh waters may be rapidly adsorbed by sediments which are significant sinks for cadmium emitted to the aquatic environment (WHO, 2011). The dissolved concentrations of Cd persist at relatively high levels in the area due to additional inputs of contaminated waters that drain the old mine workings and mine dumps (Nnabo, 2015, Igwe et al. 2012). This is supported by the Cd contents of the rocks, mine dumps and the soils (Onyeobi and Imeokparia, 2014). The mine wastes close to the mining area, are also the source of this metal. Cadmium is a priority hazardous metal and most failures to achieve its quality standard in fresh water are in base metal mining areas (Johnston et al. 2008). These localized high concentrations of Cd in the streams of Enyigba area may be related to the vicinity of the highly oxidized ore zones (Bolucek, 2007), and its moderate mobility under neutral to alkaline environments (Plant and Raiswell, 1983). In surface water, elevated concentrations of Pb were recorded from Enyigba and Ameka streams with concentrations of 0.7 and 0.3 mg/l and respectively 70 and 30 times above the WHO (2011) maximum permissible limit of 0.01 mg/l for water quality (Table 2, Figure 7). The total concentration of Pb in surface water (2.3 mg/l) is 230 times the WHO standard and contributed to the significant pollution index of heavy metals in surface water (Table 3). The average content of 0.23 mg/l of Pb in surface water is 23 times above the WHO (2011) limit for water quality (Table 5). Pb, perhaps due to its insoluble nature, decreased rapidly with distances away from the mineralization zones (Bolucek, 2007) coupled with fact that Pb, if it is in solution phase, would be highly attenuated through adsorption reactions by organic substances thereby restricting its mobility and with higher Pb in such environment (Plant and Raiswell, 1983). The dissolved concentrations of Pb persist at relatively high levels in the area due to additional inputs of contaminated waters that drain the old mine workings and mine dumps. This is supported by the Pb contents of the rocks, mine dumps and the soils ((Onyeobi and Imeokparia, 2014, Nnabo, 2015, Igwe et al. 2012). The mine wastes close to the mining area, are also the source of this metal. This water dissolves many heavy metals including Pb at high concentrations (Byrne et al. 2009; Johnston et al. 2008). Pb concentrations of up to 100 times greater than the allowable levels were also reported by Byrne et al. (2009). The stream water around Pb-Zn-Cu deposits in Guryong mines (South Korea) showed highest concentrations of Pb, Cu, Zn, Mn, Co and Ni (Kim et al. 2007). In Baia Mare Mining Basin (NW Romania), characterized by Cu-Pb-Zn sulphide ores, heavy metals such as Cu, Zn, Cd, As and Pb leached from mine wastes caused severe contamination of surface and ground waters (Bolucek, 2007), and that the the concentrations of Cu, Pb, Zn and Cd were found in higher levels in water courses due to mining and ore processing activities in the area. Despite the reduction in mining activities, the improper mines closure and poor mine wastes management still generated significant heavy metals pollution of surface waters in many areas such as Baia Mare (Bolucek, 2007), and Malluni region in Bolivia (Savarredy-Arangureen et al. 2008) Water from mine dumps are the main sources of the toxic metals and their subsequent mobilization into surface and groundwater is probably the most significant environmental impact associated with metallic sulphide mining Nash, 2002). Lead is known to fulfil no essential function in the body as it is merely harmful after uptake from food, air or water. It is a particularly dangerous metal, as it can accumulate in individual organisms and also in entire food chains, causing several health effects. In surface water, elevated concentration of Ni was recorded from surface pond and streams at Enyigba and Ohankwu with concentrations as high as 2.07 mg/l which is up to 30 times above the WHO (2011) maximum permissible limit of 0.07 mg/l for water quality (Table 2). The total concentration of Ni in surface water (9.99 mg/l) is 143 times the WHO standard and contributed to the pollution index of heavy metals in surface water (Table 3). The average content of 1.11 mg/l of Ni in surface water is 16 times above the WHO (2011) limit for water quality (Table 3). High Ni in surface waters can inhibits the growth of algae. In surface water, elevated concentration of Zn was recorded from Ebonyi River and streams from Enyigba and Ameka with concentrations as high as 10.1 mg/l and up to 3 times above the WHO (2011) maximum permissible limit of 3 mg/l for water quality (Table 2). The total concentration of Zn in surface water (35.32 mg/l) is 11.77 times the WHO standard and contributed to the pollution index of heavy metals in surface water (Table 3). The average content of 3.53 mg/l of Zn in surface water is only 1.18 times above the WHO (2011) limit for water quality (Table 3). The concentration of mobile Zn in the area will present some health effects in surface and underground water in the affected areas, where deposits of sphalerite and its mining may contribute to the high concentrations. The great mobility of Zn is exhibited here by a long dispersal pattern downstream from the mineralization zones (Bolucek, 2007).

5.2.UNDERGROUND WATER.

In underground water samples, high content of As was recorded from boreholes at Mine Road, Enyigba and Enyigba Primary School with concentrations of 0.13 and 0.09 mg/l respectively. These values are 13 and 9 times above the WHO (2011) maximum permissible limit of 0.01 mg/l for water quality (Table 4, Figure 5). The average content of 0.08 mg/l of As in underground water is 8 times above the WHO (2011) limit for water quality (Table 5). These concentrations make the water unsafe for human consumption. High content of Cd was only obtained from Enyigba Primary School borehole with concentration of 0.5 mg/l, and 167 times above the WHO (2011) maximum permissible limit of 0.003 mg/l for water quality (Table 4, Figure 6). The average content of 0.5 mg/l of Cd in underground water is also 167 times above the WHO (2011) limit for water quality (Table 5). This concentration renders this water source risky for human consumption. High content of Pb was only obtained from a borehole at Ameka village with concentration of 0.1 mg/l, and 10 times above the WHO (2011) maximum permissible limit of 0.01 mg/l for water quality (Table 4, Figure 7). The average content of 0.1 mg/l of Pb in underground water is only 10 times above the WHO (2011) limit for water quality (Table 4). This is expected as local Pb/Zn mining is very active in the area. Cidu and Fanfani (2000)'s investigation of the impact of abandoned mines on water resources in SW Sardinia area (Italy) showed that pore water in dumps exhibited high contents of Pb, Cu, Co, Ni, Cd and Zn. This was also obtainable in Humboldt Pb-Zn-Cu mines (N. Nevada) where the water sources were polluted by As, Cd, Cu, Mn, Pb and Zn from the mine dumps (Nash, 2003). However, the abundance of siderite and other carbonate minerals in Sardinia area produced a near neutral pH in the streams. High content of Ni was only obtained from a borehole at Folk Technical College, Nwakpu, Ikwo with concentration of 0.31 mg/l, and only 4 times above the WHO (2011) maximum permissible limit of 0.07 mg/l for water quality (Table 4). The average content of 0.31 mg/l of Ni in underground water is only 4 times above the WHO (2011) limit for water quality and little contribution to the overall pollution index of metals in underground water. This is because the larger part of all Ni compounds that are released to the environment will adsorb to sediments or soil particles and become immobile as a result. It becomes more mobile and enters into groundwater only in acidic environments. High content of Zn was only obtained from boreholes at Folk Technical College, Nwakpu, Ikwo and Enyigba Primary School with concentrations of 7.5 and 6.6 mg/l respectively, which are 2.5 and 2.2 times above the WHO (2011) maximum permissible limit of 3 mg/l for water quality (Table 4). This may be explained by the possibility of deep-seated Pb/Zn vein in these areas. The average content of 4.79 mg/l of Zn in underground water is only 1.6 times above the WHO (2011) limit for water quality (Table 4). Water-soluble Zn in soils can contaminate groundwater. However, Zn, if in solution phase in soil would be highly attenuated through adsorption reactions thereby reducing its mobility (Mattigod and Page, 1983). The distribution of cobalt in water from the Enyigba and Environs ranged from 0.03 to 5.44 mg/l with an average value of 2.22 ± 1.63 mg/l with the highest value of 5.44 mg/l recorded from a borehole at Enyigba Primary School. Lower values were obtained from boreholes at Folk Technical College, Nwakpu, Ikwo and Mine Road, Enyigba with concentrations of 2.4 mg/l. Other high values were obtained from streams and surface pond at Ameka village and Enyigba with values of 4.6 and 4.2 mg/l respectively (Tables 6 to 9). The highest content of *Co* in mine ponds was from Ohankwu and Enyigba areas. Elevated concentrations of Co were obtained from Ebonyi River, and streams and shale quarry pond at Enyigba. The only high content of Mn was from a borehole from Mine Road, Enyigba with a concentration of 0.41 mg/l, which is only 1.03 times the WHO (2011) maximum permissible limit (0.4 mg/l) for water quality (Table 4). Manganese compounds are very common and can be found to exist naturally everywhere in the environment as solids in soils and particles in water and air. Humans enhance Mn concentrations through industrial activities. This can enter surface and underground water. Pollution from mining activities is particularly difficult to deal with because it lasts for decades after mine closure (Bolucek, 2007) but monitoring the metals in water is important for safety assessment of the environment and human health in particular (Kar et al. 2008). In Trezebionka (Poland), where intensive mining activities took place, the mines and ground waters were reported to be characterized by higher contents of heavy metals including Cd, Cu, Co, Ni, Pb, Zn and Mn. These polluting heavy metals originated from mining and extraction activities in the area (Gajowiec and Witkowski, 1993). The groundwater was naturally enriched in heavy metals but previous mining activities resulted in highly polluted and toxic groundwater at the vicinity of the mines by Pb, Cu, Cd and Mn. In the historical mining areas of Montana and Colorado, ore-related metal concentrations in many stream reaches draining the mined areas have elevated concentrations of Cd, Pb, As, Cu and Zn that normally exceed the allowable levels for aquatic life (Nimick et al. 1999).

6. CONCLUSION

High concentration of As in water were recorded in the following locations: Surface Water – W127 from Ohankwu stream 2, W143 from Ebonyi River at Enyigba, W112 from Enyigba stream 2 and W137 from Enyigba village pond; Mine Ponds - W132 from Ameka mine pond 3, W125 from Ohankwu mine pond 3, W124 from Ohankwu mine pond 2, and W116 from Ameri mine pond 1. Underground Water – W145 from borehole at Mine road, Enyigba and W139 from borehole at Enyigba Primary School. Arsenic showed very high contamination factor in all the water samples, indicating high contamination by As, and contributed to high contamination expressed by degree of contamination, DC. Arsenic also showed high contamination factor in most water samples with high values in location W127 (surface water) from Ohankwu area, W132 (mine pond) from Ameka area, W125 (mine pond) from Ohankwu, and W115 (underground water) from Ameri. The content of As made significant contribution to the slight pollution in Ohankwu mine ponds. High concentrations of Cd were obtained from the following locations: **Surface Water -** W127 (Ohankwu stream 2), W130 (Ameka stream 1), W112 (Enyigba stream 2), W06 (Enyigba stream 1) and W114 (Ameri stream). **Mine Ponds -** W124 (Ohankwu mine pond 2), W132 (Ameka mine pond 3), W07 (Enyigba shale quarry pond), W110 (mine drain at Enyigba), W125 (Ohankwu mine pond 3) and W117 (Ameri mine pond 2). **Underground Water: -** W139 (borehole at Enyigba Primary School). Cd showed very high contamination factor in all the water samples. Cd contributed to very high pollution of surface water in Ohankwu and Ameka; mine ponds in Ohankwu, Ameka and Enyigba; high pollution in surface water in Enyigba; mine ponds in Ameka and Ameri, and moderate pollution in Ameri, and Enyigba Primary School borehole. High concentrations of Pb were obtained from the following locations: Surface Water **-** W06 (Enyigba stream 1) and W130 (Ameka stream 1). Mine Ponds **-** W123 (Ohankwu mine pond 1), W125 (Ohankwu mine pond 3), W131 (Ameka mine pond 2), W124 (Ohankwu mine pond 2), W132 (Ameka mine pond 3) and W133 (Ameka mine pond 4). Underground Water**: -** W136 (borehole at Ameka village). Pb showed very high contamination factor (pointing to high contamination) in mine ponds and underground water but very low in surface water. Pb showed high contamination factor in W123 and W125 – mine pond 1 and 3 from Ohankwu; W131 – mine pond 2 from Ameka; W124 – mine pond 2 from Ohankwu; W132 – mine pond 3 from Ameka; W115 – salt water from Ameri shaft, and W136 – Ameka village borehole. Pb made very significant contribution to the slight pollution in Ohankwu The content of Pb in water was high in surface water and low in underground water, and all indicating varying degrees contamination. The high level of contamination expressed by the concentrations of As, Cd and Pb were related to the Pb/Zn occurrence and mining in the study area. This is also shown by the positive correlation between Pb, Cu and Zn which indicates the effects of man's activities on the source environment of the metals. The metals made contribution to very high pollution of surface water in Ameka; mine ponds in Ohankwu, Ameka and Enyigba; high pollution of surface water in Enyigba, mine ponds in Ohankwu and Ameka.

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