

Geochemistry of acid mine drainage and pollution problems in Okpara coal mine, Enugu, Southeastern Nigeria

G. U. Sikakwe¹, Efosa Udinmwun² and E. P. Datok³

^{1&3} Department of Physics/Geology/ Geophysics,
Federal University Ndufu-Alike Ikwo P.M.B 1010 Abakiliki Nigeria

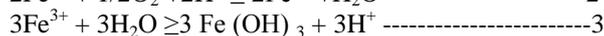
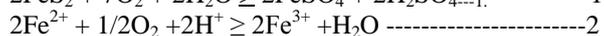
² Department of Geology, University of Calabar, P. M. B 1115 Calabar Nigeria

Abstract: In order to evaluate acid mine drainage in Okpara Coal Mine, Enugu, seasonal shallow groundwater and surface water sampling in the wet and dry seasons in nine water sample locations was carried out. Coalmine spoil dumps in 4 locations along the Orob stream and Nyaba river banks and 4 soil samples were collected across the study area. The level of acidity, turbidity, temperature, conductivity, and total dissolved solids (TDS) were measured in the field using standard equipment. Anions were determined in the laboratory by titration while heavy metals were assayed using ICP-MS. Results of the analysis indicated that the quality of water samples in both seasons ranged from acidic to very acidic (2.84-6.05). The TDS values reflect fresh water condition (TDS<1000mg/l). The mean values of F (5.08mg/l), NO₃ (567.67mg/l), PO₄³⁻ (1.08mg/l), K (12.00mg/l), Al (4.30mg/l), Fe (5.14mg/l), and Mn (3.35mg/l), recorded especially in the wet season slightly exceeded stipulations by WHO (2006) for potable water. Maximum permissible limits of F (1.5mg/l), NO₃⁻ (50mg/l), PO₄³⁻ (1.08mg/l), K (12.00mg/l), Al 0.05-0.2mg/l, Fe (0.2mg/l) and Mn (0.4mg/l) are recommended standards by WHO (2006) for potable water. The mean concentrations of heavy metals obtained from analysis of mine spoil (Fe 8871.4ppm, Mn 38.8ppm, Cu 64.14ppm, and Cr 47.14ppm) and in soil (Fe 7.18ppm, Mn 2.95ppm, Cu 1.15ppm, and Cr 1.14ppm) were above background values (Fe 3.05ppm, Mn 38.8ppm, Cu 0.71ppm and Cr 0.50ppm) obtained from coal in this study. Low pH condition (≤6) which is due to acid mine drainage, dissolves heavy metals, which is pernicious to aquatic biota. Water sources in the area are benign for irrigation purposes. Remediation of mine spoil, soil, and water of heavy metals and other pollutants using lime carbonate neutralization, ion exchange, and construction of wetland is apposite to reduce the effect of mine drainage on water sources.

Keywords: Acid mine, Drainage, remediation, Nigeria

1. Introduction

Acid mine drainage (AMD) has become a topical environmental issue, due to the devastating consequences associated with it. Acid mine drainage is common in water draining old abandoned coal and metal mines because it applies to drainage emanating from the oxidation of sulphide minerals prevalent in rocks or mine wastes. When pyrite or any other important sulphide mineral occurring in waste rocks of mines is exposed to oxygen and water, it is oxidized to sulphuric acid as shown in the equations 1 below by [1]:



As shown in (2) above iron is oxidized under acidic condition to produce Fe³⁺ and water. Hydrolysis of this Fe³⁺ (equation 3) produces ferric hydroxide (Fe (OH)₃), which is commonly found as reddish and harmful chemical species in mine sites. When the acidic water produced with harmful constituents enters water sources and soils, it become polluted by AMD. Such acidic waters from abandoned metal or coal mines have the capacity to dissolve and transport heavy metals, such as Cu, Pb, Fe, Mn, Hg, Co, Al, Ni, Cd. Apart from acid mine drainage from coal mines, noxious gases associated with coal mine are methane and Sulphur dioxide. Methane, a potent greenhouse gas which causes global warming is released from coal mining.

Sulphur dioxide (SO₂) from coal combustion produces respiratory tract ailments or even directly lethal to humans [2]. Thus, Acid mine drainage causes surface and ground water pollution downgradient of water flow in and around mine sites whether operational or abandoned [3].

The Nigerian Coal Corporation has expressed concern over the continued workability of the Okpara coal mine in the face of increased inflow of groundwater and attendant acid mine drainage problems [4]. Hydrogeological conditions and structural controls are vitally important factors that must be considered in mine planning [5]. The degree of acid drainage in a coal mine is a function of sulphur content in a coal bearing formation [6]. Besides acid mine drainage, other environmental pollution problems associated with coal mining include; high suspended particle matter in active mining areas, devegetation and the presence of noxious gases due to land subsidence and mine fire, a large portion of the land is under fire [6]. [7] traced the major problems encountered in the supply of potable water to Enugu as a result of acid mine drainage pollution caused by coal mining activities in the area due to high acidity, increased sulphate values and dissolved heavy metals.

[8] averred that heavy metals enter soil and aquatic environments via sewage sludge application, mine waste, industrial waste disposal, atmospheric deposition, and application of fertilizers and pesticides. Also [9] submitted that high concentration of trace elements such as Pb, As, Cd, Cr and

Hg in coal preclude it from being used in an environmentally friendly way.

The ultimate goal of this paper is to evaluate the degree of acid mine drainage problem caused by coal mining in Okpara mine by assessing the extent of water and soil pollution within and around the mine area. The specific objective is to ascertain the heavy metal load in the mine wastes, soil, coal and water samples. Compare how pH condition affects dissolution of heavy metals in water and soil. Show the seasonal variation of heavy metals and physicochemical parameters in water. Show the spatial variation of physicochemical parameters and heavy metals in water. Compare the heavy metal levels in water, mine wastes and soil with the background values obtained in coal samples. Recommend on the suitability of the soil for cropping and water sources in the area are for drinking and domestic uses.

2. Background to the Study

Coal was first discovered in Nigeria in 1909 near Udi in Central Eastern Nigeria [10]. The Nigeria Coal Corporation formed in 1950 operated two underground coal mines; Okpara and Onyeama mines and two surface mines Orukpa and Okaba mines located on the eastern edge of the Anambra coal basin.

Enugu coal is classified as the Lower Coal Measure with low sulphur and ash content and low thermoplastic property which makes subbituminous coal ideal for coal fired electric power plants. Okpara coal mine is the study area was opened in 1952 and formerly known as Hayes mine and later renamed Okpara Mine. The mine was operated as an underground mining. The production capacity of Okpara mine rose steadily from 150 tonnes in 1984/1985 to 1016 tonnes in [5]. The mine stopped intensive production in 1991 due to bad conduction of the sump which led to water of the mine. This coupled with poor marketing department of the Nigeria Coal Corporation led to the stoppage of production in 2004 (Personnel Communication with the Mines Manager NNC).

2.1. Study Area Description

Enugu Town in southeastern Nigeria is popularly known as the coal City. Enugu town is situated on the western edge of the Cross River plain and is dominated on the west by the Enugu escarpment (Fig. 1). The Enugu out crops occur in the plains east of the north-south trending escarpment. The formation consists of soft grey to dark grey shales and mudstone as well as the intercalation of sandstone and sandy shale [7]

Okpara Mine is around Garki about 6.5km from Enugu town along Enugu Port Harcourt expressway. Okpara mine is bounded on the North by Enugu–Ngwo and south by Agbani-Enugu PortHarcourt expressway (Fig1.). From GPS field measurements the highest elevation of about 216m above sea level is at the mine site and the lowest is about 16m at the confluence between Orob and Nyaba River. The area has a hot and humid climate with an annual temperature range of 28^oC - 23^oC. The area experience two climatic seasons of dry and wet seasons annually. The wet season is characterized by heavy rainfall with an annual rainfall over 1500mm [11].

The area has vegetation of low Greenland and the trees are scattered with less dense foliage. This type of vegetation is described as scrub forest [12]. The major streams which drain the study area are Orob stream and Nyaba River. The mine site is located at Akwuke in Awkanawna area. The mine site is on top of the valley and the streams that drain the study area Orob

and Nyaba Rivers flow down gradient. Residential buildings are located about 1.5km from the mine site. The most striking geomorphic feature in the area is the north-south trending escarpment.

2.2. Geology and Hydrogeology

The geology of the area consist of three conformable geologic formation; the Enugu shale (Campanian), the Mamu Formation, (Lower Maastrichtian) and the Ajali Sandstone. Enugu shale consist of soft to dark grey shales and mudstone as well as intercalations of sandstone sandy shales. The Ajali sandstone which overlies the Mamu Formation comprises thick friable, poorly sorted, and highly cross bedded mudstone that is white in colour but sometimes iron stained [7]. The oldest formation in Enugu coal is the Mamu Formation with a maximum thickness of thickness of 370m. it is principally made up of intercallations of sandstones, shales and mudstones with a number of coal seams and carbonaceous shales at different horizons [13] and [14]

Field evidence shows that the shales are fractured and weathered to blackish and grayish. The Ajali Sandstone has a hydraulic conductivity of (K) of 9.2×10^{-3} and a specific discharge of $1.75 \text{m}^3/\text{yr}$. The Mamu sands have a hydraulic conductivity of (k) of $9.2 \times 10^{-3} \text{cm/s}$ and specific discharge (V) of $14.5 \text{m}^3/\text{yr}$. [7]. The laterized overburden constitute the only known aquifer directly beneath the city of Enugu and has become the major source of recharge. The depth of the water table is 15m, which is a function of the local topography and the seasons [11]. At the peak of the rainy season discharge volumes are high and springs do occur. The shallow water table is an indication of aquifer susceptibility to contamination. From well site construction it is observed that the lateritic aquifer varies between 0.7m in depth and is thinly bedded and sometimes intercepted by rocks, showing that the aquifer is regularly discontinuous [11] and [13].

3. METHOD OF STUDY

3.1. Sample Collection

Water sampling was done in two seasons to reflect dry and wet seasons. The dry season sampling was accomplished between February and March while the wet season sampling was done in April and May 2007. During each sampling session, water samples were collected in prewashed plastic bottles from 9 locations within and around the mine site. The sampling bottles were rinsed with deionized water to avoid contamination that could lead to spurious results of analysis. The bottles were rinsed three times with the water to be sampled before the actual water sample was collected. The water samples were collected from sedimentation pond, mine adit, along stream and river courses draining the mine site, such as Nyaba River and Orob Stream. The sample locations were selected to reflect sources of inflow (influent), outflow (effluent), springs, sedimentation pond and a water well which served as a control and is used as drinking water source. The collected water samples were acidified to a pH of 2 with concentrated HCl to retain the metals and then preserved in a refrigerator prior to analysis to exclude microbial activity and chemical reaction. Mine dumps along river banks in the mine site were also sampled for trace metal analysis. Similarly, soil samples around the coal mine site were also collected to assess their heavy metal load due to coal mining operation.

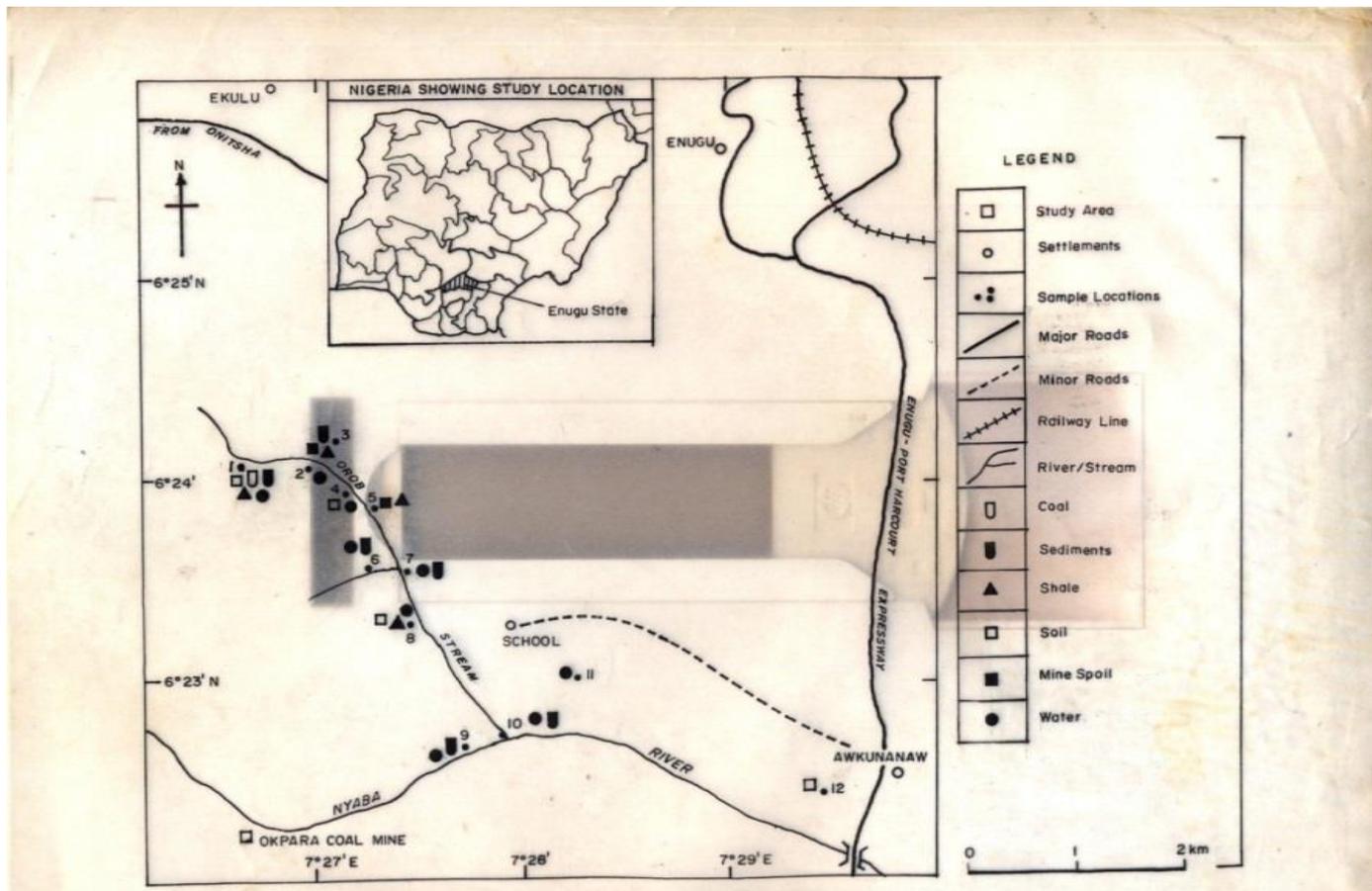


Fig. 1: Sample Location Map of Okpara Mine and Environs.

3.2. Analytical Methods

Standard methods were employed in estimation of various constituents in the mine water samples [15]. Physical properties such as pH, turbidity, temperature, Ec, Eh, total dissolved solids (TDS) were determined *insitu*, using digital Mv Redox pH meter, conductivity meter, spectrophotometer, mercury in glass thermometer respectively. Major elements, notably: Mg, K, Ca, Na, F, P, S, Cl and HCO₃, SO₄, NO₃, were analyzed by Petroc Laboratories and Department of Oceanography, University of Calabar laboratory. Anions were analyzed using chromatography and titration methods, while major cations and potentially toxic heavy metals (Fe, Al, Zn, Co, Cr, Cd, Mn, Ni, and Pb) in the water were measured using ICP-MS. Mine spoils and soil samples were analyzed for potentially toxic heavy metals using the Atomic Absorption Spectroscopy (AAS) technique from Petroc laboratories and University of Agriculture Makurdi.

4. RESULTS AND DISCUSSION

4.1. Physical Parameters

Results of the physico-chemical analysis of the sampled waters are presented in Table 1, while the statistical summary for the physical parameters, are presented alongside the WHO and SON Guidelines are presented in Table 2.

Basic statistics of measured physical parameters are presented, for wet and dry seasons, in Tables 1 and 2 respectively. The mean values of temperature for wet and dry seasons were recorded with mean and standard deviation of 26.5±0.16 and 26.8±0.207 with a

median of 26.8⁰C and 26.9⁰C respectively. Temperature ranged from 27.2⁰C to 26.5⁰C in the wet season and 27.8⁰C to 26.8⁰C in the dry season water samples. Temperature affects the solubility of heavy metals and control their mobility and dispersion. The values of temperature recorded in the two seasons were almost constant with very low standard deviation from the mean. Electrical conductivity values recorded mean and standard deviation values of 269.7±317.7 Mv in the wet season and 143±75.564 Mv in dry season. The median values of Ec in the two seasons were significantly different. A value of 277 Mv was measured in the wet season and 89 Mv was obtained in the dry season. High Ec connotes high salinity hazard which characterized acid mine drainage due to the formation of salts after the oxidation of pyrite. This concept is elucidated in equation 1. However, [6] suggested that an Ec value of 750 Mv is sufficient to suggest salinity hazard. Seasonal sampling showed mean and standard deviation values of pH, turbidity and TDS of 4.22±1.1., 14.6±16.43 NTU and 157.76±152.4 Mg/l respectively in the wet season. In the dry season the mean and standard deviation of pH, turbidity and TDS were 4.98±1.380, 42.78±30.10 NTU and 86.289±69.229 Mg/l respectively. The pH values were low in the two sampling seasons showing evidence of the oxidation of pyrite causing acid mine drainage [2]. Low TDS values depict low dissolution of sulphates, calcium, carbonates and bicarbonates minerals [17]. The turbidity level recorded was high due to suspended sediments. The mean turbidity level of 9 NTU was above 5 NTU level recommended by EPA (2006) for potable water. The mean values of pH, turbidity and TDS recorded in the area are equivalent to those reported by [7] in Ekulu river and Okpara mines which validates the credibility of this findings.

Table 1. Chemical composition of water samples from Okpara Coal Mine

SAMPLE LOCATIONS	1		2		3		4		5		6		7		8		9	
	*D	**W	D	W	D	W	D	W	D	W	D	W	D	W	D	W	D	W
Temperature	27.2	26.5	27.1	27.1	26.9	27.2	27	26.8	27.8	26.8	27	26.7	26.9	26.7	27	26.9	27.1	26.9
pH	3.5	3.5	3.8	3.7	3.6	3.5	6.1	5	5.9	3.2	3.2	6.1	6	2.8	6.2	4.8	5.9	5.5
Ec	325	334	249	277	295	318	50	12	13	336	344	50	52	1076	7	20	36	4
Turbidity	31	0	59	34	22	5	43	5	11	0	9	28	106	6	141	48	45	6
Colour	119	57	399	55	109	16	209	51	49	0	36	54	966	62	989	1005	239	78
TDS (Mg/L)	163	170	125	139.1	148	160	26	6.3	71	168	174	26.5	16.8	538	4	10	18.6	202
SO ₄ ²⁻ (Mg/L)	85	130	82	125	1.2	15	6.8	10	105	85	14	35	21	517	23	10	23	45
Cl ⁻ (Mg/L)	6.2	150	7.8	100	4.6	70	6.1	60	8.9	70	0	40	5.8	60	9.4	280	17.2	400
NO ₃ ⁻ (Mg/L)	7	792	7.5	304	4.4	480	4.8	772	8.8	563	9.7	623	7.9	405	8.6	158	13.2	1012
PO ₄ ³⁻ (Mg/L)	0.08	0.95	0.18	0.57	0	1.76	0.2	0.74	0.09	1.47	0.1	0.79	0.04	0.7	0	0.52	0.01	2.19
Ca ²⁺ (Mg/L)	10.7	10.4	12.2	9.12	14.2	1.42	5.6	5.39	10.1	8.01	7.6	6.57	12.3	20.17	8.4	3.9	11.2	14.12
Mg ²⁺ (Mg/L)	11.1	12.14	11.2	10.61	8.1	11.42	2.5	3.05	10.1	6.98	6.9	5.13	6.57	3.11	3.6	2.62	4.72	5.87
Na ⁺ (Mg/L)	9.83	12.1	10.6	9.89	17.3	11.41	6.4	7.67	8.89	7.44	6.3	7.72	12.2	8.57	8.2	6.53	31.4	54.7
K ⁺ (Mg/L)	14.7	16.61	15	17.12	4.63	16.56	0.8	1.23	14.2	8.64	2.5	3.82	3.97	15.12	2.3	1.17	10.5	27.85
Al (Mg/L)	1.27	1.69	1.77	1.45	0.32	1.76	0.2	0.28	1.08	1.74	1.7	0.79	1.68	0.7	1.7	0.52	0.54	2.19

*D - Mine water sampled during the dry season Jan-Feb 2008

**W - Mine water sampled during the wet season April –May 2008

Table 2. Statistical summary of the chemical analyses of water samples from Okpara Coal Mine, compared with the WHO and SON Guidelines for drinking-water Quality

		DRY SEASON						WET SEASON						SON (2007)	WHO (2011)
		N	MIN	MAX	MEAN	St.Dev.	MEDIA N	N	MIN	MAX	MEAN	St.Dev.	MEDIA N		
	pH	9	3.23	6.18	4.92	1.31	5.87	9	2.84	6.05	4.22	1.13	3.65	6.5 – 8.5	na
	Ec (µs/cm)	9	7	344	152.33	146.14	52	9	4.04	1076	269.67	337.02	277	1000	na
	Turbidity (NTU)	9	9	141	51.89	44.56	43	9	0	48	14.67	17.43	6	5	na
	Colour	9	36	989	346.11	374.65	209	9	0	1005	153.11	320.35	55		
	TDS (Mg/L)	9	4	174	82.93	69.67	71	9	6.3	538	157.77	161.69	160	500	na
Anions (Mg/L)	Physical Parameters Temp. (°C)	9	26.8	27.8	27.09	0.3	27	9	26.5	27.2	26.84	0.21	26.8	na	
	Cl ⁻	9	0	17.2	7.33	4.62	6.2	9	40	400	136.67	123.19	70	250	na
	NO ³⁻	9	4.4	13.2	8	2.62	7.92	9	158	1012	567.67	265.54	563		
	PO ₄ ³⁻	9	0	0.18	0.07	0.06	0.06	9	0.52	2.19	1.08	0.59	0.79	na	na
Cations (Mg/L)	Ca ²⁺	9	5.57	14.19	10.25	2.68	10.74	9	1.42	20.17	8.79	5.66	8.01	na	na
	Mg ²⁺	9	2.47	11.17	7.19	3.19	6.9	9	2.62	12.14	6.77	3.76	5.87	0.2	na
	Na ⁺	9	6.31	31.38	12.34	7.89	9.83	9	6.53	54.7	14	15.38	8.57	200	na
	K ⁺	9	0.84	14.98	7.63	5.9	4.63	9	1.17	27.85	12.01	8.95	15.12	na	na
	Al	9	0.22	1.77	1.14	0.63	1.27	9	0.28	2.19	1.24	0.67	1.45		

N-number of samples collected

Table 3. Heavy metals composition in Okpara Mine

SAMPLE LOCATIONS	1		2		3		4		5		6		7		8		9	
	*D	**W	D	W	D	W	D	W	D	W	D	W	D	W	D	W	D	W
Ba (Mg/l)	0.09	0.032	0.09	0.041	0.15	0.121	0.03	0.116	0.08	0.101	0.04	0.103	0.11	0.018	0.069	0.114	0.19	0.117
Co	0.04	0.051	0.05	0.044	0	0.048	0	0.001	0.04	0.043	0.05	0.006	0.01	0.05	0.004	0.002	0	0.004
Cr	0	0.001	0.02	0.001	0.01	0.001	0	0.001	0	0.001	0	0.001	0.01	0.004	0.002	0.001	0	0.001
Mn	2.65	2.929	2.8	2.914	0.7	2.861	0.03	0.031	2.56	2.905	2.75	0.844	0.79	17.225	0.375	0.172	0.2	0.303
Mo	0	0.004	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Ni	0.03	0.044	0.04	0.039	0.01	0.044	0	0	0.03	0.026	0.03	0.001	0.01	0.309	0.005	0	0	0
Pb	0.01	0.004	0.01	0.004	0.02	0.012	0.01	0.005	0.01	0.004	0.01	0.004	0.02	0.017	0.01	0.002	0.01	0.006
Cu	0.06	0.011	0.1	0.008	0.14	0.013	0.11	0.007	0.11	0.005	0	0.009	0.11	0.045	0.105	0.005	0.02	0.018
Zn	0.14	0.202	0.21	0.171	0.07	0.191	0.05	0.023	0.15	0.077	0.11	0.045	0.06	1.239	0.037	0.117	0.03	0.32
Fe	16.6	8.74	8.6	11.95	7.87	3.86	0.27	0.77	10.3	2.23	0.89	5.32	10.3	9.32	30.83	0.44	11.1	3.64
Al	1.27	1.69	1.77	1.45	0.32	1.76	0.22	0.28	1.08	1.74	0.67	0.79	1.68	0.7	1.68	0.52	0.54	2.19
Cd	0	0.0003	0	0.0003	0	0.0004	0	0.0002	0	0.0001	0	0.0001	0	0.0013	0.0001	0.0001	0	0.0003

Table 4 Statistical summary of heavy metal analysis in Okpara mine

Elements	N	DRY SEASON					WET SEASON					SON (2007)	
		MIN	MAX	MEAN	St.Dev.	MEDIAN	N	MIN	MAX	MEAN	St.Dev.		MEDIAN
Al	9	0.224	1.774	1.137	0.627	1.267	9	0.28	2.19	4.3	0.23	1.45	0.05-0.02
Fe	9	0.266	16.58	7.666	5.945	7.196	9	0.44	11.95	5.14	3.81	3.86	0.02
Ba	9	0.032	0.185	0.093	0.05	0.084	9	0.032	0.185	0.012	0.01	0.103	
Co	9	0.2	0.019	0.021	0.022	0.006	9	0.0005	0.051	0.028	0.028	0.043	
Cu	9	0.01	2.804	0.0183	0.0085	0.016	9	0.004	0.045	0.008	0.013	0.009	2
Cr	9	0.001	0.045	0.004	0.0058	0.002	9	0.0045	0.004	0.001	0.001	0.0006	0.05
Mn	9	0.027	0.041	1.426	1.218	0.202	9	0.031	17.225	3.35	5.05	2.861	0.4
Ni	9	0.003	0.019	0.011	0.016	0.003	9	0.0001	0.044	0.051	0.11	0.026	0.07
Pb	9	0.004	0.019	0.011	0.0004	0.01	9	0.004	0.017	0.004	0.004	0.004	0.01
Mo	9	0	0.004	0.001	0.0001	0.002	9	0	0.004	0.0001	0.001	0.0001	0.07
Zn	9	0.023	0.21	0.093	0.063	0.034	9	0.017	1.239	0.091	1.22	0.091	5
Cd	9	0	0	0	0	0	9	0.0001	0.0013	0.0003	0.0004	0.0003	0.003

N-number of samples collected

Anions such as sulphate, phosphate, nitrate, and chloride exhibited slightly different values in the wet season. The mean values of these anions were 108mg/l, 1.08mg/l, 567.67mg/l, 5.08mg/l, and 136.67mg/l respectively in the wet season. The corresponding mean values measured in the dry season such as sulphate 40.11mg/l, phosphate 0.07mg/l, nitrate 8mg/l, fluoride 0.1129mg/l, chloride 7.33mg/l. Phosphate was remarkably lower in the dry season sampling compared to the wet season. Low sulphate levels in both seasons may be attributable to inadequate pyritization and is relatively mobile in water hence its concentration despite low pyritization [18]. Phosphate is a natural constituent of water but usually very low [19]. Nitrate concentration is due to anthropogenic activities stemming from manure and fertilizer uses in cultivation. Nitrate in excess of 50mg/l is hazardous to health. Chloride is probably from coal vitrains. Fluoride occurs in industrial fumes and coal powered plants. When fluoride exceeds 4 to 6 Mg/l it reduces the prevalence of osteoporosis and collapse vertebra. Deficiency causes pain and tenderness of bones [1], [11], [19] and [20].

Major cations (Na, Ca, K, Mg and S) in the wet season sampling measured mean levels and standard deviation values of 14.±14.5, 8.79±5.33, 12.01±8.44, 6.77±3.50 and 33.89±42.23 in Mg/l respectively. In the dry season mean concentrations and standard deviations were: Sodium 12.285±7.908, calcium 10.25±2.675, potassium 7.63±5.903, magnesium 7.18±3.189 and sulphur 16.44±14.02. Low dissolution of feldspars minerals could be responsible for the low dissolution of major cations. High sulphur content in the water samples is evidence of coal mine drainage, because it is Sulphur compounds that are oxidized to produce acidity which typifies acid mine drainage. [21] reported values of Calcium 53mg/l, and magnesium 28mg/l in the Tongue River near Deckar Coal Mine, while [7] reported values consistent with this study in Okpara Coal Mine. The report on Okpara coal mine by these authors was in the time past. This work is part of mine drainage monitoring with time. This is

informed by the fact that mine drainage of abandoned or operational mines deteriorate with time.

The mean concentrations of heavy metals analysis (Table 4) in water samples in the study area shows that the mean and standard deviation of the elements in the wet season was as follows: Fe 5.14±3.81, Co 0.028±0.028, Cr 0.001±0.0001, Cu 0.008±0.013, Mn 3.35±5.05, Ni 0.051±0.11, Pb 0.006±0.004, Al 4.30±1.23, Zn 0.254±1.222, V 0.001±0.0004 (Fig. 2). In the dry season heavy metals mean levels and standard deviations were: Fe 7.66±5.945, Al 1.137±0.627, Co 0.0216±0.022, Cr 0.004±0.006, Cu 0.0183±0.0085, Mn 1.426±0.0043, V 0.0007±0.001 and Zn 0.093±0.063 (Table 2).

Aluminum, iron and manganese recorded elevated concentrations than other trace elements in water samples in both seasons. This squares with the findings of [22] and [23] who contended that iron, manganese and aluminum are common trace metals associated with coal mine drainage sites. Heavy metals exhibited higher concentrations in mine spoils and soil samples than the values obtained in water samples. This can be explained by the absorptive properties of these media [18]. The values of Al, Fe and Mn obtained in this study exceeded those reported by [8] from Ekulu mines from coal and stream sediments. This depicts improved analytical procedure or more pyritization in Okpara coal mine than Ekulu mine. Mean concentrations of heavy metals obtained in water samples during the wet season sampling were generally higher than the dry season sampling results with exception of Al and Mn. This may be due to sorption and desorption processes in the subsurface also, heavy metals and particularly Al and Mn are dissolved in low pH environments which characterized acid mine drainage in coal mines [8] and [23].

In water samples, cadmium concentration had a mean value of 0.0003mg/l in the wet season. The permissible level of 0.003mg/l is set by SON (2007) for potable water, therefore the mine drainage effect on water is not hazardous going by this standard. Cadmium is mobile under oxidizing conditions and has the same geochemical behavior with zinc [18], [24]. Its low

concentration in soil and mine spoil in this study can be attributed to co precipitation and low mobility. [8] reported a mean value of 0.036ppm in sediments from river Ekulu located in the vicinity of Onyeama mine, which is lower than the value of 0.10mg/l obtained in mine spoil and 1.370mg/l in soil in this study. Cadmium is a human Carcinogen [25].

The concentration of Pb in water samples is low relative to mine spoil and soil samples (Table 3, 4, 5 and 6). This is evident that the source of Pb in water courses is from mine spoil and soil. Generally, Pb is produce from lead sulphite (Galena PbS). Lead is a potentially toxic metal, which often causes lead poisoning. There is more concentration of zinc in mine spoil and soil samples than in water samples. This may be due to high precipitation of Zn in sulphite bearing minerals and its high mobility in oxidizing environment [18]. Zinc occurs in association with Pb and Cu. Offodile reported a mean value of 0.2ppm for Zinc in mine waters Onyeama Mine compared to a mean value of 0.093 and 0.091mg/l measured in the dry and wet seasons respectively in this research. Zinc deficiency causes bone disorders, joint weakness and skin dermatitis, loss of fertility, chronic arterial diseases and lung cancer but the mean values of zinc recorded in water samples does not pose a health threat compared to SON (2007) standard of 5mg/l for potable water. In water samples, Copper had a mean concentration of 0.008ppm and 0.0183ppm in the wet and dry seasons respectively. The mean concentration of copper in mine spoil and soil was higher than in water due the absorptive properties of these media. Copper is generally immobile in basic pH conditions and mobile in acidic conditions [18]. The low concentration of copper in acidic condition may be due to co precipitation. The mineral pyrite is the main source of copper and pyrite is prerequisite for acid mine drainage.

Chromium recorded mean concentrations of 0.001ppm and 0.004ppm in wet and dry season samplings respectively. Chromium has low mobility in water. This justify it low concentration in water. Its high concentration in soil (Table 5) may be due to sorption [18]. A pH of 3-6.5 and reducing conditions is a barrier to chromium mobility [18]. Generally, the source of chromium is from chromite. Nickel possess a mean concentration of 0.051mg/l and 0.0183mg/l in wet and dry water samplings. In mine spoil and soil samples, Nickel had mean concentration of 9.6ppm and 0.72ppm respectively. Nickel can be readily mobilized from sulphide bearing fine grained sediments into drainage [18]. Nickel is found in the mineral forsterite Mg (Ni) SiO₂. Excess intake of Nickel causes dermatitis. Due to low acidic conditions at mine site, metals that were once part of the host rock are solubilized and exacerbate the lethal effect of low pH on terrestrial and aquatic biota. Concentrations of common elements such as Zn, Cu, Al, Fe and Mn are spontaneously elevated in water with low pH [26]. This explains why Cu, Al, Fe, Zn and Mn had higher concentrations in the seasonal water samplings. (Fig. 2 and 3)

4.2. Spatial Variation of Physicochemical Parameters and Heavy Metals in Water Samples

Temperature was almost uniform (26.5⁰C-27.2⁰C) in the wet season (Fig. 4) and ranged from 26.8⁰C -27.8⁰C in the dry season (Fig. 5). The pH was low in both seasonal samplings in all the locations (Fig. 4 and 5) with exception of locations 6 in the wet season locations 4, 7 and 9 in the dry season. Low pH shows acidity due to acid mine drainage. Location 6 is a tributary to Orob River (Fig. 4 and 5). The difference in values between wet and dry seasonal samplings is due to the degree of pyrite oxidation. [23] obtained pH values ranging from 4-7 in

Pennsylvania coals. Electrical conductivity is highest (1076 μ s/m in location 7 (confluence) in wet season and 218 μ s/m in location 3 (stream channel) in the dry season (Fig. 4 and 5). Low turbidity values in the area could be ascribed to little runoff, because high values suggest impurities due to high runoff. Turbidity was nil in locations 1 and 5 in the wet season. In the dry season turbidity was highest in location 2, 4, 7, 8, 9 (59, 43, 106, 45, and 59 NTU) due to little runoff. Total dissolved solids (TDS) in the wet season were low at locations 4 (63mg/l). Location 1, 2 and 5 had values of 170, 139 and 158mg/l (Fig. 4). Whereas in the dry season TDS had lowest values in location 5 (7.1mg/l), with a highest value in locations 1, 2 and 3 (163, 125 and 148mg/l). Measured value of TDS in coal mine in Colorado by [1] was 500mg/l, which is above the findings in this study. High TDS connotes the presence of bicarbonates, carbonates and sulphates in water [17].

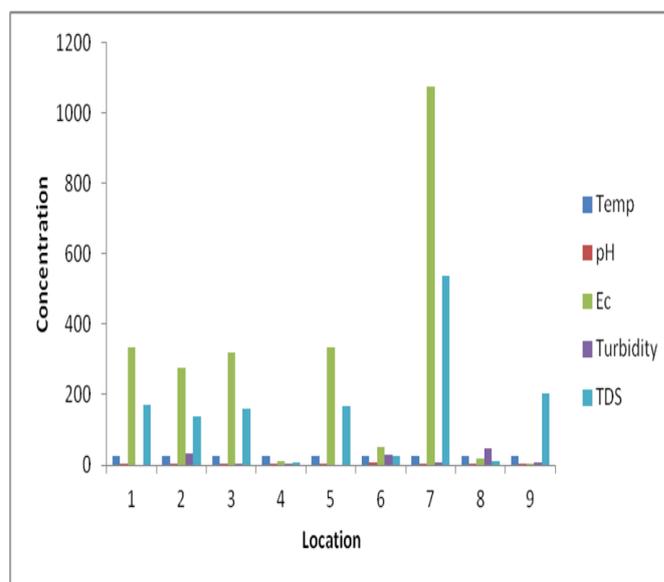


Fig. 2 Spatial variation of physical parameters in water in the wet season

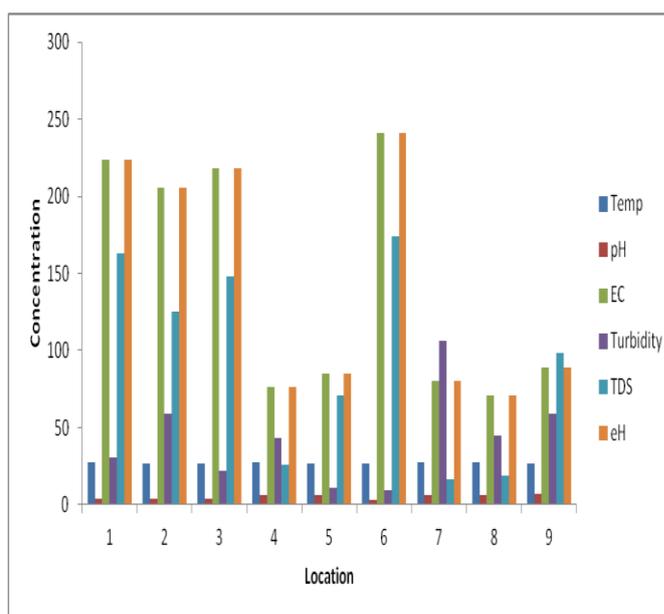


Fig. 3 Spatial variation of physical parameters in water in the dry season

In the wet season fluorine had a highest value of 45mg/l at location 9 adjudged to be above potable water standards by

WHO (2006). Dry season sampling recorded lower values of fluorine. Almost all the locations had zero concentration of fluorine except locations 7 and 9 indicated 1.01 and 0.07mg/l respectively. On the contrary, [27] recorded values of fluorine as high as 74.4mg/l in coal mine at China. The source of fluorine is the mineral fluorite. High phosphate of 2.19mg/l at location 9 in the wet season could be due to anthropogenic activities. Phosphate was drastically low in all the locations in the dry season. Phosphate is a natural constituent of natural waters. The values of phosphate in the wet season were low in locations 1, 2, 4, 6, and 7. In the dry season phosphate was least in location 3, next to locations 5, 6, 7, and 8 proximate to the mine area. There is high concentration of potassium in location 9 in the wet season (Fig. 6) and a correspondingly high value in location 9 in the dry season (Fig. 7). Low geochemical mobility explains its low concentration in other locations. Potassium rich fertilizers are the likely source of potassium in soils. High concentration of chloride was 400mg/l in location 9 in the wet season, but low in the dry season. High chloride concentration can be attributed to rock salt. Chloride has high mobility in water. [13] obtained a chloride value of 3.5ppm in Enugu coal mines which is lesser than values of 7.33mg/l and 136.67mg/l recorded in the dry and wet seasons respectively in this study. Garbage and fertilizers are the sources of chloride since location 9 is a well in the nearby village. Nitrate concentration peaked at location 9 (1012mg/l) and least at location 8 (158mg/l). In the dry season nitrate had very low concentration, probably due to low runoff from fertilizer sources. High nitrate concentration at location 9 could be due to nitrogenous fertilizers and leguminous plants. [28] associated nitrate released from coal gasification in Texas USA to ammonium reduction by bacteria and from fertilizers. Sulphate concentration in the wet season was lowest (10mg/l) in location 4 and 8 while the highest concentration (517mg/l) was obtained at location 7 (Fig. 9). In the dry season sulphate recorded least value (1.2mg/l) in location 3 and highest concentration in location 5 (105mg/l). Locations with high value of sulphate are indicative of pyrite oxidation causing acid mine drainage [29]. [7] recorded sulphate value of 430mg/l in Okpara Coal Mine.

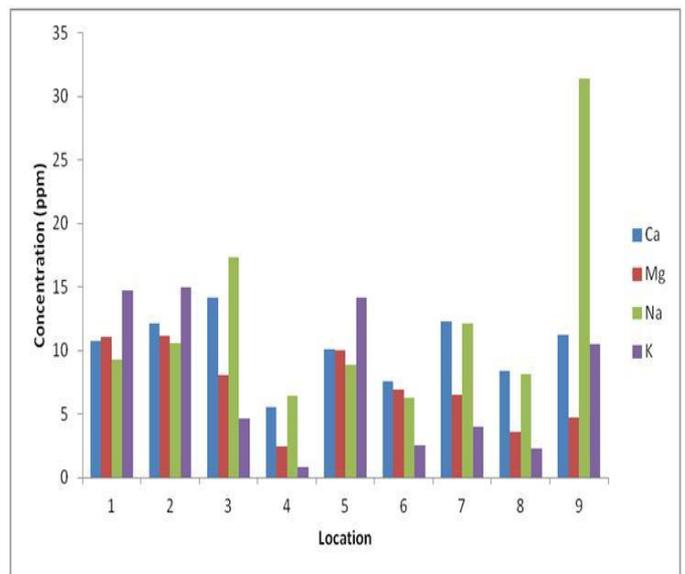


Fig. 5 Spatial variation of major cations in water in the dry season

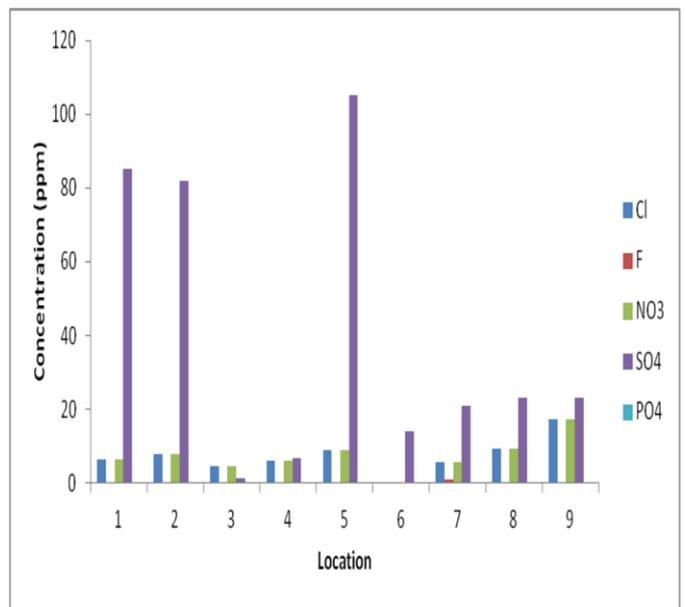


Fig. 6 Spatial variation of anions in water in the dry season

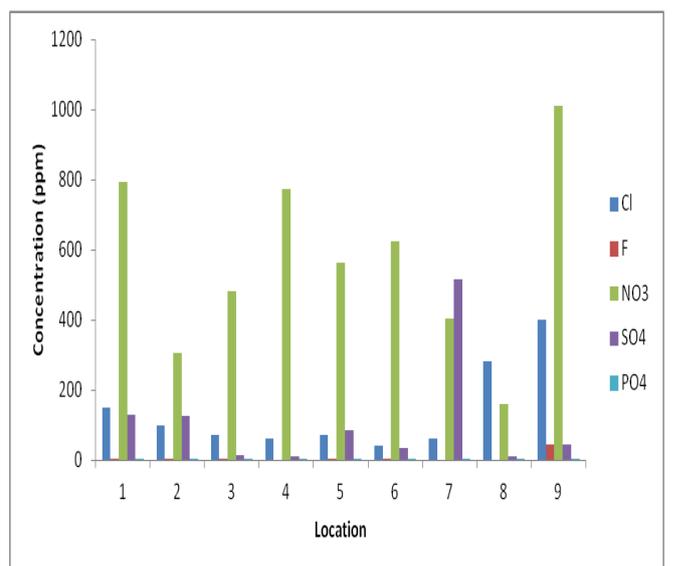


Fig. 7 Spatial variation of anions in water in the wet season

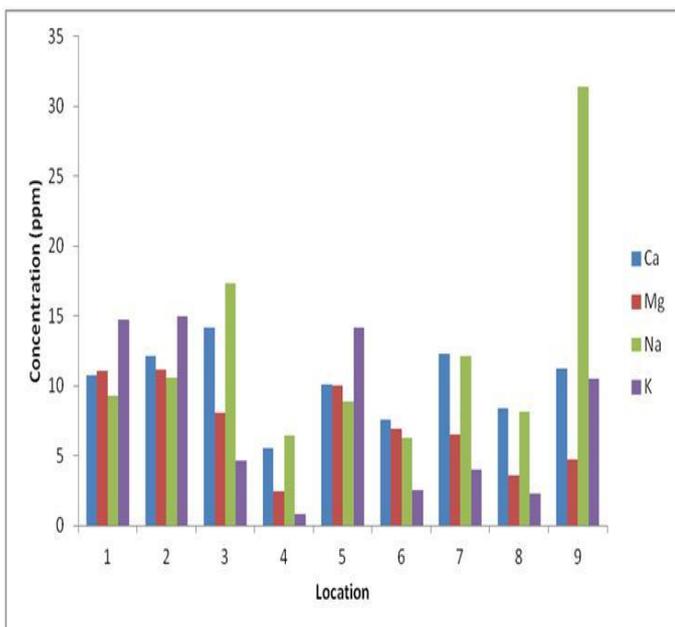


Fig. 4 Spatial variation of major cations in water in the wet season

The highest calcium concentration was recorded at location 9 and a least value of 1.4mg/l in location 4. The source of calcium is salt called gypsum. Sodium has a high mobility and has a highest concentration in location 9 (well). The source of sodium is nepheline. Magnesium is maximum (11.42mg/l) in location 3 (effluent). This is due to coal mine drainage. The least value in the wet season is in location 8 and in the dry season location 4. Magnesium concentration portrays reduction with increasing distance from the mine adit. The source of magnesium is carnelite [30].

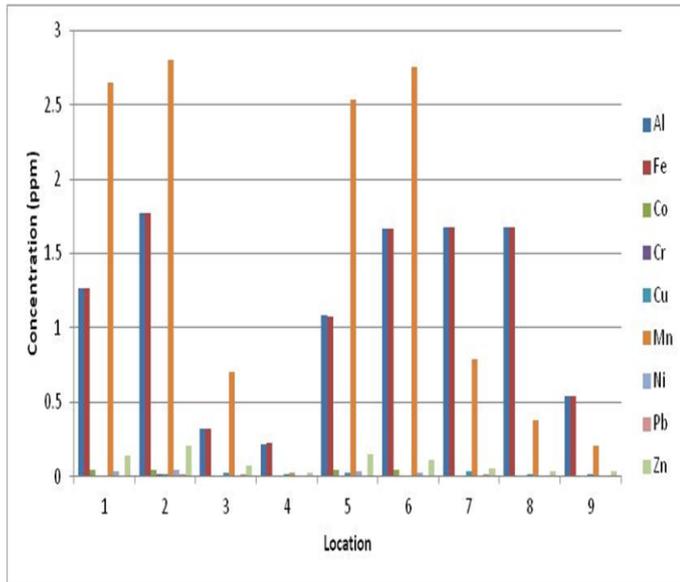


Fig. 8 Spatial variation of heavy metals in water in the dry season

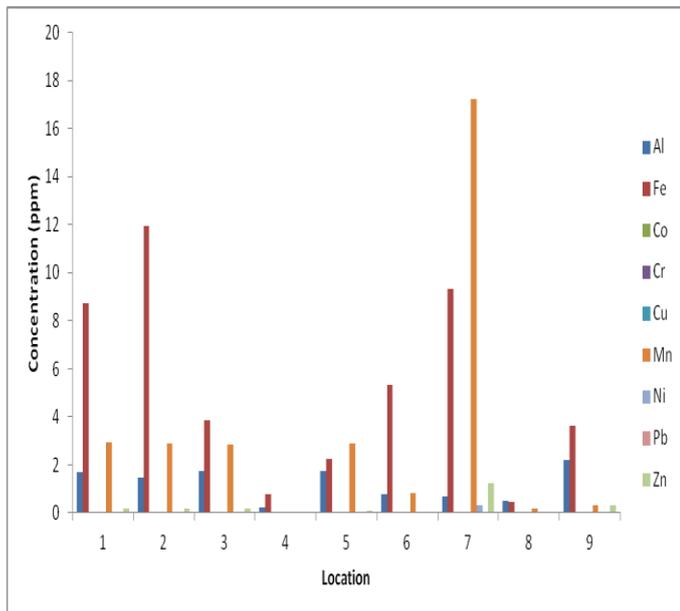


Fig. 9 Spatial variation of heavy metals in water in the wet season

The maximum concentration of manganese in wet season (17.23mg/l) was obtained at location 7 (confluence) and lowest value (0.03mg/l) at location 4. In the dry season manganese had highest concentration of 2.804mg/l at location 2 and least value of 0.202mg/l at location 9. This reflects the decrease in concentration with increasing distance from the mine site. High iron and manganese concentration are preponderant heavy metals in the study area in both seasons (Figs. 8 and 9). This is

due to pyrite oxidation causing acid mine drainage. [13] reported a value of 0.03ppm of iron at Awgu in Enugu. The source of iron is from pyrite (FeS), siderite (FeCO₃) and hematite. Aluminum is common in lateritic soil. The soil in the area is lateritic. Aluminum has low geochemical mobility. Aluminum concentration is highest in location 2 (1.19mg/l) and least concentration in location 4 (0.28mg/l) in the wet season. In the dry season, Aluminum indicated maximum value of 1.774mg/l in location 2 and least value (0.22mg/l) in location 4. In acid mine drainage site Al is converted to toxic Al³⁺. [23] obtained a mean value of 26mg/l in Pennsylvania coals. Aluminum is from the mineral bauxite.

The heavy metals Cd, Pb and Cr have negligible concentration in 0.00mg/l in all in water samples. The source of Cd is clay and shale. Chromium and Lead are from clay sediments [18]. The highest concentration of Nickel (0.309mg/l) in the wet season was obtained at location 7 and a value of 0.038ppm at location 5 in the dry season. Weakly acidic conditions immobilize Nickel. High concentration of Zinc at location 7 and 5 in wet and dry season respectively may be due to reducing conditions [18]. Zinc has high mobility under oxidizing and reducing low pH conditions. [32] reported values of 0.13µg/l, 0.18µg/l and 17.10µg/l for Cr, Pb and Zn respectively in surface nearby water coal mines in Guryongsgan Formation.

4.3. Spatial Variation of Heavy Metals in Soil and Mine Spoil

Tailings piles, ponds, mine wastes rock dumps and coal spoils are an important source of acid mine drainage. Stockpiles and mines that are situated close to water courses without any barrier can cause degradation of water quality. The variation of common toxic heavy metals released from coal such as Pb, Ni, Cd, Fe, Cu, Cr, Mn and Zn were investigated.

There is higher concentration of heavy metals in mine spoil than in soil. (Tables 3 and 4). The concentration of Pb in soil was almost uniform, but slightly elevated at location 1 and above background values obtained in coals and black shale (Table7). This is probably due to the fact that heavy metals are concentrated in the top soil [32]. The source of lead is galena [18]. Iron had the highest concentration in mine spoil heap 4 (near confluence). The concentration of iron was widely different in mine spoil but with little variation in soil. Higher values in soil and mine spoil than in water samples were due to their adsorptive capacity for these elements. In soil (Table 5), the highest value of iron was 8.56 at location 2 (near mine pond) and least value (5.60ppm) at location 1 (overburden soil).

Table 5. Summary of levels of concentration (ppm) of heavy metals in soil

Parameter	MEAN	STD	MINIMUM	MAXIMUM
Fe	7.177	1.052	5.6	8.56
Zn	5.292	0.054	4.86	6.10
Mn	2.950	0.003	2.61	3.30
Pb	4.602	0.49	4.11	5.30
Cd	1.370	0.132	1.22	1.59
Cr	1.14	0.046	1.08	1.15
Ni	0.712	0.38	0.08	1.05
Cu	1.15	0.05	1.10	1.17

Table 6. Summary of levels of concentration (ppm) heavy metals in mine spoil

Parameter	MEAN	STD	MINIMUM	MAXIMUM
Fe	8871.4	5422.05	6200	154000
Zn	189.8	295.27	28	780
Mn	2.60	1.20	1.0	44.0
Pb	23.72	4.15	18	29
Cd	0.10	0.00	0.1	0.1
Cr	47.14	4.21	41.7	51.6
Ni	9.60	0.49	87	98
Cu	64.14	16.35	43.2	90.2
Co	3.32	0.36	2.9	3.8

Table 7. Background values of the level of heavy metals (ppm) in coal

Parameter	MEAN	STD	MINIMUM	MAXIMUM
Fe	3.05	0.58	2.58	3.86
Zn	2.68	0.43	2.15	3.20
Mn	0.95	0.14	0.82	1.15
Pb	1.50	0.27	1.27	1.87
Cd	0.65	0.09	0.56	0.77
Cr	0.50	0.10	0.39	0.63
Ni	0.28	0.06	0.22	0.37
Cu	0.70	0.15	0.55	0.91

Cadmium recorded a constant value of 0.1ppm in mine spoil with a slight variation in soil. Cadmium is common where there has been zinc and lead mining because zinc and cadmium has the same geochemical behavior. [8] obtained a mean value of 0.036ppm for Cd in coal samples from Onyeama mine. Sources of cadmium are sphalerite and smithsonite [24]. In mine spoil the highest concentration of copper (90.2ppm) was recorded at location 1. Soil samples had the highest concentration of copper (1.23ppm) in location 2 and the least concentration (1.10ppm) in location 3 and 4. The source of copper is chalcopyrite.

High concentration of Chromium (51.6ppm) was obtained at location 1 and least value (41.7ppm) at location 3 in mine spoil. Chromium concentration in soil was low in all the locations this may be due to leaching. The concentration of Chromium in soil was fairly uniformed. Fang et al [33] reported a mean value of 180µg/g in soil samples around a coal mine at Guryongsan Formation. The source of Chromium is from the mineral Chromite. It can also be precipitated from smectites [18]. Manganese is commonly found in coal mine sites in association with Fe and Al. manganese exhibited high concentration due to its availability at acid mine drainage sites [23]. [21] obtained a value of 0.05ppm for manganese in mine spoil at Decker Coal Mine. In mine spoil (Table 6), the highest concentration of zinc was recorded at location 1 (near mine pond). This is due to mobility at pH of 5.8 is oxidizing condition. Higher concentration of zinc in the soil is due to its mobility [21]. The source of zinc is sphalerite. The concentration of heavy metals recorded in this work is higher than those obtained in previous work in the study area. This may be due to the sensitivity of the instrument (ICP-Ms) used in relative to AAS used by previous investigators.

The low concentration of heavy metals in mine pond location 1 and 9 as explained by [34] is due to the fact that heavy metals are weakly hydrolysed in aqueous solution in addition to dilution by rains. This makes the particulate metal system

content to settle to the bottom. Heavy metals are dissolved at low pH condition of heavy metals. This may be due to the metals leaching from the water and sorbed in soil [34]. The mean values of heavy metals recorded in the background values of coal samples (Table 7) are lower than those obtained in Soil and mine spoil (Tables 5 and 6 respectively). This could be attributed to acid mine drainage on soil and mine spoil

5. CONCLUSION

The oxidation of pyrite is the principal factor responsible for acidic condition at mine sites. On the other hand sulphite oxidation causes the mobilization of heavy metals in water which combine to cause acid mine drainage. Carbonate causes buffering thereby decreasing the acidity of the mine site. Mine spoil and contaminated soil, which are not treated, when there is overflow are drained into receiving rivers and streams causing elevated acidity and heavy metal dissolution. This condition hampers photosynthetic activities in the receiving water courses which is harmful to aquatic lives in such water bodies. Water quality within the mine site is degraded due to acid mine drainage. Water bodies down gradient from the mine exhibit moderate acidity and heavy metal concentration. In coalmine sites there is a preponderance of heavy metal concentration such as Al, Fe, Mn, Ni and Cu, which are potentially toxic metals.

Seasonal water sampling from a mine site unfolded that the favourable season for acid mine drainage is the wet season due to overland flow. The water quality is also influenced by the geologic and hydrogeologic condition prevailing at a given site. Acid mine drainage is better appreciated by seasonal water sampling; mine spoil and soil in a mine site. Mine spoil and soil recorded higher heavy metal concentration than water samples. This implies that the source of heavy metal contamination is from mine spoil. The soil within the mine site is suitable for cultivation. Heavy metals are supposed to be dissolved at low pH. The low metal concentration obtained in the study area despite low pH was due to leaching of the metals to the subsurface. Using a more sensitive analytical instrument such as ICP- MS guarantees a reliable heavy metal analysis compared to AAS.

6. REFERENCES

- [1] R.A. Zielinski, J.K. Otton and C.A. Johnson, Sources of salinity near a coal mine spoil pile North Central Colorado. *Journal of Environmental Quality* Vol 30 pp 1237-1240. 2001.
- [2] L.M. Cathles, Acid Mine Drainage. *Journal of Earth and Mineral Sciences* Vol 51 No 4 pp 39. 1982.
- [3] S. Geldenhius, F.G. Bell, F. G, Acid Mine Drainage at a Coal Mine in Eastern Transvaal South Africa. *Environmental Geology* pp238-239. 1998.
- [4] G.I. Nwankwor, B. Egboka, I.P. Orajaka, I. P, Groundwater occurrence and flow pattern in Enugu coal mine area. *Hydrological Sciences Journal* Vol 5 No 33 pp465-482. 1988.
- [5] H.N. Dialah, A review of some of the future and possible solutions facing the Nigerian coal industry. *Symposium on 20th Annual Conference of the Nigerian Mining and Geosciences Society* publication pp 17-18. 1994.

- [6] R.K. Tiwary, B.B. Dhar, Environmental pollution from coal mining activities in Damodar River Basin India. *Mine Water and the Environment* Vol 13 pp1-10. 1994.
- [7] H.I. Ezeigbo, B.N. Ezeanyim, Environmental pollution from coal mining activities in the Enugu area Anambra state Nigeria *Mine Water and Environment*. Vol 2 pp58-59. 1993.
- [8] E.O. Adaikpo, G.E. Nwajei, J.E. Ogala, Heavy metals concentration in coal and sediments from River Ekulu in Enugu coal city of Nigeria. *Journal of Applied Science and Environmental Management* 9 (3) 5 - 6. 2005.
- [9] C.R. Ward, Coal Geology and Technology. *Geological Magazine*. 122 (6), 4 - 9. 1984.
- [10] K.E. Nwabufu-Ene, Non-oil mineral exploration in Nigeria. *Journal of Science and Technology*. 1, 16 - 17. 1993.
- [11] O.S. Onwuka, K.O. Uma, H.I Ezeigbo, Potability of shallow groundwater in Enugu Town southeastern Nigeria. *Global Journal of Environmental Sciences* 1 (2) 34 - 37. 2004
- [12] O. Areola, An introduction in Aerial Photo-interpretation in the African Continent. Evans Brother Nigeria Limited. 108p. 1985.
- [13] M.E. Offodile, Groundwater study and Development in Nigeria (9) ed Macon Geology and Engineering Services Ltd Jos Nigeria. 364 - 393. 2002.
- [14] G.S. Nwajide and T.J.A Reijers, Geology of Southern Anambra Basin. In T.J.A. Reijers (Ed.), selected chapters on geology (131 - 140). Port Harcourt Shell Petroleum Development Company. 1996.
- [15] American Public Health Association, American Water Works Association, and Water Pollution Control Federation, Standard Methods for the examination of water and wastewater, twentieth ed. Washington, DC. 1998.
- [16] T.N. Nganje, C.I. Adamu, A.N. Ugbaja, E.A. Amah, Evaluation of hydrogeochemical characteristics of groundwater. *Journals of Geochemistry* Vol 29 pp 400-401. 2010.
- [17] M. Keating, Environmental impact from coal Clean Air Task Force (CATF) Spectrum printing and Graphics: In Ellem Beum, and Army Hennen and Brue Hell (eds) pp 1-3. 2001.
- [18] F.R. Siegel, Environmental Geochemistry of Potentially Toxic Metals. Springer Barker Heldenberge New York Barcelona, Honkey, London Mine Par Tokyo, pp 277-280. 2002.
- [19] G.J. Udom, E.O. Esu, S.J. Ekwere, Quality status of groundwater in Calabar Municipality in Southeastern Nigeria. *Global Journal of Pure and Applied Sciences*. 2 (2), 4-5. 1996.
- [20] D.B. Willock, Water Engineering Evans Base Technology Ltd. Printers Ltd Series Consultants pp43. 1983.
- [21] G.K. Pagenkopf, C. Whitworth, W.A. Varvoast, Influence of spoil material on Groundwater Quality *Energy Communications* Vol 3 No 2 pp 115-126. 1997.
- [22] E. Earle, G. Callaghan, Impact of mine Drainage on aquatic life, water uses and manmade structures coal mine drainage productions and pollution prevention Pennsylvania Department of Environment in Tim Kanu, Scott Barnes, William Heller, Charles, Miller and Jory Terium (eds) pp 4-8. 1998.
- [23] A.W. Rose, A. Cravotta, Geochemistry of Coal Mine Drainage prediction and pollution prevention Pennsylvania Department of Environment. In Tin Kanu, Scott Barneds, William Hetter, Charles Miller and Jony Tarantino (eds) pp 7-9. 1998.
- [24] I. Thorton, Impact of Mining on the Environment, some local regional and global issues. *Applied Geochemistry* Vol 11 pp 355-360. 1996.
- [25] E.A. Keller, Geologic Aspect of Environmental Health. *Environmental Geology*. Vol 2 (ed) Charles printing Company Ohio pp50-65. 1976.
- [26] E.A. Keller, Geologic Aspect of Environmental Health. *Environmental Geology*. Vol 2 (ed) Charles printing Company Ohio, 50 - 65. 1976
- [27] M. Ando, T. Miloko, M.S. Shousni, W.T. Toshikazu, S.S. Kondo, J.I. Rongbi, L. Chacke, C. Shoun, Health effects of Indoor Flouride pollution from coal burning in China. *Environmental Health Perspective* Vol 106 pp 239-241. 1998.
- [28] M.J. Humenick and C.F. Mattox, Groundwater pollutants from underground coal gasification. *Water Research*, 3, 463 - 467. 1977.
- [29] C. Chick, Acid mine drainage –causes, effects and solutions. Retrieved June 24, 2008 from <http://www.essaydepot.com/essayme/159/index.php>. 2002.
- [30] J.D. Hem, Study and interpretation of the chemical characteristics of national water. United States Geological Survey water Supply Paper, 3, 1104 - 2301. 1985.
- [31] N.C. Woo, M.J. Cho, K.S. Lee, Assessment of groundwater quality and contamination on Uranium bearing blacks hales in Goesen Boein Area. *Environmental Geology*, 40; 261 - 264. 2002.
- [32] A.A. Levinson, Introduction to exploration Geochemistry. Applied publishing limited Wilmete Illinois pp 142-143, 187. 1974.
- [33] W. Fang, R. Hu, and P. Wu, Influence of black shales on soils and edible plants in the Ankang area, Shanxi Province China. *Journal of Chinese Academy of Sciences*, 3, 36 - 39. 2001.
- [34] Balkema, A. Rotterdam, and A. Brookfield, Mineral Deposits process to processing: proceedings of the fifth Biennial SGA Meeting and the Tenth Quadrennial AAGOD Meeting London pp 1172. 1999.