

*Full Length Research Paper*

# **Influence of mine drainage on water quality along River Nyaba in Enugu South-Eastern Nigeria**

**T. N. Nganje<sup>1\*</sup>, C. I. Adamu<sup>1</sup>, E. E. U. Ntekim<sup>1</sup>, A. N. Ugbaja<sup>1</sup>, P. Neji<sup>2</sup> and E. N. Nfor<sup>3</sup>**

<sup>1</sup>Department of Geology, University of Calabar, Calabar, Nigeria.

<sup>2</sup>Department of Chemistry, Cross River State University of Technology, Calabar, Nigeria.

<sup>3</sup>Department of Chemistry, University of Buea, Cameroon.

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**Major and Trace elements concentration were measured in water samples collected in and around Okpara coal mine in Enugu southeastern Nigeria to investigate the influence of mine drainage on the quality of water. The cations and trace elements were determined by ICP- MS while the anions were measured by spectrophotometer and titration methods. Field parameters such as pH, temperature and conductivity were determined in the field using standard equipment. The results show that the water is acidic to moderately acidic (pH 2.84 to 6.69) with pH increasing along the flow direction. The mean values of pH (4.66 (dry), 4.22 (wet), Color (334.34 TCU (dry), 153.11 TCU (wet) and turbidity (53,67 NTU (dry), 17.43 NTU (wet) as well as iron (6.35 mg/L(dry), 5.14 mg/L(wet), aluminum(1.14 mg/L(dry), 4.30 mg/L(wet), manganese (1.43 mg/L(dry), 5.36 mg/L (wet) and nickel, 0.053 mg/L (wet) recorded in the dry and wet seasons are above levels recommended by WHO for drinking water and other domestic purposes. Mean levels of fluoride (5.4 mg/L) with ranged of 0.00 to 45 mg/L, potassium (12 mg/L) with ranged of 1.17 to 27.85 mg/L and nickel (53.10 µg/L) with ranged of 1.50 to 309.30 µg/L, as well as maximum levels of chromium (100 µg/L) with ranged of 0.05 to 100 µg/L , chloride(400 mg/L) with ranged of 40 to 400 mg/L, nitrate(1012 mg/L) with ranged of 158 to 1012 mg/L and sulphate (517 mg/L) with ranged of 10 to 512 mg/L obtained in the wet season are above the WHO maximum permissible level. Generally, the levels of the elements decrease with distance away from the mine waste except for nitrate and fluoride. Thus the quality of the water is most probably influenced by acidic mine drainage and its impact on human health and the environment could be severe. Microbial assessment and element speciation are recommended for further quality assessment in the study area.**

**Key words:** Major, trace elements, water quality, mine drainage, Enugu, Nigeria.

## **INTRODUCTION**

Drainage from underground coal mines, surface mines and coal refuse piles is the oldest industrial pollution in the Enugu coal area which is characterized by numerous surface water, hand dug wells and shallow unconfined aquifer and as such the water sources are prone to contamination from coal mining activities. The potential for acidic mine drainage and the release of toxic elements from mine waste exist throughout the Enugu coal region. Acidic mine drainage poses a major environmental hazard to fresh water resources worldwide and has enhanced levels of heavy metals and the pH is low due to the weathering of sulphide minerals. Acidic mine

drainage water could come from mine ponds and spoils heaps into soils, surface water and groundwater as well as into stream sediments and surrounding vegetation (Blodau, 2004). Acidic mine drainage may occur especially if the bedrock is fractured and exposed, the climate is warm and moist and the thick vegetation cover is removed (Bain et al., 2000; Amenita et al., 2001; Zielinski et al., 2001; Moncur et al., 2006). Contaminated water constitutes health risk, as this could result to excess accumulation of heavy metals in humans leading to phototoxic effects.

About 11% of the global sulphate flux from the continent to the oceans comes from mining activities alone (Banwart et al., 1998). The influx of untreated acidic mine drainage into streams can severely degrade both habitats and water quality and often produced an

\*Corresponding author. E-mail: [ntonzi@yahoo.com](mailto:ntonzi@yahoo.com).

environment devoid of most aquatic life and unfit for healthy habitation. The severity of the damage depends on factors such as the volume and chemistry of the drainage and the size and buffering capacity of the receiving stream (Kimmel, 1983).

The geochemistry of acidic mine drainage has been the subject of numerous investigations. Some documented cases include that of Kimmel (1983), Alpers and Blowes (1994), Nordstrom and Alpers (1999), Frommichen et al. (2004), Geldenhaus and Ball (1998), Jenkins et al. (2000), Bachmann et al. (2001), Fontbole (2001), Holmstrom et al. (2001), USGS, USEPA (2002), D.E.P (2002), Ehrlich (2004), Denimal et al. (2005), Ata and Kudas (2006) and Egiebor and Oni (2007). In the study area, at the end of the mining activities in 2004, the mine was left un-reclaimed; water bodies collected in them forming perennial mine ponds. Untreated water from these mines ponds and those from the underground mine are drained into the surrounding streams, agricultural land and the nearby Nyaba River. The unfavorable repercussion of coal mine drainage in the Enugu area has been documented by Ezeigbo and Ezeanyim (1993) and Offodile (2002). The present study is to investigate the influence of acidic mine drainage on the quality of water along River Nyaba in the vicinity of Okpara coal mine and also to examine their spatial and temporal variation.

#### Description of study area

Okpara coal mine was opened in 1952 by the Nigerian Coal Cooperation (NCC). Production declined from a peak of 3040 tons in 1984 to 1016 tons in 1990 and was closed down (Dialah, 1996; Skeup, 1983; NCC, 1989). The mine was later reopened in 1999 and operated till 2004/2005 when it was abandoned due to economic problems. The area is situated between latitudes 06° 20' and 06°25' and longitudes 07°25' and 07°30'. The study area is drained by the river Nyaba and its tributaries (Figure 1).

The study area is located within the tropical climatic region with temperatures in the range of 23 - 30°C. The area is characterized by two seasons: a dry season which starts from November to March with harmattan with dusty haze from the Sahara region between December and early February and the rainy season which lasts from April to October. The rains are usually heavy and the annual mean value is about 1500 mm (Onwuka et al., 2004). The natural vegetation is the tropical rainforest type which has largely changed to guinea savannah due to farming and deforestation.

The coal mine spoils which are not treated and are scattered around the area consist of a mixture of variable fragmented carbonaceous shale, sandstones, clay and coal. Pyrite and marc site are found to be associated with these materials. The Ajali sandstone is the major aquiferous unit in the area and it contributes almost all the groundwater entering the Okpara coal mine (Ezeigbo and Ezeanyim, 1993). According to Onwuka et al. (2004) the lateritic overburden which varies in thickness from 20 - 30 m constitutes another major source of recharge in the area. The depth of the water table is between 5 - 7 m and is a function of local topography. The shallow water table is prone to aquifer susceptibility to contamination.

#### MATERIALS AND METHODS

Thirty six water samples were obtained from surface water, mine

ponds and hand - dug well in the dry season (January, 2007) and wet season (April, 2007) within and around the vicinity of the Okpara coal mine for the study (Figure 1). Sampling sites were selected to reflect sources of inflowing, intermediate and out - flowing water. The water samples were collected below the surface and filtered using 0.45 µm Millipore filters into sterilized polyethylene bottles tied at the necks with clean twine rope to avoid collecting the metal rich surface films. Sample bottles were rinsed at the sampling site with the water to be sampled before collection. Water collected for major and trace metal analysis was preserved by acidifying with a few drops of HNO<sub>3</sub> acid to achieve a pH of ≤ 2. The samples used for anions analysis were not acidified but were preserved in a refrigerator prior to analysis to exclude microbial activity. Water analyses were carried out using standard procedures. Field analyses were made for parameters such as Temperature, pH, Turbidity, Electrical Conductivity and Color. Temperature and Conductivity were measured using WTW 96 meter, Turbidity with Turbidity meter, pH with WTW pH meter and Color with lauvibond comparator. NO<sub>3</sub><sup>-</sup>, SO<sub>4</sub><sup>-</sup>, F<sup>-</sup> and PO<sub>4</sub><sup>-</sup> were determined by spectrophotometer. Cl<sup>-</sup> and HCO<sub>3</sub><sup>-</sup> were determined by titration. Major cations (Ca, Mg, Na, K) and other trace elements such as As, Be, Ba, Cr, Cu, Zn, U etc. were analyzed using ICP - MS (Perkin Elmer Elan 6000). Precision was achieved by triplicate analyses of the same sample and standards and the mean value s was taken.

## RESULTS AND DISCUSSION

### Seasonal variation

The mean, standard deviation, median, minimum and maximum values for the physico - chemical parameters and trace elements are presented in Tables 1 and 2, respectively. Large standard deviations as obtained for most of the parameters for both season except for Ag, Be, Cd, Mo, U and V, may probably be due to some analytical errors and the variation in geology.

The maximum levels for all the physical parameters except for temperature and TDS were obtained in the rainy season. The minimum and maximum values of temperature correspond to the ambient temperature of the area as quoted by Onwuka et al. (2004). The mean values for electrical conductivity (334.33 µs/cm(dry) and 337 µs/cm(wet) and TDS (65.54 mg/l (dry) and 157.77 mg/L (wet) are within the WHO (1993) admissible values of 1400 µs/cm(conductivity) and 1000 mg/L(TDS) for both seasons indicating that the water is good with regard to these parameters. The mean values obtained for pH 4.66 (dry) and 4.22 (wet) in both season are above the WHO (1993) admissible value of 6.5 to 8.5 indicating that the water is moderately acidic. The acidic nature of the water may be associated to the weathering of the sulphide minerals from the mine spoils and discharges from the mine which are pumped into River Nyaba. The mean values obtained for color of 334.33 TCU (dry) and 153.1 TCU (wet) and turbidity of 53.67 NTU (dry) and 14.67 NTU (wet) for both season are above the WHO (1993) admissible level of 15 TCU (color) and 5 NTU (turbidity). The discharge from the underground mine and leaching from the mine heaps may be contributing to the color and turbidity of the water. The maximum

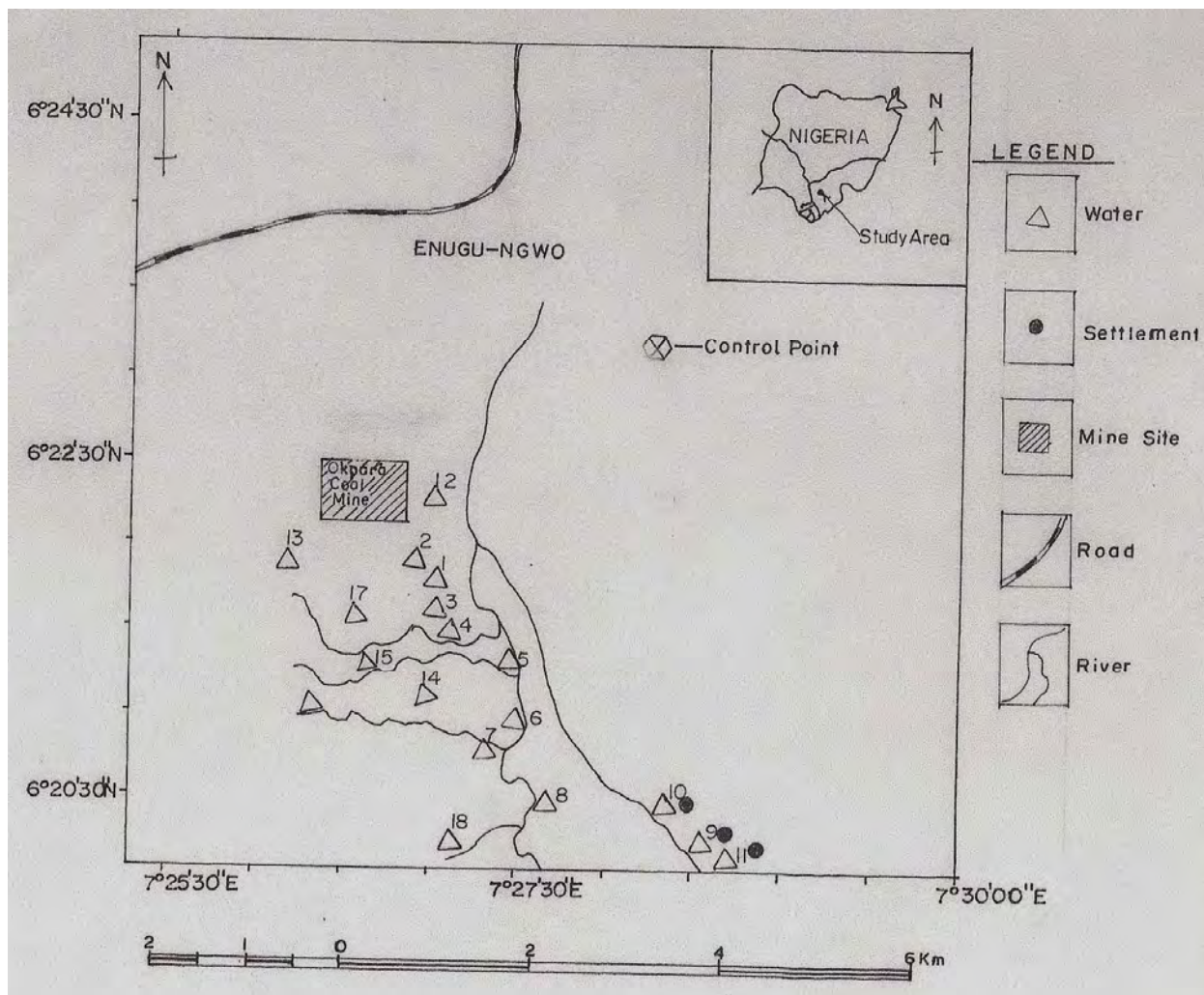


Figure 1. Map of the study area showing sample location.

Table 1. Descriptive statistics of physico - chemical parameters alongside WHO (1993) maximum permissible limits.

Parameters	Dry season					Wet season					WHO limit
	Mean	S.D	Median	Min	Max	Mean	S.D	Median	Min	Max	
Colour (TCU)	334.33	381.11	119	36	989	153.11	320.35	55	0.00	1005	15
EC (µs/cm)	168.67	141.09	195	7	344	269.67	337.02	277	4.04	1076	1400
Temp (°C)	27.12	0.28	27.10	26.9	27.80	26.84	0.213	26.80	26.50	27	-
TDS (mg/L)	65.54	68.31	18.6	4	174	157.77	161.69	160	6.3	583	1000
Turb (NTU)	53.67	44.48	45	9	141	14.67	17.43	6	0.00	48	5
pH	4.66	1.44	3.84	3.18	6.69	4.22	1.13	3.65	2.84	6.05	6.5-8.5
Cl (mg/L)	118.57	69.14	100.00	40	250	138.89	122.01	90	40	400	250
F (mg/l)	0.128	0.33	0.010	0.00	1.01	5.04	14.99	0.40	0.00	45	1.5
NO <sub>3</sub> (mg/L)	104.87	259.54	8.60	4.40	792.0	167.67	265.54	5.63	158	1012	50
PO <sub>4</sub> (mg/L)	0.063	0.067	0.040	0.00	0.18	1.08	0.59	0.79	0.52	2.19	5
SO <sub>4</sub> (mg/L)	46.67	37.76	23	10	105	119.11	156.54	85	10	517	250
Ca (mg/L)	10.25	2.68	10.73	5.57	14.19	9.9	4.97	9.12	3.90	20.17	200
Mg (mg/L)	7.19	3.19	6.90	2.47	11.17	6.80	3.80	5.80	2.62	12.14	100
K (mg/L)	6.52	0.624	3.90	0.53	14.83	12.01	8.95	15.12	1.17	27.85	10
Na (mg/L)	12.34	7.89	9.83	6.31	31.83	14.00	15.38	8.57	6.53	54.70	250

**Table 2.** Descriptive statistics of trace elements in water alongside WHO (1993) maximum permissible limit and average freshwater content.

parameters	Dry season					Wet season					WHO (1993) permissible limit (mg/L)	Average Fresh water content (ppb)*
	Mean	S.D.	Median	Min	Max	Mean	S.D.	Median	Min	Max		
Ag (µg/L)	19.79	34.35	0.53	0.25	104.4	0.078	49.92	0.03	0	0.5		0.3
A <sup>s</sup> (mg/L)	1.14	0.62	1.27	0.244	1.77	4.30	9.88	1.45	0.28	30.59		0.1 - 0.01
As (µg/L)	79.73	44.18	102	1.7	104	0.3378	0.4694	0.04	0.1	1.1	0.05	2
B (µg/L)	29.56	21.11	28.00	7	76	27.78	21.3	27	9	79		10
Ba (µg/L)	92.99	49.49	84.85	32.62	185.27	69.43	52.13	73.33	24.56	191.15	0.7	9.3
Be (µg/L)	11.67	33.13	0.62	0.05	13.59	13.24	32.82	1.16	0.05	1.85		5.5
Cd (µg/L)	0.433	0.101	0.4	0.32	0.57	0.35	0.392	0.3	0.05	1.36	0.003	0.032
Ce (µg/L)	8.063	4.81	8.82	1.54	17.43	33.32	77.59	8.06	1.73	239		0.2
Co (µg/L)	21.70	22.27	6.33	0.30	48.48	68.62	133.53	42.83	0.51	419.40		0.1
Cr (µg/L)	4.38	6.03	1.80	0.60	19.40	12.03	33.01	0.700	0.50	100	0.05	1
Cu (µg/L)	18.26	8.70	15.80	9.40	36.20	13.47	12.72	8.80	4	45.6	2.0	3
Fe (mg/L)	6.35	5.45	7.19	0.277	16.58	5.14	4.03	3.86	0.44	11.95	0.3	100
Li (µg/L)	10.10	6.9	0.80	1.50	20.50	18.59	27.86	10.30	1.30	90.60		4
Mn (µg/L)	1425.9	1217.9	786.76	26.98	2804.3	3353.8	5361.9	2861	31	17225	0.05	15
Mo (µg/L)	0.144	0.053	0.100	0.10	0.20	11.23	33.29	0.10	0.10	100		1.5
Ni (µg/L)	18.30	16.14	8.70	2.70	40.5	53.10	97.78	26.60	1.50	309.30	0.02	1.5
Pb (µg/L)	10.88	4.37	10	5.70	19.40	6.38	4.79	4.10	2.3	16.60	0.01	3
Si (mg/L)	8.31	1.73	7.69	5.89	10.81	8.50	6.02	6.23	4.52	23.89		6.5
U (µg/L)	0.83	0.376	0.73	0.42	1.45	23.22	68.93	0.70	0.48	199		5
V (µg/L)	0.83	0.73	0.40	0.20	2.10	0.53	0.397	0.40	0.20	1.50		2
Zn (µg/L)	93.23	62.61	0.72	29.80	210.5	253.82	382.88	171.10	16.8	1239	3	20

\* Adapted from Giblin (1994).

concentration for most of the major anions and cations are obtained in the rainy season. The order of relative abundance for the anions is  $\text{NO}_3^-$  (1012 mg/L) >  $\text{SO}_4^-$  (517 mg/L) >  $\text{Cl}^-$  (400 mg/L) >  $\text{F}^-$  (45 mg/L) >  $\text{PO}_4^-$  (2.19 mg/L) while for the major cations the order is Na (54.70 mg/l) > Al (30.59 mg/L) > K (27.85 mg/L) > Si (23.89 mg/l) > Ca (20.17 mg/L) > Mn (17.23 mg/L) > Fe (16.58 mg/L) > Mg (12.14 mg/L). Only the mean levels of concentration of Fe (6.35 mg/L, 5.14 mg/l, Mn (1.43 mg/L, 3.35 mg/L),  $\text{NO}_3^-$  (104.8 mg/L, 167.7 mg/L) for both seasons,  $\text{F}^-$  (5.04 mg/L) and  $\text{K}^+$  (12.01 mg/L) in the rainy season are above the WHO (1993) admissible values of 1.5 mg/L ( $\text{F}^-$ ) and 10 mg/L ( $\text{K}^+$ ). All other values of major anions and cations are within this limit. The elevated levels of Fe and Mn may be related to the co precipitating effect of Fe and Mn-oxides/hydroxides. Fe and Mn are considered as the common heavy metals of mine drainage.

The major source of Fe is most probably the pyrite and marcasite gangue found in the Enugu coal seams as well as the associated shales in the area mined. When pyrite ( $\text{FeS}_2$ ) is oxidized Fe is released coating the water and sediments with the characteristic yellow or orange color (Keller, 2000), U.S.G.S, U.S.E.P.A. (2002) which is observed in the study area.

The high values of cations and anions (Na > Al > K >

Ca > Mg and  $\text{NO}_3^-$  >  $\text{SO}_4^-$  > Cl > F >  $\text{PO}_4^-$ ) are contrarily to those reported by Turbak et al. (1979) (Ca > Mg > Na > K and  $\text{HCO}_3^-$  >  $\text{SO}_4^-$  > Cl) for mine drainage. The elevated levels of Na and K are probably as a result of dissolution of feldspathic minerals found in the sandstone and shale in the study area. Al rarely occurs in water at concentrations greater than a few tenths of milligrams per liter (Collagham and Earle, 1998). Higher concentration in the water in the study area may be as a result of drainage from coal mines, acid precipitation and breakdown of clays and aluminosilicates in shale (Hem, 1986). According to Rosemand et al. (1992), dissolved Al > 0.5 mg/l will generally eliminate all fish and many micro-invertebrates and will also coat the stream surface causing slippery surfaces and difficulties for insects to maintain their position in the current. The high level of  $\text{NO}_3^-$  (1012 mg/l) greater than F (45 mg/l) is unusual because although nitrates are of immense biological importance, it does not contribute significantly to the anionic composition unless they are highly enriched (Wetzel, 1983). High nitrates in the rainy season are attributed to leaching from fertilized farmyards and probably to denitrification of  $\text{NH}_3$  which may have resulted from underground coal gasification. Coal mine spoils can be sources of dissolved Mn, Na, Ca, Mg,  $\text{NO}_3^-$ ,  $\text{SO}_4^-$ , and Cl which can contribute to the salinization of local soils

(Zenlinski et al., 2001). High  $\text{SO}_4$  is as a result of dissolution of sulphide minerals. Jung (2001) also attributed high concentration of  $\text{SO}_4$  in stream water in the Au – Ag mine in Korea to the oxidation of pyrite.

65% of the maximum concentration obtained for trace elements were found in water collected during rainy season and these are in the order of Al(30.59 mg/l) > Mn(17.23 mg/L) > Co (419.9  $\mu\text{g/L}$ ) > Ni (309.3  $\mu\text{g/L}$ ) > Zn (253.82  $\mu\text{g/L}$ ) > Ce (239.88  $\mu\text{g/L}$ ) > U (199  $\mu\text{g/L}$ ) > Ba (191.15  $\mu\text{g/l}$ ) > Li (90.6  $\mu\text{g/L}$ ) > B (79  $\mu\text{g/L}$ ) > Cu (45.5  $\mu\text{g/l}$ ) > Pb (16.6  $\mu\text{g/L}$ ) > Cd (1.36  $\mu\text{g/L}$ ). Mo showed no variation with season and constitutes 5% of the trace elements analyzed, 30% of the maximum concentration was obtained for Ag (104.42  $\mu\text{g/L}$ ) > Cr (19.4  $\mu\text{g/L}$ ) > Be (13.59  $\mu\text{g/L}$ ) > V (2.10  $\mu\text{g/L}$ ) > As (1.1  $\mu\text{g/L}$ ) in the dry season. The source of these elements (major and trace) found in water sample in the rainy season especially in tropical humid region as in the study area, may be due to the interaction of acidic rain water with the mine spoils scattered around containing these trace elements and effluents from the underground mine which is emptied into the nearby River Nyaba and its tributaries. With the exception of Mo, U, V (dry season) and V (wet season) the mean values for all the trace elements are above the average fresh water content quoted by Giblin (1994). In addition the acidic nature of the water may enhance the mobilization of these elements. However, Cu and Zn are essential trace elements for plant and animal life including humans but at higher concentration they are considered toxic like others such as As, Cd, Pb, U, and V etc, (Savinov, 2003) and may affect aquatic life.

Many authors (Countin-Nomade et al., 2003; Dold and Fontbote 1998; Fostel et al., 1998; Fukushi et al., 2003; Mincage et al., 2005; Savage et al., 2001) have reported that secondary Fe and clay minerals have a large capacity for adsorption and co - precipitation of As and other heavy metals. Consequently, they are considered as the main solid - phase control on the mobility of potentially toxic elements in mine effluent. According to Jung (2001), the dispersion pattern of metals varies depending upon their solubility and mobility in the aqueous environment. The low metal and high acid metal water in the rainy season are due to the influx of acid rain water and the dissolution of sulphide minerals.

### Spatial variation

Dispersion pattern showing the level of variation of parameters are shown on Figures 2 and 3. For physicochemical parameters (Figure 2) the lowest and highest values for color were recorded at locations 5 and 8. The highest value for TDS, turbidity and lowest pH values were recorded at location 7. Meanwhile the highest values for electrical conductivity and pH were obtained at location 9. While low values for color and turbidity were obtained at location 5; location 8 recorded the maximum pH value. The maximum values for color and turbidity were above

the WHO (1993) limit.

The variation of major anions and cations are shown in Figure 2. For the anions the minimum values for  $\text{NO}_3$  and  $\text{SO}_4$  were recorded at location 8 ( $\text{NO}_3$ ) and locations 4, 8 and 9 ( $\text{SO}_4$ ) while the maximum values for  $\text{NO}_3$  and  $\text{SO}_4$  were recorded at locations 9 and 7, respectively. The maximum values of  $\text{NO}_3$  and  $\text{SO}_4$  obtained at location 9 and 7 are above the WHO (1993) admissible values. The values obtained for F and  $\text{PO}_4$  are below WHO (2004) admissible values for all location except at locations 6, 9, 10, 11 and 14. The lowest value for  $\text{PO}_4$  was obtained at location 7 while the highest value was obtained at location 9. The maximum value of F at location 9 is above the mean value of 5.04 mg/L and the WHO (1993) acceptable value. For chloride the lowest values were obtained at locations 6 and 9 but the maximum value is above the mean value indicating contamination. The relatively high concentration of nitrate, fluoride and phosphate at location 9 (shallow dug well) which is in the down stream area reflect to some extent, inflow of surface water and anthropogenic effluents derived from application of chemical fertilizers and livestock manure for cultivation mainly along the stream banks. High concentrations of sulphate were recorded around the mine area containing mine spoils and areas receiving effluent from the underground mine. For the cations, the lowest and highest concentrations of Na were recorded at locations 5 and 9 and these concentrations were below the WHO (1993) limit of 250 mg/l. The highest and lowest values for K were recorded at location 9 for the wet and dry seasons respectively. The maximum concentration is above the WHO 1993 acceptable limit. The lowest values 2.47 mg/L (Mg), and 5.67 mg/L (Ca) were obtained at locations 4 (Mg, Ca). While the highest concentration of 12.14 mg/l(Mg) was recorded at location 1(pond water).

The dispersion pattern showing the variation of some trace elements in Figure 3 shows that about 74% of the highest concentrations (Al, B, Be, Cd, Ce, Co, Cu, Fe, Li, Mn, Ni, Si, U and Zn) are obtained at location 7(influent water from the mine). At location 2 (also influent water from the mine), 5.2% of the highest concentration is recorded for Mo. 5.2% of the highest concentration was obtained for Ba at location 9. The highest concentrations of Cr and Ag are recorded at location 3 (effluent water from the mine pond) and that of V and Pb are found at locations 6 and 8 (stream) constituting about 10.4 and 5.2%, respectively. There is a general trend of decreasing concentration downstream away from the source of the contamination. Locations 2 and 7 represents water from the underground mines (influent), while location 3 (effluent) water from the mine pond. Location 6 is water along river Nyaba which is downstream of locations 2 and 3 and may have been contaminated by discharge from locations 2 and 3 which drains from the mine and are pumped into the river. 70% of the minimum concentration of (Ag, As, B, Be, Cd, Cr, Cu, Mo, Ni, Pb, U, V, and Zn) were found at locations 8 and 18 which are down stream, 25% of Ba, Ce, Co, Li, were obtained at location 4(spring)

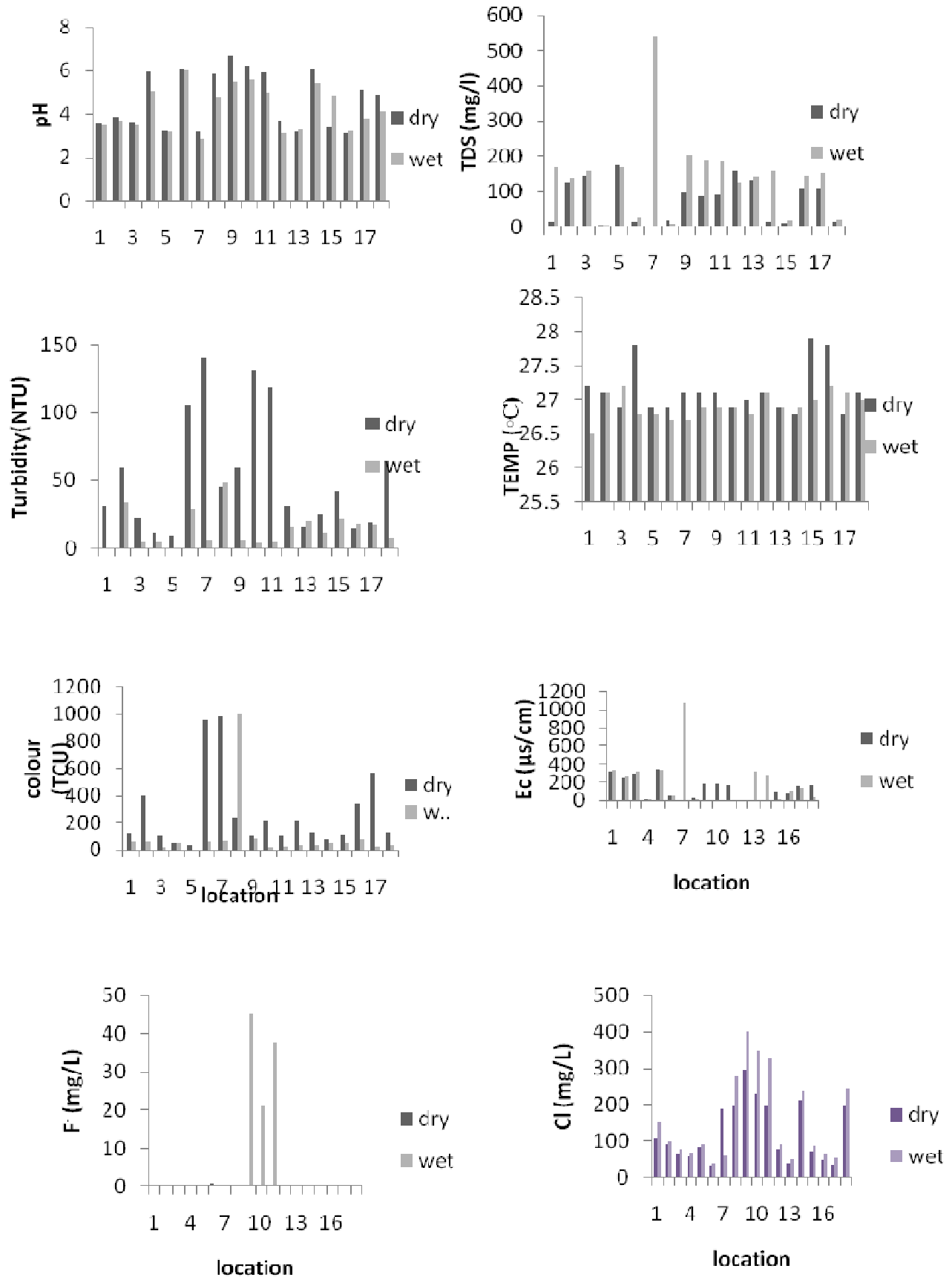


Figure 2. Spatial and temporal variation of physico-chemical parameters in water along River Nyaba.

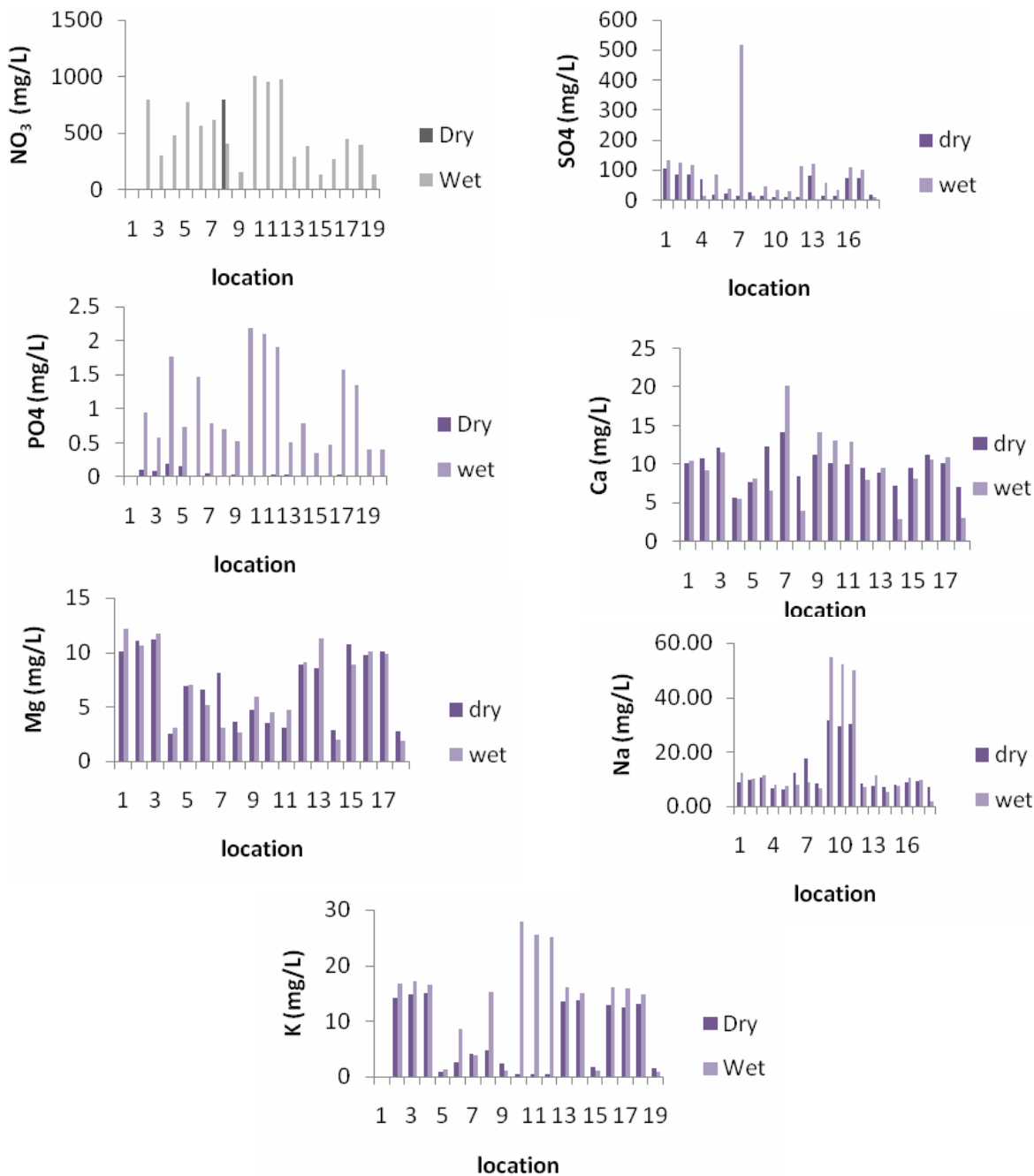


Figure 2. Contd.

and 5% of Cr was obtained at locations 9, 10 and 11(hand dug wells). The above data show no defined pattern of variation.

pH is an important physical parameter characterizing mine drainage. According to Rose and Cravotta (1998), the pH of mine water is in the range of 2 to 3.5. Locations 7, 5, 15 and 1 have values within this range indicating mine drainage. Locations 2, 3, 12 and 13 are slightly above this range. While locations 7, 2, and 1 are influent from the underground mine, locations 3, 13, 17

and 5 and 15 are effluent and water from the streams. The pH value of 2.84 at location 7 is similar to values obtained for pH in groundwater from the Okpara mine by Ezeigbo and Ezeanyim (1993) and Offodile (2002). The acidic nature of the water is attributed to the weathering of sulphide minerals and effluent from the underground mine. Elevated levels of NO<sub>3</sub>, Cl and F at location 9 which is a shallow well in the nearby village may be probably due to the anthropogenic influence resulting from ponded mine effluent through seepage. According to Appelo and

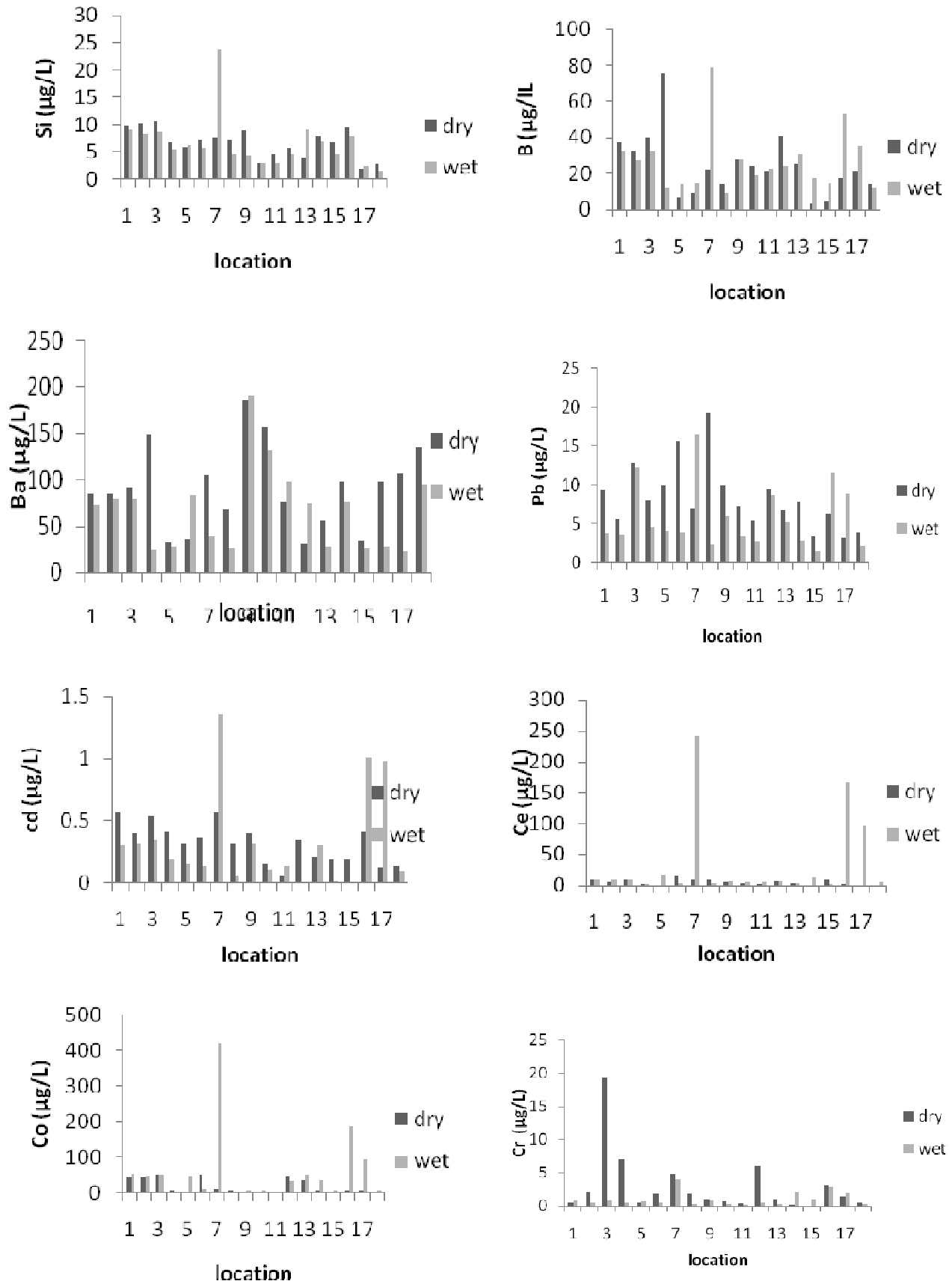


Figure 3. Spatial and temporal variation of trace elements in water along River Nyaba.



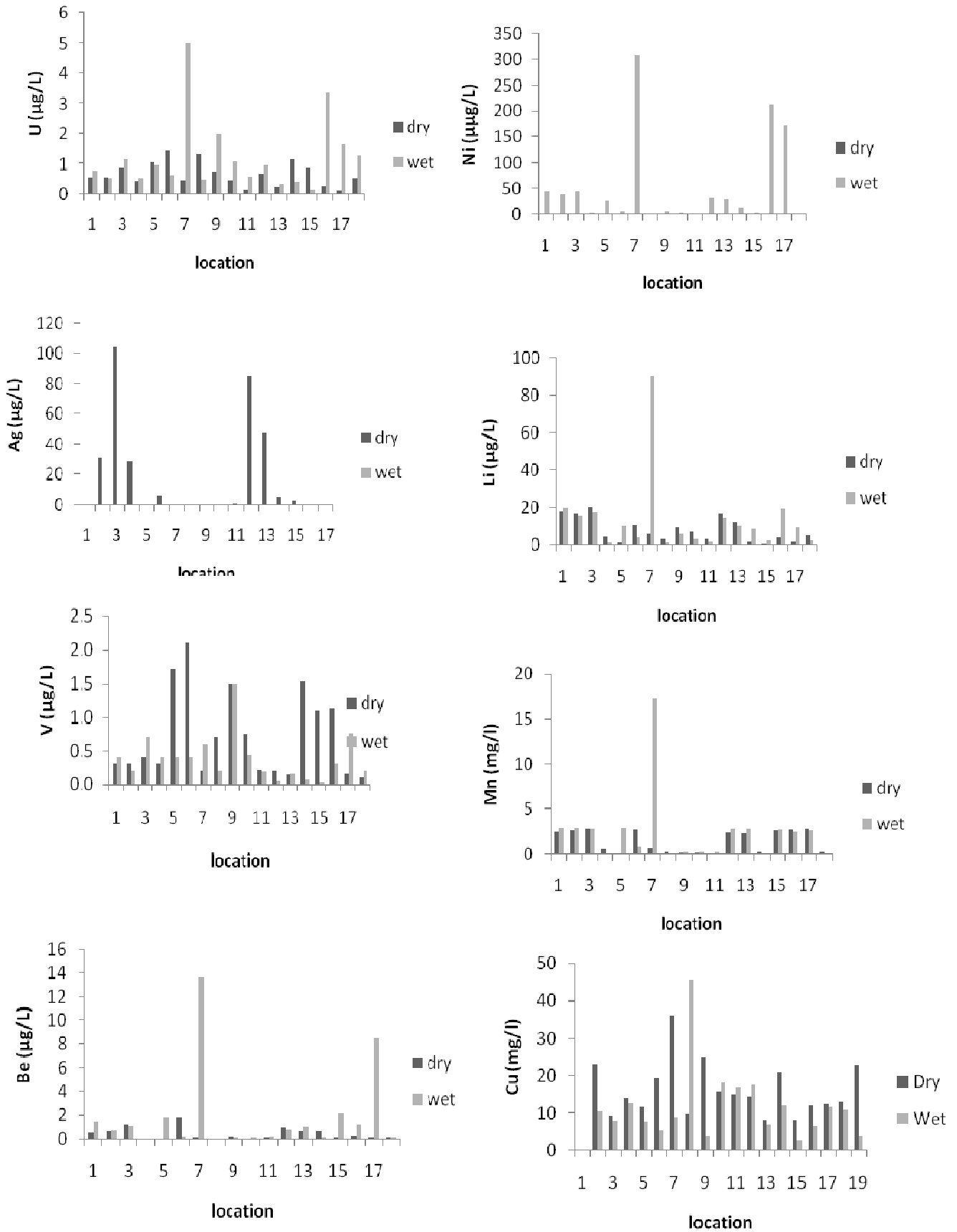


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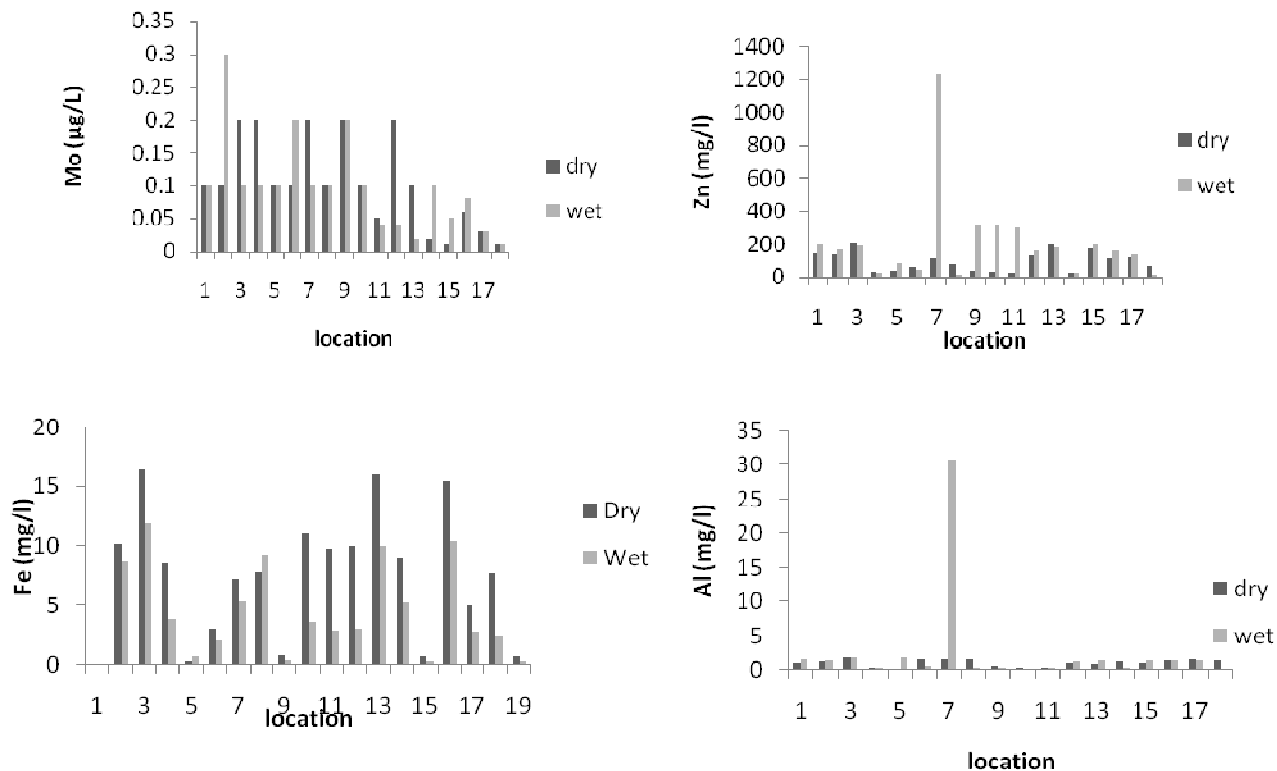


Figure 3. Contd.

Table 3. Relationship between pH and metal load.

Class	Metal load (mg/l)	pH	Description
1	> 100	< 3.0	High acid - extreme metal
2	1 - 100	< 3.0	High acid - high metal
3	< 1	< 3.0	High acid - low metal
4	> 100	3.0 - 5.5	Acid extreme metal
5	1 - 100	3.0 - 5.5	Acid - high metal
6	< 1	3.0 - 5.5	Acid - low metal
7	> 100	> 5.5	Near neutral - extreme metal
8	1 - 100	> 5.5	Near neutral - high metal
9	< 1	> 5.5	Near neutral - low metal

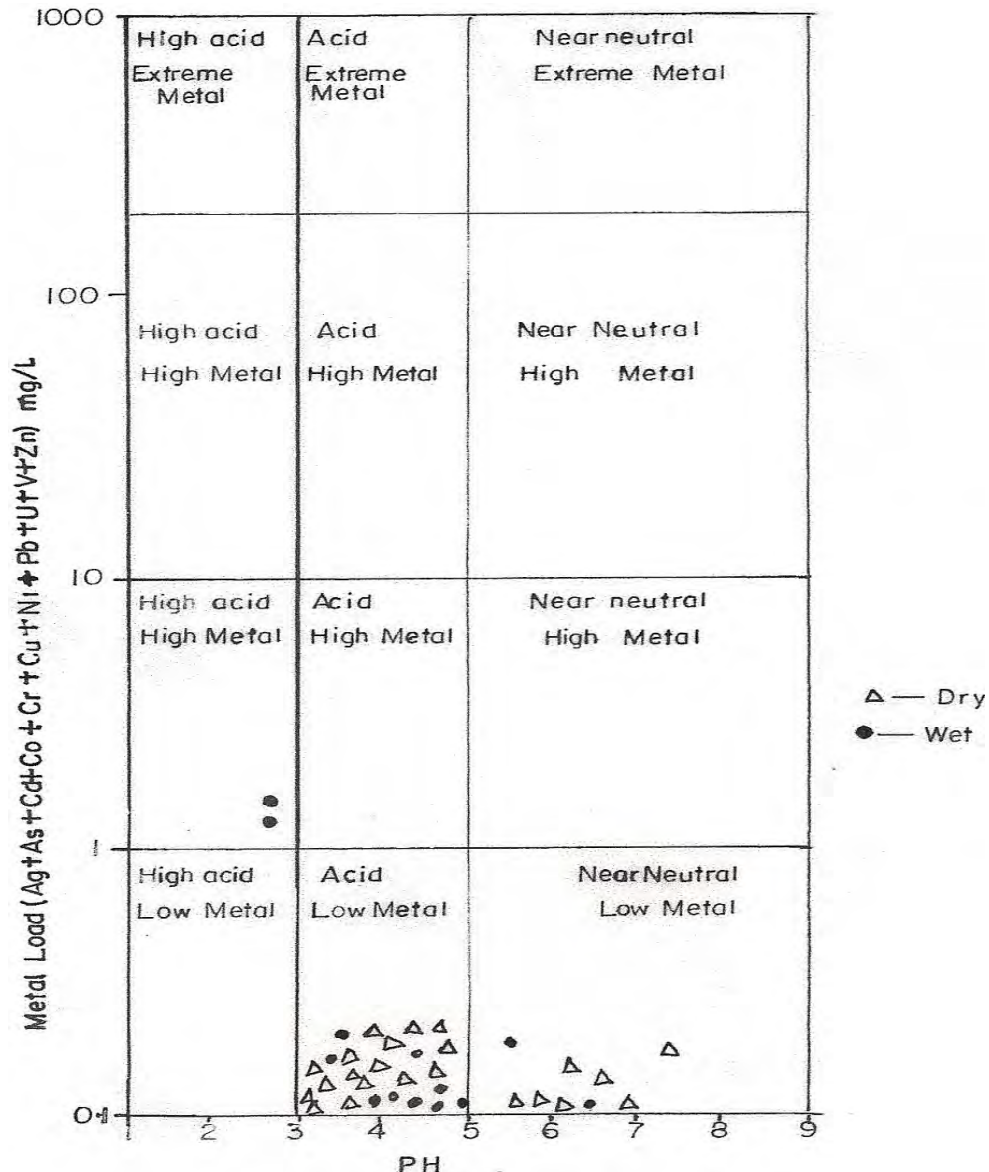
Adapted from Edet et al. (2004).

Postma (1996), metals are highly mobilized under moderate acid and acidic conditions. The presence of nitrate and sulfate bacteria biomass may also contribute to elevated level of metals in the water samples investigated.

**Evaluation of water type**

The relationship between pH and metal load as described by Edet et al. (2002) and (2004) was used to classify the water in the area. The metal load based on heavy metal

Content was defined as as + Cd + Co + Cr + Cu + Ni + Pb + Se + Sr + Tl + U + V + Zn. In this study the metal load was calculated as Ag + As + Cd + Co + Cr + Cu + Ni + Pb + U + V + Zn. On the basis of water type classification scheme (Table 3) by Edet et al. (2004) the water type in the study area (Figure 4) varied from near neutral low metal (spring water) to acid low metal in tributaries to the River Nyaba. High acid high metal (inflowing water) in the wet season constitute about 88.89% of the water type and high acid high metal water type at location 7 is associated with the acidic nature of the water from the underground mine. Locations 4, 8, 9,



**Figure 4.** Classification of water samples based on the plot of metal load and pH and their seasonal variation.

10,11 and 18 (Figure 4) show a change in water type from near neutral low metal to acid - acid low metal while location 7 varied from acid low metal to high acid metal.

**Conclusion**

The study evaluated the temporal and spatial variations as well as water contamination by effluents derived from an abandoned coal mine using chemical analysis of water samples. Results show that the water is acidic to moderately acidic with mean pH values of 4.66 (dry) and 4.22 (wet) in both season. Higher values of dissolved Cl (400 mg/L), K (27.85 mg/L), Fe (16.58 mg/L) and Mn

(17.23 mg/L) were observed close to the mine area and might have impacted color (1076 CTU) in the water. On the other hand, the relatively enhanced values of NO<sub>3</sub> (1002 mg/l), and F (45 mg/L) were observed in a shallow well down stream from the mine dumps. On the whole, the chemical quality of the water was found to be outside the WHO (1993) standard for pH, color, turbidity Al, Fe, Mn and Pb for both seasons. Mean levels of F (5.4 mg/L), K (12 mg/L) and Ni (53.10 µg/L), as well as maximum levels of Cr (100 µg/L), Cl (400 mg/L), NO<sub>3</sub> (1012 mg/L) and SO<sub>4</sub> (517 mg/L) obtained in the wet season are above the WHO maximum permissible level. The relative abundance of ions in the mine area showed the trend NO<sub>3</sub> > SO<sub>4</sub> > Cl > F > PO<sub>4</sub> for anions and Na > Al >

K > Si > Mn > Ca > Mg for major cations. The trend for trace elements is Co > Ni > Ce > U > Ba > Li > B > Cu > Pb > Cd. The high concentration of sulphates was most probably derived from weathering and oxidation of sulphide minerals. The NO<sub>3</sub> is probably sourced from the indiscriminate application of nitrate fertilizer in the area. Hence the high concentration away from the mine.

Concentrations of cations, anions and trace elements as well as levels of physical parameters were observed to decrease in the dry season. The higher concentrations in the wet season might be attributed to dissolution and leaching of substances into the drainage system by the heavy rainfall within the catchment area. The distribution of contaminants in the mine area appears to be controlled by dissolution under acidic conditions and the removal by dilution. High acid - high metal type was observed close to the mine waste. At some locations the water type changed from near alkaline to acid low metal downstream of the mine waste away from the source. High acid high metal (inflowing water) and acid low metal in the wet season constitute about 88.89% of the water type. The quality of the water is significantly influenced by acidic mine drainage and its impact on human health could be severe. In further assessing the quality of drinking water in the area, microbial concentration and speciation of elements are hereby recommended.

## REFERENCES

- Ata A, Kodas S (2006). Acid mine Drainage (AMD): Causes, treatment and case studies. *J. Cleaner Prod.* 14: 1139 - 1145.
- Appelo CAJ, Postma D (1996). *Geochemistry, groundwater pollution Rotterdam/Brook field.* A A Balkema.
- Amienta MA, Villusenor G, Rodriguez R, Ongley LK, Mango H (2001). The role of arsenic - Bearing rocks in groundwater pollution at Zimapan Valley, Mexico. *Environ. Geol.* 40: 571 - 581.
- Aples CN, Blowes DW, Nordstrom DK, Lamber JL (1994). Secondary minerals and acid Mine water chemistry. In: Blowes DW and Lamber (eds). *Environ. Geochemistry of sulphide mine.* Waste Miner. Assoc. Canada pp. 247 - 270.
- Bachmann TM, Friese K, Zachmann DW (2001). Redox and pH conditions in the water column and in the sediments of an acidic mining lake. *J. Geochem. Explor.* 73: 75 - 86.
- Bain JG, Bloes DW, Robertson WD, Frind EO (2000). Modelling of sulphide oxidation with reactive transport at a mine drainage site. *J. Contamin Hydrol.* 23 - 47.
- Banwart SA, Destouni G, Malmstrom M (1998). Assessing mine water pollution from laboratory to field scale. In: *Proceedings of the groundwater quality conference held at Tübingen Germany* pp. 307 - 311.
- Blodau C (2004). Evidence for a hydrologically controlled iron cycle in acidic and iron rich sediments. *Aquat. Sci.* 66: 47 - 59.
- Countin - Nomade A, Bril H, Neel C, Ienaim JE (2003). Arsenic in iron cements developed within tailings of a former metaliferous mines - engualles, Aveyron. France. *Appl. Geochem.* 18: 395 - 408.
- Callaghan T, Earle J (1998). Impacts of mine drainage on aquatic life, water uses and man made structures. In: Ridge T and Seil JM (eds), *Coal mine drainage prediction, and pollution prevention in Pennsylvania* pp. 1 - 22.
- Denimal S, Bertrand C, Mudry J, Paquette Y, Mochart M, Steinmann M (2005). Evolution of the aqueous geochemistry of mine pit lakes - Blanzay - Montceau - les - Mines coal basin (Massif Central, France): origin of sulfate contents; effects of stratification on water quality. *Appl. Geochem.* 20: 825 - 839.
- Dold B, Fontbote L (1998). Element cycling and secondary mineralogy in porphyry copper tailings as a function of climate. Primary mineralogy and mineral processing. *J. Geochem Explor.* 74: 3 - 55.
- Edet AE, Offiong OE (2002). Evaluation of water quality pollution indices for heavy metal contamination monitoring. A case study from Akpabouyo - Odukpani area, lower Cross River Basin (Southeastern Nigeria). *Geol. J.* 40: 1 - 10.
- Edet AE, Merkel BJ, Offiong OE (2004). Contamination risk assessment of fresh groundwater using the distribution and chemical speciation of some potentially toxic elements in Calabar (Southeastern Nigeria). *Environ Geol.* 45: 1025 -1035.
- Egiebor NO, Oni BO (2007). Acid rock drainage formation and treatment: a Rev. *Asia Pacific J. Chem. Eng.* 2: 47-62.
- Ehrlich HL (2004). Beginnings of rational bioleaching and highlights in the development of biohydrometallurgy: A brief history. *Euro. J. Min. Process. Environ. Prot.* 4: 102-112.
- Ezeigbo HI, Ezeanyim BN (1993). Environmental pollution from coal activities in the Enugu area Anambra State, Nigeria. *Mine Water Environ.* 12: 53 - 62.
- Fostel AL, Brown GE, Tingle TN, Parks GA (1998). Quantitative arsenic speciation in mine tailings using X - ray absorption spectroscopy. *Am. Miner.* 83: 553 - 568.
- Frommichen R, Went-Potthoff K, Friese K, Fischer R (2004). Microcosm studies for neutralization of hypolimnic acid mine pit lake water (pH 2.6). *Environ. Sci. Technol.* 38: 1877 - 1887.
- Fukashi K, Sasaki M, Sato T, Yanase N, Amano H, Ikeda H (2003). A natural attenuation of arsenic in drainage from an abandoned arsenic mine dump. *Appl. Geochem.* 18: 1267 - 1278.
- Geldenhaus S, Ball FG (1998). Acid mine drainage at a coal mine in the eastern Transvaal South Africa. *Environ. Geol.* 34(213): 234 - 242.
- Giblin A (1994). Natural water as a sample media in drainage geochemistry. In: Hale M and Plant JA (eds) *Handbook of exploration geochem.* Elsevier, Amsterdam. Table 8- 1, p. 291.
- Hem J (1986). Study and interpretation of chemical characteristics of natural water. USGS water supply paper 2245: 263.
- Holmstrom H, Salmon UJ, Carlsson E, Petrov P, Ohlander B (2001). Geochemical investigation of sulphide bearing tailings at Kristineberg, Northern Sweden, a few years after remediation. *Sci. Total Environ.* 273: 111 - 133.
- Jenkins DA, Johnson DB, Freeman C (2000). Mynydd parys Cu - Pb - Zn mines: mineralogy, microbiology and acid mine drainage. In: Cotter - Howells JD, Campbell LS, Valsami - Jones E, Batchelder M (eds) *Environmental mineralogy: microbial interactions, anthropogenic influences, contaminated land waste management.* The mineral. society series, UK 9 pp. 161 - 180.
- Jung MC (2001). Heavy metal contamination of soils and waters in and around the Imcheon Au - Ag mine, Korea. *Appl. Geochem.* pp. 1369 - 1375.
- Kimmel WG (1983). The impact of acid mine drainage on the stream ecosystem. In: Majumdar SK, Miller WW (eds), *Pennsylvania coal: Resources, Technology and Utilization.* Acad. Sci. Publisher, USA, pp. 424 - 437.
- Moncur MC, Ptacek CJ, Blowes DW, Jambor JL (2006). Spatial variations in water composition at a Northern Canadian lake impacted by mine drainage. *Appl. Geochem.* 21: 1799 - 1817.
- Nordstrom DK, Alpers CN (1999). Geochemistry of acid mine waters. In: Plumlee GS, Logsdon M.J (eds), *The environmental geochemistry of mineral deposits. Part A: Processes, Techniques and Health Issues.* Rev. Econ. Geol. 6A: 133 - 160.
- Offodile M (2002). Groundwater supply and development in Nigeria. *Mecon Geol. Eng. Serv. Ltd. Jos Nig.*
- Onwuka OS, Uma KO, Ezeigbo HI (2004). Potability of shallow groundwater in Enugu Town, Southeastern, Nigeria. *Glob. J. Environ. Sci.* 3(1): 33-69.
- Rose AW, Cravotta CA (1998). Geochemistry of coal mine drainage. In: Ridge T and Seil JM (eds) *Coal mine drainage prediction and pollution prevention in Pennsylvania* pp. 1 - 22.
- Savinov VM, Gabrielsen GW, Savinov TN (2003). Cadmium, Zinc, Copper, Arsenic, Selenium and mercury in seabirds from the Barents sea: levels, inter - specific and geographical differences. *Sci. Total Environ.* 306: 133 -158.
- Turbak SC, Olson GJ, Mcfeters GA (1979). Impact of western coal

mining – 1: Chemical investigations of a surface coal mine sedimentation Pond. *Water Res.* 13: 1023 – 1031.  
US Geological Survey (U.S.G.S) (2002) . Mine drainage. <http://geology.er.usgs.gov/eastern/environment/drainage.html>.  
US Environmental Protection Agency (U.S.E.P.A) (2002). What is acid mine drainage.<http://www.epa.gov/region03/acidification>.

Zielinski RA, Otton JK, Johnson CA (2001). Sources of salinity near a mine, a coal mine spoil pile, North – Central Colorado. *J. Environ. Qual.* 30: 1237 –1248.