

Physico-chemical parameters and heavy metals in River Pompom in Okehi Local Government Area of Kogi State, Nigeria

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The use of rivers for various purposes has resulted in their deterioration. Water quality involves integrating chemical and biological monitoring methods to evaluate the negative potential human health impact. Water samples from river Pompom in the vicinity of the Nigerian iron ore deposit at Itakpe, Nigeria, were analyzed for pH, turbidity, odour, conductivity, total suspended matter, total dissolved solid, biochemical oxygen demand, chemical oxygen demand, Cd, Cu, Ni, Pb and Zn to determine its suitability for drinking. Water samples were digested with HNO₃ and Flame Atomic Absorption Spectroscopy technique was used for the determination of concentration level of heavy metals while the physicochemical parameters were determined by gravimetric and titrimetric methods. Comparing the results obtained with Nigeria (Federal Environmental Protection Agency, FEPA) and WHO permissible guidelines for drinking water the concentration of Cu, Ni, Pb and Zn were found to be within safe limits. The pH, TDS and conductivity were found to be within the WHO safe limits of drinking water. Microbiological characteristics and element speciation are recommended for further quality assessment in the study area.

Keywords: Drinking water, heavy metal, water quality, aquatic ecosystem

INTRODUCTION

The use of rivers for various purposes has resulted in their pollution with the result that water quality data is needed to integrate the chemical and biological information to evaluate the potential impacts to the aquatic ecosystem. Water quality data include variables that have significant impact on designated water use such as chemical and microbiological characteristics, those affecting the taste and odour and those with indirect effect (pH, COD, BOD, TSS, TDS, conductivity etc.) (WHO, 1993, Kucuksezgin et al., 2008). Water quality guidelines provide toxicological threshold values to protect humans and aquatic organisms. Regular monitoring leads to revisions in water quality guidelines in order to adjust them to suit the potential of pollution reduction offered by new technologies and new scientific

knowledge. Thus criteria are continually being reviewed and revised. Arsenic intake in drinking water for example was globally re-evaluated with Canada decreasing maximum allowable level from 50 to 25 µg/l and the US from 50 to 10 µg/l (Kapaj et al. 2006).

Natural levels of metals have significantly increased in the last decades with increase in industrial activities. Water contaminations deserve attention due to its environmental hazardous effects, risk to human health and economical damages. Of the wide diversity of pollutants affecting water resources heavy metals are of particular interest due to their strong toxicity even at low concentrations. They have been reported to cause various human health related problems such as cancers, cardiovascular and neurological disease and effects on aquatic life (UNECE, 1995, Lawson, 2011). Mollusks species was reported to disappear in Lapus River as a result of the presence of large amount of heavy metals (Cordos et al., 2003).

The occurrence of heavy metals in water bodies can be of natural origin such as eroded minerals, leaching of

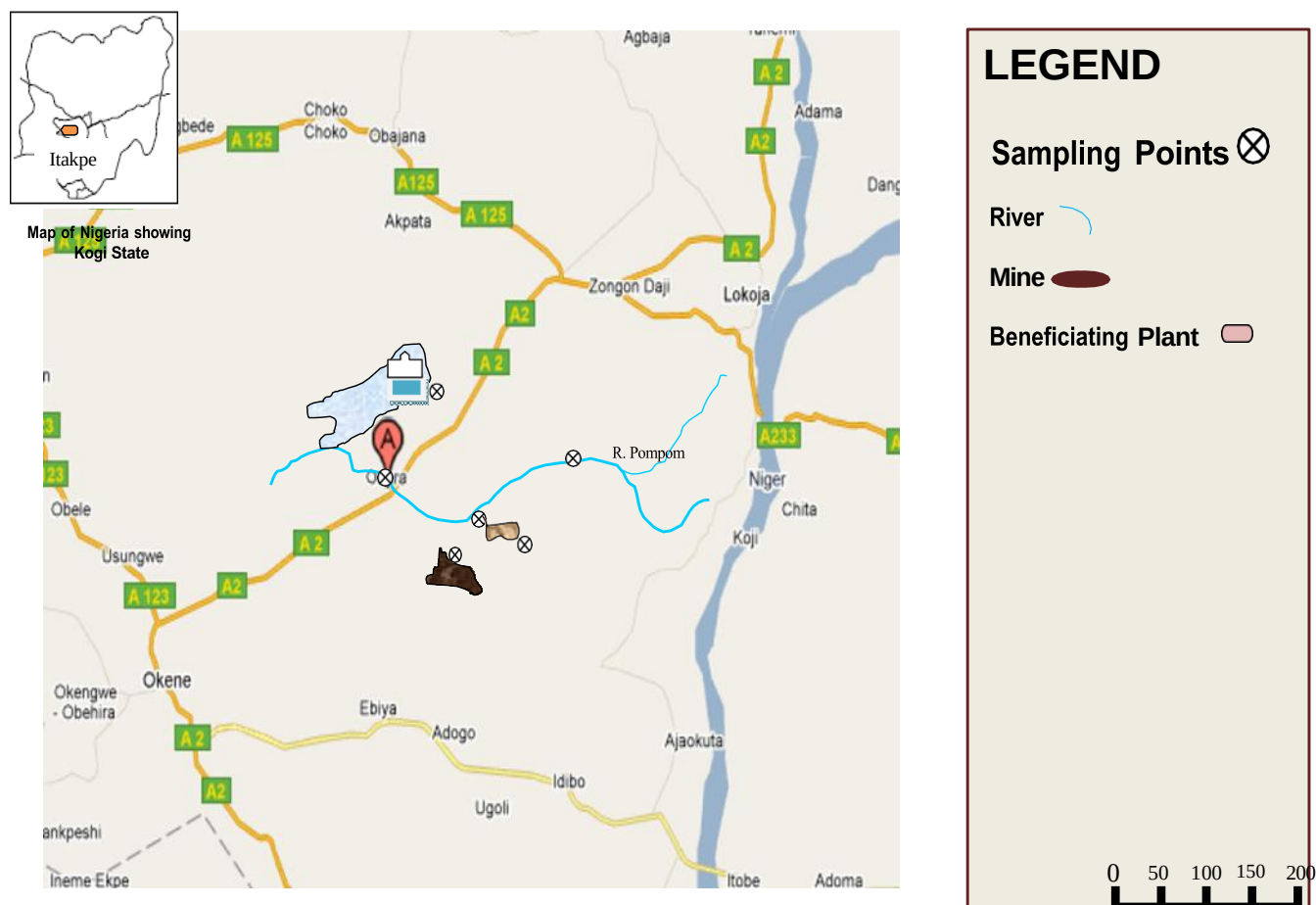


Figure 1. Map of Itakpe Mining Environment Showing Sampling Areas

ore deposit or anthropogenic through mining, agriculture, industrial or domestic effluents and so on. Mining operations causes oxidation of sulphidic mine waste, which leads to the release of metal pollutants into rivers (Makhoukh, 2011, Cordos et al., 2003). High levels of these metals and physicochemical changes in water have been reported in mining areas. In the United States of America's Bureau of Mines indicate that over 19,000 km of rivers and streams are negatively impacted by mine water and in Europe watercourses negatively impacted by mine water exceeds 5000 km (Ashraf et al., 2012). Such effects can have negative impact on the aquatic ecosystem and/or make water unsuitable for established or potential uses. The study of behaviour of heavy metals may be sensitive indicators for pollution levels in the water environment. Thus accurate determinations of heavy metals and other physical and chemical parameters in aquatic environment are of ultimate importance for water quality monitoring.

Globally, estimates of the impacts and the extent of the problem on water quality have been reported for a number of countries. The objective of this study is to determine physical and chemical properties of River

Pompom in the vicinity of the Nigerian iron ore deposit at Itakpe, Nigeria, in order to assess pollution impact through the determination of pH, turbidity, conductivity, total suspended substances, total dissolved solid, biochemical oxygen demand, chemical oxygen demand and concentrations of Cd, Cu, Ni, Pb and Zn.

MATERIALS AND METHOD

Studies was carried out in the Itakpe mining community in Okehi Local Government Area of Kogi State, Nigeria which lies within longitude $6^{\circ} 16'E$ and latitude $7^{\circ} 36'N$. Mining began in 1979 and Beneficiation in 1993. Mining stopped in 2008 with mine waste left untreated. River Pompom flows across the mining environment and the river serves for irrigation, drinking, domestic and grazing purposes. In addition to pollutants from its uses the component of metals present in tailings, waste effluents and agricultural soils are sources of heavy metal distribution to the river. All the water samples were collected from the river Pompom twice in the year. A total of 150 water samples were collected at three different

Table 1. Mean Physiochemical properties of river Pompom water

	L2	L3	L4	WHO (1984)	FEPA(2007)
pH	6.92	7.23	7.15	7-9.2	6.5-8.5
Conductivity ($\mu\text{S}/\text{cm}$)	187.40	154.20	259.00	200-600	N/A
Odour PtCoAPHA)	54	120	21	Unobjectionable	Unobjectionable
Turbidity (FTU)	7	18	0	5	5
TSS (mg/l)	8	17	2	N/A	30.0
TDS (mg/l)	89	74	122	500	500
BOD (mg/l)	35.48	86.69	104.98	6	N/A
COD (mg/l)	75	171	203	N/A	N/A

N/A= not available

Table 2. Concentration (mg/l) of metals in the water samples in dry and rainy season

Metal	Location	Dry Season	Rainy season	Mean (RS and DS)	WHO (1993)	FEPA (2007)
Cd	L2	<0.01	0.06 $\pm$ 0.04	0.03 $\pm$ 0.003 0.027-0.033	0.003	0.003
	L3	<0.01	0.06 $\pm$ 0.04			
	L4	<0.01	0.04 $\pm$ 0.01			
	Mean	<0.01	0.05 $\pm$ 0.03			
Cu	Range	-	0.02-0.08	0.05 $\pm$ 0.01 0.04-0.06	2	1
	L2	<0.01	0.08 $\pm$ 0.05			
	L3	<0.01	0.08 $\pm$ 0.05			
	L4	<0.01	0.10 $\pm$ 0.03			
Ni	Mean	<0.01	0.09 $\pm$ 0.04	0.01 $\pm$ 0.001 0.009-0.011	0.02	0.02
	Range	-	0.05-0.13			
	L2	<0.01	0.01 $\pm$ 0.01			
	L3	<0.01	0.01 $\pm$ 0.01			
Pb	L4	<0.01	0.01 $\pm$ 0.004	0.01 $\pm$ 0.001 0.009-0.011	0.01	0.01
	Mean	<0.01	0.01 $\pm$ 0.01			
	Range	-	0.00-0.02			
	L2	<0.01	0.01 $\pm$ 0.01			
Zn	L3	<0.01	0.01 $\pm$ 0.01	0.04 $\pm$ 0.01 0.03-0.05	3	3
	L4	<0.01	0.01 $\pm$ 0.01			
	Mean	0.03 $\pm$ 0.01	0.04 $\pm$ 0.01			
	Range	0.02-0.04	0.02-0.06			

locations [L2 (downstream), L3 (industrial waste entry) and L4 (up stream)] (Figure 1). The dry season (DS) samples were collected in January 2010 while the rainy season (RS) samples were collected in July 2010.

Water samples were collected by immersion of the container below water level. The containers were completely filled with water. The collected water samples were not filtered prior to analysis. 1% HNO_3 solution was added to acidify the sample to a pH of < 2 as preservative. The same treatment was given to the blank sample. Each water sample was analyzed for the hydrochemistry parameters following APHA et al. (APHA, AWWA and WEF, 1998, APHA, 1985). USEPA (HACH, 2008) methods were used to digest the water samples for the determination of concentration level of heavy metals.

The extract was analyzed using AAS. The same procedure was carried out on blank samples. Spiking of the sample was done using standards of various concentrations of each studied metal.

Atomic Absorption Spectrophotometer (AAS) model 210VGP, Buck Scientific Incorporated USA was used for the determination of heavy metals in this work.

RESULTS

Physiochemical properties of water samples from river Pompom collected at points along its length is shown in Table 1 while Table 2 shows metal levels in the river Pompom water samples. Recovery studies gave

84-110 %. All the studied variables had no specific pattern of variation. The river water samples pH ranged 6.92 to 7.23. The values of conductivity ranged from 154 to 259 with a mean of 200 ($\mu\text{S}/\text{cm}$). The highest conductivity was at the upstream (L4 259 $\mu\text{S}/\text{cm}$). Turbidity ranged 0 to 18 (FTU), TSS ranged 2 to 17 (mg/l), TDS ranged 74 to 122 (mg/l), COD ranged 75 to 203 (mg/l), BOD ranged 34 to 105 (mg/l). The highest value of conductivity, TDS, COD and BOD were observed at L4. The highest turbidity, TSS, pH and odour were in L3. The levels of pH, Conductivity and TDS were low in comparison to the corresponding maximum acceptable limits in drinking water WHO (1984).

Water samples of the river Pompom were analyzed for Cd, Cu, Ni, Pb and Zn. The studied heavy metals in water ranged Cd <0.01 to 0.05, Cu <0.01 to 0.09, Ni <0.01 to 0.01, Pb <0.01 to 0.01 and Zn 0.03 to 0.04 mg/l. (Table 2). The highest metallic levels were observed in the rainy season with copper having the highest level 0.01-0.09 mg/l while the lowest metal concentration levels were observed during the dry season for Cu, Cd and Ni <0.01 mg/l). The seasonal average concentrations of the studied heavy metals were Cd 0.03, Cu 0.05, Ni 0.01, Pb 0.01 and Zn 0.04 mg/l

ANOVA analyses comparison of L2 water between DS and RS shows no significant difference ($p>0.05$) in Ni and Pb while there was significant difference ($p<0.05$) in Cd, Cu and Zn. For L3 water between DS and RS there was no significant difference in ($p>0.05$) Ni, Pb and Zn while there was significant difference in ($p<0.05$) Cd and Cu. For L4 water between DS and RS there was no significant difference ($p>0.05$) in Cd, Ni, Pb and Zn while there was significant difference ($p<0.05$) in Cu.

DISCUSSION

Water quality is defined in terms of the physical, chemical and biological content of water. Water quality guideline provides basic information about water quality parameters and ecologically relevant toxicological threshold values to protect specific water uses. Water quality is influenced by the geology, mineralization, climate, atmospheric deposition, industrial discharge and physiochemical properties of rivers (WHO, 1984, Traichaiyaporn and Chitmanat, 2008, UNICEF, 2008, Makhoukh et al., 2011). Rivers associated to sandstones for example have a poor flow while pH is affected by run off from surrounding rocks (Loredo et al, Lawson, 2011). The flow rate of a water body can significantly affect its ability to assimilate and transport pollutants. This can vary within a day, as well as from day to day and season to season depending on hydrometeorological influences and the nature of the catchment area (Rehana and Mujumdar, 2011). Changes in water quality brought about by human activity will usually be superimposed on natural sources of variation. Thus the most likely sources of

variation in water quality include: flow variation, seasonal variation, trend and components.

The river water samples exhibited near neutral pH (6.92 to 7.23). The observed pH of the water under study in both seasons is within the WHO (1984) standard. Tailings promotes the formation of acidic mine drainage which results in increase in acidity. The near neutral pH levels observed could be due to the dilution factor as water flows downstream. According to Loredo et al (2009) mine drainage and spoil heap leachates show high acidic conditions, which are easily neutralized when they reach streams or rivers with enough flow to produce a dilution of pollutants. Furthermore not all mine water is characterized by low pH, some may contain elevated concentrations of metals at near neutral or alkaline pH values (Ashraf et al., 2012). Studies of drainage water from the Kamioka mine was found to be weakly basic (Laws, 2003). In neutral pH, increased acidity and metals contribute to degradation of physical habitat, as a result of the precipitation of large quantities of aluminum and iron as insoluble hydrous oxides (Besser et al., 2009).

The acidity of a water body influences the concentration of metals by altering their availability and toxicity (Lawson, 2011). Water pH is reported to influence size and activities of aquatic organisms, methylation of elements, availability, toxicity and concentration of metals in water bodies. Lower pH extremes can result in the death of many aquatic organisms while higher pH extremes can result in precipitation reactions and can also kill aquatic organisms. Furthermore acidity and heavy metal contamination in aquatic and terrestrial ecosystems causes a reduction in both species diversity and the total biomass composition of such systems (Deepali et al., 2009, Lawson, 2011, Ashraf et al., 2012).

The highest odour was reported at L3. Water odour is usually the result of decaying organic matter such as phytoplankton and aquatic plants. Industrial wastes and pH are reported to influence the production of odour (Chapman and Kimstach, 1992, 1996).

The conductivity levels were within the maximum acceptable limits in drinking waters (WHO, 1984). Conductivity for a given water body, is related to the concentrations of total dissolved solids and major ions. Thus it is sensitive to variations in dissolved solids and indicator of the mineral content of the water body. The observed conductivity values decreased down stream and are within the conductivity range of most freshwaters. (Chapman and Kimstach, 1992, 1996) The main source of TDS is the mining activity going on in the study area. The high conductivity upstream suggests that hydrogen ions were generated from sulfide oxidation which could be the contamination source. (Lawson, 2011, Loredo et al (2009). Loredo et al (2009) reported levels between 882 and 1753 (S.cm-1) in Lena River, in a mine site in Spain. The observed decrease down stream could be due to the amount of ions being transported which depends on the several factors such as volume of water flow, type of

chemical reaction, tidal effect and dilution.

TSS ranged 2 to 17 (mg/l). The TSS was highest in L3. Suspended particulate matter consists of material originating from the surface of the catchment area, eroded from river banks and resuspended from the bed of the water body and their source can be attributed to runoff from the mine, fertilizers and pesticides used in farms, industrial wastes and algae growth. According to Cordos et al 2003 polluting elements from mining are in suspension forms. In mining environment a single hydrological event can increase the suspended particulate matter load concentrations by at least one order of magnitude (Cordos et al., 2003). TSS varies seasonally according to biological activity in the water and surface run-off carrying soil particles. TSS provides a means of transport of toxic heavy metals which may be an irritant for some fish through clogging of the gills and death. Longer term impacts of high suspended solids include alteration of in-stream dynamics and receiving water bodies (e.g. blocking channels and filling river pools), potential flooding problems and loss of aquatic flora and fauna habitat (Cordos et al 2003, Chapman and Kimstach, 1992, 1996).

The turbidity was highest in L3. The high concentration of suspended matter in L3 influenced the high turbidity observed at that location. The observed turbidity of the water under study in both seasons at L2 and L3 were above the WHO (1984) standard. Turbidity represents the extent of light penetration through the water column. The significance of suspended solids relates largely to the effects on light penetration into the water. Thus turbidity is mainly due to particles in suspension, and therefore typically corresponds to the total suspended solid concentration in a stream. It may also be the result of dissolved metals or dissolved organic matter. Water plants need light for photosynthesis. If suspended particles block out light, photosynthesis and the production of oxygen for fish and aquatic life will be reduced. If light levels get too low, photosynthesis may stop altogether and algae will die. Turbidity affects the aesthetics, water transparency and gas solubility of water bodies (Lawson, 2011, Begum and Harikrishna, 2008, UNICEF, 2008). Limiting light availability can also irritate fish while high levels of turbidity can shield pathogens from disinfectants (UNICEF, 2008).

Total dissolved solids ranged 74 to 122 ($\mu\text{g/ml}$). These observed values are directly proportional to the conductivity values in the different locations. The TDS is below the WHO (1984) standard. The dissolved solids encompass particles that are transported in solution and are a measurement of inorganic salts, organic matter and other dissolved materials in water. The concentration and composition of TDS in natural waters is determined by the geology of the drainage, atmospheric precipitation and the water balance (evaporation-precipitation). In streams directly affected by metal-rich acid drainage,

most toxicity can be attributed to exposure to dissolved metal (Besser et al., 2009). The concentration of metals dissolved in water may give a misleading picture of the degree of contamination and hence under estimation of the total metal concentration in the water. High TDS waters may interfere with the clarity, colour and taste of water. A high total dissolved solid indicate hard water and is reported to have effect on the taste and also indicate the presence of toxic minerals in drinking water (UNICEF, 2008, Lawson, 2011). High TDS indicate the water is unfit for irrigation and drinking purposes. Drinking water with high concentrations of TDS has been reported to cause health problems affecting alimentary canal, respiratory system, nervous system, coronary systems, miscarriage and cancer (Deepali et al., 2009).

The COD ranged 75 to 203 (mg/l) and BOD ranged 34. to 105 (mg/l). The highest COD and BOD were observed at L4. The BOD observed is higher than the WHO value. COD and BOD are used to measure the susceptibility to oxidation and biochemically degradability of the organic and inorganic materials present in water bodies. The low levels of BOD observed down stream could be as a result of water flow. According to Rehana and Mujumdar (2011) increase in streamflow of 0 to 20% effluents could cause BOD levels to go down drastically as a result of changes in precipitation. High BOD levels in water bodies could affect survival of gill breathing animals present. (Deepali et al., 2009)

All the studied metals were observed to be present. Sources of these metals may be attributed to the nature of the catchment area, industrial waste discharges, water runoffs, agricultural wastes (fertilizers, pesticides and herbicides), geological weathering of parent rocks and atmospheric sources (UNICEF, 2008). Cd is reported to be a component of pesticide and fertilizer (Laws, 2003). Substances such as volcanic gases and natural gases (carbon dioxide, oxygen, sulphur dioxide and nitrogen), when in the air dissolves in rain and as runoff, dissolves soil and rocks picked up as water flows. The main air quality issues with mining are dust particles and combustion of fossil fuels used in mining activities which releases Pb into the atmosphere. Emission of Pb to the atmosphere from burning of fossil fuels is reported to be roughly 6,000 tonnes per year (Laws, 2003). Pb is potentially health hazardous and toxic to most forms of life. Large concentrations in dust can lead to exacerbating respiratory disorders such as asthma and irritating the lungs and bronchial passages. Pb is also reported to be responsible for chronic neurological disorders in fetuses and children (Lawson, 2011). Volatilization of Cd from fertilized agricultural lands introduces significant amounts of Cd to the atmosphere which through runoff gets into the aquatic ecosystem (Laws, 2003). Cd is reported to cause neurotoxin, hypertension, carcinogenic, teratogenic, mutagenic, liver and kidney dysfunction. The impacts to aquatic life may range from their immediate kills to impacts affecting

growth, behaviour or ability to reproduce. (Adelekan and Alawode, 2011). Thus metals get into the river through the atmosphere (as rain, dust or seaspray).

The observed metallic levels were generally low in the dry and rainy period. The highest metallic levels were observed in the rainy season with copper having the highest level. This could probably be due to Cu been a component of pesticide. Previous research reports Zn and Cu as components of pesticides which attach to organic materials which can be released through surface runoff during the RS (Sankar et al, 2010). Other reasons for the observed higher metallic level during the RS may be due to Acid mine drainage (AMD), the interaction of acidic rain water with the mine spoils scattered around containing trace elements mixed with other pollutant sources such as agricultural and effluents from plant which is emptied into the River. Hg and CN have been reported to be part of the components of reagent used in mineral processing (Ato et al., 2010, Cordos et al., 2003). Hg at very low concentration is highly toxic. Inorganic Hg could be methylated in the water environment and lead to levels in fish and other high-level predators which pose a human health risk (Loredo et al., 2000). The most serious publicized example of methyl Hg fish contamination exposure is the Mina Mata Bay, Japan Hg poisoning, during which many people died and pregnant women who ate polluted fish manifested no symptoms of the poison but gave birth to infants with severe developmental disabilities (Laws, 2003). CN affects all components of the aquatic ecosystem: change in water quality, decrease in a number of fish species and some of the microalgae and mollusks species have been reported to disappear (Cordos et al., 2003).

AMD occurs as a result of oxidation in underground mine workings, waste rock dumps, mill tailings piles, ore stockpiles, spent ore piles from heap leach operations, and in other residue deposits which present a high surface area to water and air during mining. Series of chemical reaction results in water discharges high in acidity containing dissolved heavy metals which can react with the ferric ions produced to oxidize other metal sulphides which contain significant concentrations of other metals (Ashraf et al., 2012, Besser et al., 2009). These metals carried by water can travel far contaminating stream and ground water. Carnon River from Wheal Jane Mine, in the United Kingdom for example, affected by receiving waters, was reported to have Zn and Cd concentrations reaching 540 mg/l and 600 mg/l, respectively (Ashraf et al., 2012). Mining also results in the loss of vegetation and topsoil which causes flooding, and the water emerging from the debris contains toxic solutes which include metals. Thus mine water is complex in nature and of widely varying metallic composition.

AMD may persist for many decades to thousands of years. Studies of an abandoned mine in South Africa were found to still discharge AMD into an adjoining river

after 49 years and this resulted in adverse effects on vegetation and the near total destruction of aquatic life in the seepage area (Ashraf et al., 2012). Problems with AMD are contamination of drinking water, contamination of food chain through contamination of agricultural lands and aquatic plants and animals if untreated. With the water Cd concentration of 0.03 mg/l the Pompom river will be a threat to agriculture in the mining environment. According to a UNESCO report 10 µg/ml Cd in irrigation water can lead to 1 µg/ml Cd in soil, because essentially all Cd in the water accumulates in the soil (Kyaw et al., 2008).

The levels of pH, Conductivity and TDS were low in comparison to the corresponding maximum acceptable limits in drinking water WHO (1984). Cu, Ni, Pb and Zn metallic levels were within the WHO and FEPA acceptable guidelines for drinking water. Cd level of 0.03 mg/l is higher than the WHO recommended for drinking water.

CONCLUSION

The systematic monitoring accomplished in the stream of the area of Itakpe mine works makes evident the presence of anthropogenic hydrogeochemical anomalies in the area, which represent an important environmental impact, reflected mainly by the high concentration of Cd. The highest metallic levels were observed in the rainy season. Based on the results of water quality analysis, River Pompom water did not meet the standards for use set by Federal Environmental Protection Agency (FEPA), of Nigeria and WHO permissible guidelines for drinking water. The findings will assist relevant agencies on the need for pollution control. Although the effects of mining activities on riverine biota currently are limited, our results show that there is potential for effects to occur with proposed growth in mining activities. Microbiological characteristics and element speciation are recommended for further quality assessment in the study area.

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