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Research Article

Concerns over Heavy Metal Concentrations in Ebonyi River Used for Domestic Purposes Confirmed in Abakaliki, Southeastern Nigeria

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ABSTRACT

The heavy metal concentrations in Ebonyi River used for domestic purposes in Abakaliki, Southeastern Nigeria was studied at the teaching and research centre, Department of Soil Science and Environmental Management, Ebonyi State University, Abakaliki. The river was sampled in a completely randomized design (CRD); with three months of the year serving as sources of variation and three replicate samples per sampling period. The harvested rain water for the corresponding months of investigation served as control. The heavy metals of interest were: zinc, lead, copper and chromium. Other physico-chemical properties of the water like colour, temperature, total solids, total dissolved solids, total suspended solids, amongst other parameters were added. The data were subjected to analysis of variance (ANOVA) for CRD. The highest zinc concentration of 144.92 mg l^{-1} was in the month of September while there was no zinc in control (rainwater). The zinc order of increase was September>October>November>Control. Similarly, the highest lead concentration of 5.70 mg l^{-1} was in the month of October and nil in control; with the order of increase being September>November>October>Control. The highest copper concentration of 0.21 mg l^{-1} was in the month of September and none in control; with order of increase being September>October>November>Control. On the other hand, the highest chromium of 1.32 mg l^{-1} was in the month of November and 0.96 mg l^{-1} in control (rainwater). The order of increase in chromium was November>September>October>Control. It was found that copper and chromium failed the World Health Organization (WHO) standard; while zinc and lead concentrations passed the WHO test. The order of increase in total solids was September>November>October>Control; while the order for total dissolved solids was October>November>September>Control. That of total suspended solids was September>November>October> Control. The order of magnesium concentration was November>September>October>Control; while calcium was October>September>November>Control. That of phosphorus was September>October>November>Control; while total hardness was September>October>November>Control. The river passed WHO total hardness limits. The disposal of untreated wastes to ebonyi river was condemned. The occasional assessment of the river for biophysico-chemical properties and heavy metal concentrations was recommended in view of over 3 million citizens connected directly and indirectly to the river as major source of domestic water.

Key words: Water quality, Fresh water pollutants, Industrial activities, Water ways, Heavy metal pollutants

INTRODUCTION

The Nigerian inland water bodies have been subjected to various forms of degradation arising from pollution. The Ebonyi River of Ebonyi State, Nigeria is one of such endangered inland water bodies (Njoku and Keke, 2003). The river is source of water for drinking and domestic purposes. It has also been used for total and supplemental irrigation especially in the area of vegetable forcing in the state (Igboji, 2000; Igboji, 2015).

Several effluents are discharged from domestic and industrial activities into the river with tributaries from river benue, river niger and cross river of Nigeria. Most of these effluents are loaded with heavy metals that affect aquatic and human lives (Njoku and Keke, 2003; Clark, 2001). A lot of work support pollution as bane of physico-chemical characteristics of water, sediments and fish stocks. One of such is heavy metals. The concern about heavy metals is based on the persistence in the environment, being not easily degraded either through biological or chemical means unlike most organic

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pollutants. Some workers (Abowei and Sikoki, 2005) lament on the ability of the water bodies to be rendered unsuitable for its intended uses. This, according to the workers is a serious health threat to citizens that depend on them. They noted increased urbanization and industrialisation as the basis for increased levels of heavy metal in our waterways. Other workers like Baird (2001) and Abida *et al* (2009) supports their accumulation in the soil, sediment and water bodies.

The concentration of these pollutants have been linked to location of water sources, reaction rate of the water, effect of agricultural activities such as pesticides residues, extent of discharge of waste from industry into the water body as well as sewage (Holkes, 1985). Past and present governments of Nigeria and donor agencies have supported water supply programmes in the country. Notwithstanding, all these efforts, access to safe and affordable water supply in Nigeria are not fast improving (Layaunda, 2007; Omutunde, 2012). These have forced many families in Abakaliki to resort to unsanitary water sources which are prone to pathogenic and disease infections. Generally, public water supply is becoming scarcer in Nigeria. In most cities where they are operational, they are usually unreliable and poor due to incessant power failure, general mismanagement of public funds and inability of utilities to recover operating costs (Ezenwaji, 2014).

With an increasing population of Ebonyi State up to the tune of 3 million, there is higher demand for potable water (Njoku, 2014). Other alternatives available to the people are borehole and rain water. The former is very expensive while the later is frustrated with lack of facilities to harvest rainwater during the rainy season which span from April to November every year. Another major problem of natural waters is the concentration of heavy metals. There is considerable dearth of information on the metal pollution status in rivers. Hence, this current work has linked similar ones on highlighting the concerns of highly neglected but vital area of water pollution in developing countries – heavy metal pollution.

MATERIALS AND METHODS

Geographical and Climatic Information

Abakaliki lies within Longitude 08° 06¹ E and Latitude 06° 19¹ N at an altitude of 128 meters above sea level. It lies within the derived savannah belt of South eastern Nigeria. The mean annual rainfall for 25 years (1977-2012) was 154.75 mm spread across April – November; while the mean annual minimum and maximum temperatures for same period were 23.58 and 32.40°C respectively; with higher and lower temperatures during the dry and rainy seasons respectively. On the other hand, the average annual sunshine hours for same period was 5.13, while the mean annual relative humidity@09/15 hrs was 80.2 and 59.93% respectively; with higher and lower relative humidity during rainy and dry season respectively. The rainfall, temperature, and relative humidity of the area are presented in Figures 1, 2 and 3 (NMI, 2015). The soil is shallow with consolidated parent materials within 1m of the soil surface classified as *Dystric Leptosol* (Anikwe *et al*; 1999).

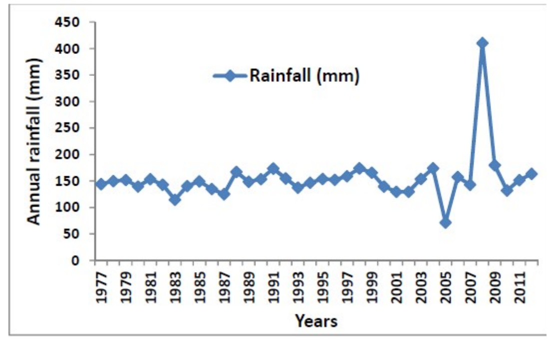

Fig. 1: Annual rainfall for Abakaliki (1977 – 2012) – mm

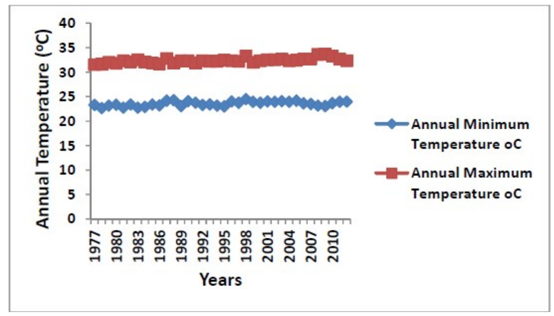

Fig. 2: Annual minimum and maximum temperature for Abakaliki (1977 – 2012) - °C

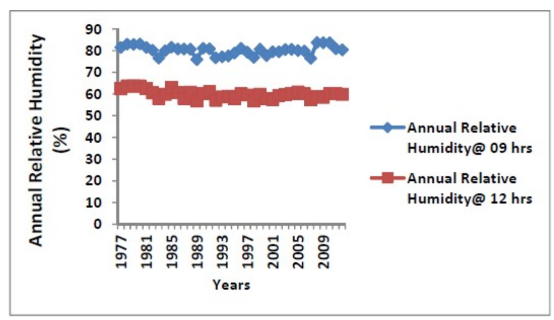

Fig. 3: Annual relative humidity@09/12 hrs at Abakaliki (1977-2012) - % Sampling procedure

The water samples were collected from identified points across Ebonyi River in line with the procedure described by APHA (1995). Sampling was at depth of 0 – 30 cm for three months – September, October and November. Each sampling area was replicated three times on each occasion; with corresponding rainwater harvested for these periods as control. The samples were collected using plastic bottles preserved with ice packs in a cooler; except that for heavy metal estimation that was preserved with 1% HNO_3. At point of collection, in-situ temperature was taken using digital thermometer, allowing 5 minutes for stabilisation of readings.

Laboratory procedure/methods

The water physico-chemical properties were analyzed using the methods described by Association of Official Analytical Chemists (2012). For example, water colour was determined by the use of Lovibond Nessleriser with colour disc, especially Hagen disc and recorded as % transmittance. For total solids, about 50 ml of each sample was measured into an already weighed beaker and evaporated to dryness for 1 h at 103°C on a steam bath, cooled in desiccators and recorded for constant weight. Total solids (mg l^{-1}) were calculated thus: W_1 – W_2/volume of sample used; where W_1 was the weight of dried residue + beaker and W_2 was the weight of empty dish. On the other hand, total dissolved solids were measured by shaking sample vigorously, taking 50 ml and transferring into weighed evaporation dish. The sample was evaporated to dryness on a steam bath. The evaporated sample was then dried for 1 h in an oven and cooled in desiccators. The drying was repeated until constant weight was obtained. The total filterable residue at 110°C was calculated thus: A – B/volume of the sample used x 100; where A was the weight of dried residue + dish and B was the weight of dish. The total suspended solids were got by calculations using the values of total solids and total dissolved solids as follows: TSS = TS – TDS (mg l^{-1}) where TSS was total suspended solids; TS was total solids and TDS was total dissolved solids.

Similarly, water pH was measured with pH meter after standardization with buffer 7.0 solution. For phosphorus level about 10 ml of neutralized sample was pipette into 50 ml volumetric flask, followed by 4 ml of 1.25% ammonium molybdate and 4 ml of 10N H_2SO_4 before shaking. Then followed by 6 drops of stannous chloride, shaking and dilution with distilled H_2O to 50 ml mark. Then allowed to stand for 30 minutes for colour development. The absorbance was read using spectrophotometer at a wavelength of 650_{nm}. Thus, phosphorus was calculated based on concentration x dilution factor x 1000 (mg l^{-1}).

To measure magnesium level, about 10 ml of sample was measured into 250 ml conical flask, followed with 5 ml of NH_3-10 buffer solution and a pinch of hydroxylamine and potassium cyanide. Then Erichrome Black T solution was used as indicator and titrated with 0.01M EDTA until the colour change from black to blue. Then Mg was calculated thus: TV x 0.2432/volume of sample used x 1000 (mg l^{-1}) where T was titre value. For calcium, about 10 ml of sample was measured into a beaker, followed by 5 ml of KOH and 3 ml of 10% hydroxylamine and a pinch of potassium cyanide. Then followed by pinch of Potton and Reeders reagents as indicators and titration with 0.01M EDTA till colour change from brown to green. The Ca was calculated thus: TV x 0.4/volume of sample used x 1000 (mg l^{-1}) where TV is titre value. The total hardness was measured by taking 50 ml of sample into conical flask, adding 1 ml of buffer 10 solution and 1 ml of $NaSO_4$ solution. Then 3 drops of Erichrome Black T was added as indicator and titrated with 0.01M EDTA solution till colour change from red wine to blue black. The total hardness was calculated thus: TV x 0.01 x 100/volume of sample used x 1000 (mg l^{-1}); where TV was titre value.

The heavy metal concentrations were analyzed using the photospectrometric method as described by AOAC (2012). For zinc concentration, about 20 ml of sample was measured into a beaker, followed by 2 ml of buffer NH_3-10 and 2 drops of Erichrome Black T indicator and titration with 0.01 M EDTA until colour change from red wine to blue. The Zn concentration was calculated thus: TV x 0.6534/volume of sample used x 1000 (mg l^{-1}) where TV was the titre value. For lead (Pb) concentration, about 10 ml of the sample was measured into a beaker followed by 0.5M of 10% $NaSO_4$; then 25 ml of 1:2 ammonium: potassium cyanide solution. Then using distilled H_2O to make up 50 ml mark. The absorbance was read using spectrophotometer at 430_{nm}. The absorbance was interpolated using standard graph of lead (Pb) concentration. The Pb concentration was calculated thus: concentration x dilution factor x 1000.

For copper measurement, about 10 ml of the sample was measured into a beaker; followed by 5 ml of ammonium hydroxide. Then distilled H_2O was used to make up to 50 ml mark and the absorbance read with spectrophotometer at 620_{nm}. The absorbance was interpolated using standard graph of Cu. The calculation was: concentration x dilution factor x 1000 (mg l^{-1}). For the determination of chromium (vi), about 10 ml of the sample was measured into 10 ml calibrated flasks; followed by 0.5M acetate buffer (pH 4.8) and 0.5M 0.1% hydroxylamine hydrochloride solution. After 2 minutes, another 0.5M 0.05% sulphanilamide was added to each flask and the mixture allowed to stand for 2 minutes, followed by addition of 2 ml 0.1% saccharin and 1.5 ml of 4M NaOH. The contents were diluted to mark with distilled water and mixed very well. After 5 minutes the absorbance of the sample was read at 390_{nm} with reference to blank reagent. For chromium (iii) determination, about 10 ml of the sample was measured into 10 ml calibration flasks, followed by 0.5ml of saturated bromine water and 0.5 ml of 4.5M KOH. The solution was allowed to settle for 5 minutes, followed by addition of 2.5 ml of 0.5M H_2SO_4 and 0.5 ml of 5% sulposalicyclic acid. The absorbance of the solution was measured at 390_{nm} against blank.

Statistical and data analysis

The data were subjected to analysis of variance (ANOVA) for completely randomized design (CRD). Further means testing was done with Fishers Least Significant Difference (F-LSD) as described by Steel and Torrie (1980). Further comparison was done with World Health Organisation (WHO) standards (WHO; 1996; WHO; 2008; WHO; 2011; WHO; 2015).

RESULTS

Heavy metal concentration of Ebonyi River

There was significant difference (P = 0.05) in the Zn concentrations for the periods studied. The month of September recorded the highest Zn concentration of 144.92 mg l^{-1}; while control (rainwater) had none. The coefficient of variation (cv) amongst the months was 68.66%. The concentration was within the limit of 5 mg l^{-1} set by WHO (1996). In terms of lead (Pb) concentrations there was also significant difference (P = 0.05) amongst the period assessed with highest Pb concentration of 5.70 mg l^{-1} for the month of September and nil for control. The cv amongst periods was 14.91%. The Pb concentration was above the limit of 0.01 mg l^{-1} set by WHO (2011) for domestic water. The results showed highest copper concentration of 0.21 mg l^{-1} for the month of September and none in control. The Cu concentrations were within the range of 1.0 mg l^{-1} set by WHO (2011). On the other hand there was significant difference (P = 0.05) in the chromium concentrations amongst periods of monitoring; with the month of November giving the highest chromium concentration of 1.3 µg l^{-1} and rainwater (control) giving the least value of 0.96 µg l^{-1}. The cv amongst the periods investigated was 6.94%. Nevertheless, chromium concentration for the river and rainwater samples passed the permissible level of 50 µg l^{-1} set by WHO (2011) and Nkono and Asubiojo (1997) – Table 1.

Chemical properties of Ebonyi River

There was significant difference (P = 0.05) in the level of water pH amongst the periods assessed. The highest pH of 7.0 was in control (rainwater) while the least value of 6.55 was in October. The cv amongst the period covered was 0.39%. The pH fell within the range of 6.5 – 8.5 permissible by WHO (2011) for domestic water. In terms of magnesium, there was significant difference (P = 0.05) amongst the periods with the month of November giving the highest value of 129.04 mg l^{-1} and nil in control. The cv amongst these periods was 27.83%; with values being above the 50 mg l^{-1} set by WHO (2011) standard; except for rainwater (control). There was significant difference (P = 0.05) in the calcium concentrations amongst the months investigated with the month of October giving the highest value of 263.19 mg l^{-1} and none in control. The values fell within the permissible levels of 200 mg l^{-1} set by WHO (1993; 2011; Wikipedia, 2015). The phosphorus level was significantly different (P = 0.05) amongst the periods assessed with highest level of 1.41 mg l^{-1} was recorded in the month of September and least value of 0.22 mg l^{-1} in rainwater (control) – Table 2.

The results showed that total hardness was significantly different (P = 0.05) amongst the periods of comparison with the month of September giving the highest total hardness of 41.33 mg l^{-1} and nil in control. The cv amongst the periods compared was 28.82% and all values for total hardness were within WHO (2011) and Wikipedia (2015) permissible limits (Table 2).

Physical properties of Ebonyi River

In terms of colour based on % transmittance as tested there was significant difference (P = 0.05) amongst the periods tested with the month of September giving the highest value of 0.27% and none in control. The cv amongst the periods was 21.91% and remained within the standard of 0% set by WHO (1993). There was significant difference (P = 0.05) in water temperature amongst the various periods investigated with the month of October recording the highest value of 28.67°C; while the least value of 20°C was in rainwater (control). The cv amongst period was 1.58% and all values; except rainwater failed WHO (2011) permissible limit of 20 - 23°C.

There was significant difference (P = 0.05) in the level of total solids, total dissolved solids and total suspended solids for the periods assessed with the month of September recording the highest TS of 1.26 mg $l^{-1}$and TSS of 1.22 mg l^{-1} respectively. The least TS and TSS was in rainwater (control) which gave 0.33 and 0 mg l^{-1} respectively. The highest TDS of 1.11 mg l^{-1} was in the month of October and least TDS of 0.3 mg l^{-1} in the control. The cv amongst months for TS, TSS and TDS were 14.47%; 39.83% and 46.0% respectively. All the values for TS, TSS and TDS fell within permissible levels of 500; 50 and 500 mg l^{-1} set by WHO (1993) as in Table 3.

Table 1: Heavy metal concentration of Ebonyi River (mg l^{-1})

Source of variation	Zn	Pb	Cu	Cr
	.....mg l^{-1}.....		.......µg l^{-1}.......	
September	144.92	5.7	0.21	1.25
October	131.12	5.04	0.16	1.08
November	129.82	5.09	0.05	1.32
Rainwater (control)	0	0	0	0.96
Mean	101.47	3.96	0.11	1.15
SE	29.77	0.59	0.09	0.08
FLSD(0.05)	68.66	1.38	0.21	0.19
CV (%)	29.34	14.91	85.71	6.94
WHO Standard	5.0	0.01	1.0	50

Table 2: Chemical properties of Ebonyi River (mg l^{-1})

Variation	pH	Mg	Ca	TH	P
September	6.74	118.27	129.25	41.33	1.41
October	6.55	76.93	263.19	38.6	0.73
November	6.57	129.04	11.61	30	0.70
Rainwater (control)	7	0	0	0	0.22
Mean	6.72	81.06	101.01	27.48	0.77
SE	0.03	22.56	29.2	7.92	0.33
F-LSD(0.05)	0.06	52.02	67.34	18.26	0.77
CV (%)	0.39	27.83	28.90	28.82	43.14
WHO std	6.5-8.5	50	200	500	Na

Table 3: Physical properties of Ebonyi River (mg l^{-1})

Variation	TS	TDS	TSS	Colour	Temp
	......mg l^{-1}.....			.......%......	....°C…
September	1.62	0.40	1.22	0.27	27.67
October	0.84	1.11	0.27	0.23	28.67
November	1.08	0.60	0.48	0.23	27.33
Rainwater (control)	0.33	0.30	0.03	0	20.00
Mean	0.97	0.60	0.50	0.18	25.92
SE	0.14	0.24	0.23	0.04	0.41
F-LSD(0.05)	0.32	0.55	0.53	0.09	0.94
CV (%)	14.47	39.83	46	21.91	1.58
WHO std	500	500	50	0	20-23

DISCUSSION

Heavy metal concentrations in Ebonyi River

The failure of Pb test in Ebonyi River confirms these concerns for heavy metal pollution of Ebonyi River. Even though Zn, Cu and Cr passed the test, their presence also signifies danger to the users especially the indigenes that use it as a source of drinking and domestic water. Similarly, aquatic organisms are not spared. According to Baird (2001) Pb does not become an environmental problem until it dissolves to yield the ionic form (hence why its presence in water is detested). It easily dissolves in water to yield the ionic form. Likewise the worker informs us that Pb used in the solder of domestic copper water pipes and Pb used for decades and centuries to construct water pipes themselves can dissolve in drinking water, particularly if the water is quite acidic or if it is particularly soft. The Ebonyi River pH and hardness supports this assertion and that is why the critical Pb level is of concern (even though the sources were not totally clear in this investigation). But it is likely that geology and anthropogenic activities of states like Benue, Niger, Cross River, Anambra; Imo whose rivers tributaries feed Ebonyi River may have accounted for the heavy metal concentration. In view of the fact that ebonyi and most of these states are naturally endowed with Pb, Zn, Cu and other solid minerals. The activities of welders, automobile mechanics, painters, plumbers are not ruled out as their presence dots every nook and corner of these states including ebonyi.

Hence, Baird (2001) informs the public of the need to avoid drinking water drawn from older standing fountains or in the pipes of older dwellings. According to the worker, water in such plumbing systems should be allowed to run for 60 seconds before being used for human consumption. On the part of Ebonyi River, irrespective of the dilution arising from the flow rate; there are still concerns of the critical levels. The scientist gave some natural remedies that try to contain Pb in natural water. One of which is presence of carbonate ions that informs water hardness. According to the expert; this ions together with oxygen forms an insoluble layer containing compounds such as $PbCO_3$ on the surface of Pb. This layer prevents the metal underneath from dissolving in the water that passes over it. This type of science has been explored in some countries like England and USA where soft water and networks of old Pb pipes add phosphates to drinking water in order to form a similar protective coating on the inside of the lead pipes and so reduce the concentration of dissolved Pb. This technology may not be affordable for ebonyi people in view of financial challenges of government and people. The author (Baird, 2001) confirms that Pb in water is more fully absorbed by the body than is lead in food. That explains the danger of exposure to Pb in water when compared to other sources like food and air and in view of the fact that many other sources of Pb have been phased out in many developed countries of the world. For the worker, many domestic water treatment systems successfully remove the great majority of Pb from drinking water. This is an over generalisation as that of local treatment plants in ebonyi does not have the facilities for removing heavy metals.

Chemical properties of Ebonyi River

Apart from Mg other chemical parameters in this work passed the WHO test which is consoling. The fact that the water is soft is good for the indigenes of ebonyi state in view of lean resources and technology available for treating water hardness. In another account, Baird (2001) attributes the entering of Ca from either $CaCO_3$ in the form of limestone or from mineral deposits of $CaSO_4$, as the major sources of much of the Mg in water. Others include dolomite ($CaMgCO_3$); gypsum ($CaMgSO_4$). For the expert, hardness is an important characteristic of natural waters, since Ca and Mg ions form insoluble salts with the anions in soaps, thereby forming a “scum” in washwater. Hence, that is why water is termed to be hard when it contains substantial concentrations of Ca and/or Mg ions. Hence, calcareous water is hard. According to this worker, many areas possess soils that contain little or no carbonate ion and thus its dissolution and reaction with CO_2 to produce HCO_3 does not occur. Such soft water (as the case of Ebonyi River) typically has a pH much closer to 7.0 (as in Ebonyi River) than does hard water, since it contains few basic anions. However, according to this expert, there are lakes with little dissolved Ca or Mg but with relatively high concentrations of dissolved sodium carbonate (Na_2CO_3). Such lakes, according to the scientist have a very low degree of hardness but are high in alkaline. Interestingly, according to this worker, people who live in hard water areas are found to have a lower average death rate from heart disease than do people living in areas with very soft water. The worker adds that the assertion is not clear as whether the advantage of drinking hard water stems from its supply of Mg ion to the body or from the protection that hard water provides from the presence of other ions such as Na and those of the heavy metals. Therefore in this regard there may be some benefits of heavy metals as allayed in this work, but the carcinogenic effects arising from heavy metal accumulation in body tissues calls for no loose ends. Hence, the concerns in this part of the region with increasing cancer and other defective cases still posses the greatest challenges of the people, whether they are coming from water, air or soil sources.

Physical properties of Ebonyi River

Apart from temperature the Ebonyi River passed the standard set by WHO for the physical parameters tested. However, temperature is not a major limitation for water quality. Since the river passed the standards set for total solids, total dissolved solids, total suspended solids and colour which are good. Water in rivers and lakes that is not in contact with carbonate salts, according to Baird (2001) contains substantial fewer dissolved ions than are present in calcareous waters. The concentration of Na and K ions, according to the scientist may be as high as those of Ca, Mg and HCO_3 ions in these fresh waters. Even in areas with no limestone in the soil, according to the worker; the waters contain some bicarbonate ion due to the weathering of alumnosilicates in submerged soil and rock in the presence of atmospheric carbon dioxide. The concentration of sodium ion in water is of interest since high consumption of it from water and salted food are believed to increase one’s blood pressure, which may lead to cardiovascular disease. On the other, excessive sulphate of over 500 mg l^{-1}, according to Baird (2001) may cause laxative effect in some people. The scientist warns that some varieties of bottled drinking water, which people presumably drink in preference to tap water in view of health concerns of sulphate ion in tap water, sometimes exceed the recommended values of some ions. Several of the well known bottled water, according to this worker exceeded the drinking water standards for sulphate, fluoride or chloride.

Conclusions

The results of this study are an indication of the water quality of Ebonyi River and its unsuitability for domestic purposes. The results showed the level of physicochemical properties and heavy metal concentrations. Hence, there should be purification before it is fit for drinking. Although, the water can be used untreated for irrigation, construction, washing of cars and other domestic wares. The disposal of untreated wastes inside and along the river was condemned. It was also recommended that regular microbiological assay of the Ebonyi River be done to safeguard health of the indigenes and aquatic life. The Ebonyi State Water Corporation and Ministry of Environment were challenged on these teething issues.

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