Surface and Ground Waters Concentrations of Metal Elements in Central Cross River State, Nigeria, and their Suitability for Fish Culture

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Abstract

One of the requirements for fish farming is good water quality, void of pollutants. Some heavy metals such as Magnesium, Calcium, Zinc and Iron, which are important in daily life processes, could become pollutants above the required concentrations. Others such as Mercury (Hg), Arsenic (As), Silver (Ag), and Cadmium (Cd) are not required by organisms even at low concentrations. Surface and ground water were investigated for heavy metals concentration to establish their suitability for fish culture. Three surface water bodies (a river, stream and fish pond) and ground water stations (dugout well and two bore holes) were sampled. Heavy metals were analyzed spectrophotometrically at different wave lengths. Data were collated and subjected to analysis of variance which showed that heavy metal concentration in order of abundance was pond, river, stream, dug out well and the bore holes. Heavy metals were therefore, more concentrated in surface water than in ground water (p < 0.05). Surface water contain run off from within their basins while ground water contain what has been sieved into it from the surrounding. Hardness which is a measure of Calcium (Ca) and magnesium (Mg) salts were higher in ground water compared to surface water. Heavy metal concentration were Cu = 0.06 - 0.97 mg/l, Cd = 0.0 - 0.0013 mg/l, Zn = 0.04 – 2.97 mg/l, Ni = 0.0 – 0.43 mg/l, Mn = 0.1 – 3.67 mg/l, Fe = 0.95 – 5.11 mg/l and Al = 0.02 - .02 mg/l. Though heavy metals have no safe concentration for living organisms, the metals were observed to be lower than concentrations recommended by several bodies including Food and Nutrition Board (USA) and Food and Drug Administration Control (NAFDAC in Nigeria).

Keywords: Surface water, ground water, metal elements, physico-chemical parameters, fish culture, Central Cross River State

1. Introduction

Heavy metals are chemical elements with a specific gravity that is at least four to five times the specific gravity of water at the same temperature and pressure (Garbarino et al., 1995; Duruibe et al., 2007). Metal elements are those with positive valances and occupy group I to III in the periodic table. Thirty five elements including antimony, arsenic, bismuth, cadmium, cerium, chromium, cobalt, copper, gallium, gold, iron, lead, manganese, mercury, nickel, platinum, silver, tellurium, thallium, tin, uranium, vanadium, and zinc concern us as "heavy metals (Glanze, 1996). We are constantly in contact with heavy metals while carrying out our daily activities, due to the necessity of some of them in our daily life as kitchen utensils, packaging materials, fuel components (Lead), and component of locomotives (Aluminum used in plane and boat constructions due to its strength to weight ratio); as well as important parts of enzymes and circulatory pigments (Iron, Zinc, Calcium and Magnesium) (Nolan, 2003). Small
amounts of these elements are actually necessary for good health, but large amounts of any of them may cause acute or chronic toxicity. Exposure to unsafe levels of these metals has been shown to pose health problems, for instance, metal fumes of Zinc oxide, Magnesium, Cobalt and copper oxide have been shown to cause Monday morning fever, zinc shake, neuropathies, pneumoconiosis and hepato-renal degenerations; characterized by headache, fatigue, cough and metabolic taste. Heavy metal toxicity can result in damaged or reduced mental and central nervous function, lower energy levels, and damage to blood composition, lungs, kidneys, liver, and other vital organs (Kaye et al., 2002). Long-term exposure may result in slow and progressive physical, muscular, and neurological degenerative processes such as muscular dystrophy and multiple sclerosis (International Occupational Safety and Health Information Centre, 1999). It has been difficult to state what concentration of heavy metal that is safe; different agencies state different levels for a particular metal (Duruibe et al., 2007). Therefore, Duruibe et al. (2007) points out that the most dangerous are those inhaled or taken orally or those absorbed through skin break. Fish and other aquatic organisms are constantly immersed in water containing pollutants. They absorb the pollutants through skin, gut (from food) and respiratory surfaces (Bull et al., 1981; Wegu et al., 2006). Death caused by toxicity or poisoning of living organisms is as old as living things themselves. Living organisms can strive only in optimal environmental conditions. Extreme concentrations of naturally occurring substances has been reported as being harmful to living organisms (Offem and Ayotunde, 2008; Hornung et al., 2009; Ayotunde et al., 2011; Ada et al., 2011; Ayoola, 2008; Ayoola and Ajan, 2008; Jiraungkoonskul et al., 2002; 2003; Idodo-Umeh, and Oronseye, 2006). Among the poisons are heavy metals. Farming activities usually center on helping preferred organism(s) to grow well especially in the absence of harmful or hazardous substances. This is usually done by removing the toxins from the environment or culturing the organisms in selected areas where the toxins are not found.

As there is increasing need for improving output from fish production due to ever increasing population, investigation is required in the aspect of typing the different water bodies in Central Cross River State based on their harmful metal elements concentrations. This activity shall reveal these water bodies’ safety and suitability for fish culture, having in mind that water is the only medium in which fish grows. Its availability and suitability become matter of importance.

2. Materials and methods

The research was carried out in Obubra Local Government of Cross River State, Nigeria (latitude 6° - 7° N and longitude 8° - 9° E of the equator). The area is situated within the middle reach of Cross River; the river therefore has influence on the area. Samples were collected from six stations, designated as station 1, 2 and 3 for surface waters and 4, 5 and 6 for ground waters respectively. Samples were collected from the river using a local fisherman dugout canoe. Samples were collected 30 cm below the surface using 1 litre plastic containers with screw cap at the middle of the river. Sampling was done once a month for twelve months. The samples for the heavy metal analysis were collected in sterilized plastic bottles rinsed with HNO₃ and taken to the laboratory of the Cross River State Water Board Commission, Calabar for metals analysis, while physicochemical parameters were determined in situ.

Mercury in glass thermometer was used to take the temperature of the surface water. For the underground water, temperature was measured immediately after the water was pumped out from the bore hole. pH meter model Mether loledor MP 220 was used to determine the level of acidity of the water. Conductivity was determined using conductivity meter (model: HANNA H18733). The conductivity meter probe was rinsed with distilled water and inserted into the sample in a beaker and the value read off.

Total hardness was estimated using titrimetric method (AOAC, 2002; Wurts, 2009). Dissolve oxygen concentration was obtained by using WTW OXI 196 while turbidity was determined using a Secchi disc in the field and meter (model: HANNA H193703) was used for the determination of turbidity in the laboratory.
Water from bore holes was allowed to rush for about 3 minutes before a midstream portion was taken to avoid collection of rust from pipe walls. Well water was collected in clean plastic buckets. Water samples in the plastic containers were preserved in the refrigerator at 0°C for subsequent analysis. 1.5 ml of concentrated HNO₃ was added to each 1 litre of sample to adjust the pH to 2.0. Samples containing particles of organic materials were digested in two grams (2 g) of equal volumes of nitric acid and sulphuric acid (2.0 ml) in a beaker placed on a hot plate and heated until the whole quantity was dissolved. The digested sample was then cooled and was adjusted to 100 cm³ with de-ionised water. Spectrophotometric method (Spectrophotometer model VIS SPEC 6100, PHOTOLAB, made in Germany) was used for the determination of the concentrations of the following heavy metals: Copper (Cu), Cadmium (Cd), Nickel (Ni), Iron (Fe), Zinc (Zn), Aluminum (Al), Manganese (Mn) and Lead (Pb) at different wavelength as shown in Table 1. Analysis of variance was used to compare the concentration levels of the various metals, hardness, conductivity, and other physico-chemical properties. Duncan’s multiple Range Test (DMRT) was used to determine the significant differences at (P<0.05) among means.

3. Results

The physic-chemical parameters were displayed in Table 2. Significant differences exist in physico-chemical properties between the different water bodies (p < 0.05). Figure 1 shows the map of Cross River State, Nigeria indicating the study area, Obubra.

The relative concentrations of these metals in the various sampling stations or water bodies are displayed in Figures 2 to 9. There were significant differences (p < 0.05) between the concentrations of the various metals between the sampling stations as displayed in Figures 2 - 9.
Table 1. Recommended allowable concentrations (ppm) values in portable water by different bodies

<table>
<thead>
<tr>
<th>Institutional body</th>
<th>cadmium</th>
<th>copper</th>
<th>nickel</th>
<th>lead</th>
<th>iron</th>
<th>zinc</th>
</tr>
</thead>
<tbody>
<tr>
<td>WHO (WHO, 1985)</td>
<td>0.005</td>
<td>3.00</td>
<td>-</td>
<td>0.05</td>
<td>0.30</td>
<td>5.00</td>
</tr>
<tr>
<td>FEPA (FEPA, 2003)</td>
<td>&lt;1.00</td>
<td>&lt;1.00</td>
<td>-</td>
<td>-</td>
<td>&lt;1.00</td>
<td>&lt;1.00</td>
</tr>
<tr>
<td>USEPA (USEPA, 1987)</td>
<td>0.008</td>
<td>0.10</td>
<td>-</td>
<td>0.0058</td>
<td>0.10</td>
<td>0.0766</td>
</tr>
<tr>
<td>USEPA 2007 (regarded as clear water)</td>
<td>30</td>
<td>1500</td>
<td>420</td>
<td>300</td>
<td>-</td>
<td>2800</td>
</tr>
</tbody>
</table>

Source: Ayotunde et al. (2012)

Figure 2. Relative concentrations of Copper in the various water bodies
[Means having the same letters show that the concentrations were statistically the same (p < 0.05)]
Table 2. Some physicochemical properties of different water bodies. Means which carry the same superscript are statistically the same while those with different superscripts are statistically the different (p < 0.05)

<table>
<thead>
<tr>
<th>Station</th>
<th>Temperature (°C)</th>
<th>pH</th>
<th>Conductivity</th>
<th>Total hardness</th>
<th>Dissolved Oxygen</th>
<th>Turbidity</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 River</td>
<td>27.03b ± 0.033</td>
<td>5.643e ± 0.006</td>
<td>21.06f ± 0.233</td>
<td>12.64f ± 0.14</td>
<td>2.113c ± 0.036</td>
<td>7.493b ± 0.523</td>
</tr>
<tr>
<td>2 Dugout well</td>
<td>27.00ab ± 0.00</td>
<td>5.10f ± 0.06</td>
<td>289.3c ± 0.666</td>
<td>175.6c ± 1.6</td>
<td>1.113c ± 0.026</td>
<td>1.84d ± 0.07</td>
</tr>
<tr>
<td>3 Earthen pond</td>
<td>27.00ab ± 0.00</td>
<td>6.006d ± 0.003</td>
<td>101.6e ± 1.466</td>
<td>61.0e ± 0.88</td>
<td>0.69d ± 0.136</td>
<td>12.41a ± 0.776</td>
</tr>
<tr>
<td>4 Stream</td>
<td>26.93ab ± 0.033</td>
<td>6.193c ± 0.066</td>
<td>61.73e ± 0.266</td>
<td>37.04e ± 0.16</td>
<td>0.80d ± 0.06</td>
<td>1.73d ± 0.14</td>
</tr>
<tr>
<td>5 Bore hole</td>
<td>27.03b ± 0.033</td>
<td>6.77b ± 0.013</td>
<td>705.3b ± 1.666</td>
<td>423.2b ± 1.0</td>
<td>3.243a ± 0.193</td>
<td>0.70d ± 0.046</td>
</tr>
<tr>
<td>6 Bore hole</td>
<td>27.00ab ± 0.00</td>
<td>7.215a ± 0.015</td>
<td>817.5a ± 0.555</td>
<td>490.5a ± 0.3</td>
<td>3.15a ± 0.04</td>
<td>5.33c ± 0.095</td>
</tr>
</tbody>
</table>

Figure 3. Relative concentration of Cadmium present in the different water bodies

[Means with the same letters are statistically the same (p < 0.05)]
Figure 4. Relative concentration of Zinc present in underground and surface waters

[Same letters signify statistically insignificant different means (p < 0.05)]

Figure 5. Relative concentration of Nickel present in underground and surface waters

[Means with different letters are statistically different (p < 0.05)]
Figure 6. Concentration of Aluminum in surface and underground waters
[Same letters signify statistically insignificant different means (p < 0.05)]

Figure 7. Concentration of Iron in waters in Obubra
[Same letters signify statistically insignificant different means (p < 0.05)]
4. Discussion

It is not expected that water from the bore hole should have higher oxygen concentration than the surface water. Oxygen concentration in bore hole water was higher possibly due to the splashing action of the water as it falls from the nozzle of the tap, thereby mixing with atmospheric oxygen (Lassee, 1995; Sverdrup et al., 2006). There was no significant difference in temperature (p < 0.05) between ground and surface waters. However, differences in temperature existed between sample stations, which did not follow any defined pattern as ground or surface water. The variation was local rather than being affected by depth and could have been influenced by vegetation cover of stream or pond. These temperatures were optimal for culture of warm water fishes (Mills, 1986). Conductivity, basicity and total hardness observed to be higher in the ground waters (p < 0.05). Conductivity is influenced by temperature and salinity of water. The underground water in this study area is hard water which does not produce leather with soap. Total hardness is a measure of the quantity of Magnesium, Calcium and Iron salts (Sienko and Plane, 1976).

Different metals have different modes of poisoning depending on their chemical form. As Hornung et al. (2009) pointed out, barium sulfate is nontoxic, but its salts are rapidly absorbed and cause fatal hypokalemia. Some metals poison by emitting particles rather than poison by binding to cell proteins. Others only become potentially poisonous in the presence or absence of other metals (Herbert and Vandyke, 1964; Jones, 1983; Rompala et al., 1984).

The concentration of metals observed here were lower than the safe concentrations reported in Medscape (2012) for the soil with proximity to water bodies. The soil contains dissolved metals, which constantly and easily sip into the water bodies. Medscape (2012) reported concentrations of some metal in the soil to be higher than concentrations recorded here in water. The concentration of these elements falls within the same range as those recorded by Ayotunde et al. (2012). They observed the concentration of iron to be 0.009 ppm, copper to be 0.015 ppm, lead to be 0.0002 ppm, cadmium to be 0.0006 ppm and zinc to be
0.009 ppm. These range as also found in this investigation was below danger levels for aquatic organisms. Ayotunde et al. (2012) pointed out that sediments can be sensitive indicators of aquatic environment contamination. For instance, Copper was 0.2 ppm in the bore hole to 0.7 ppm in the river; Cadmium concentration in this area (0.0 to 0.0013 ppm) was lower than 0.0 to 2.0 ppm; Nickel was 0.0 to 0.043 ppm which is lower than the average of 2.0 to 750 ppm; and Lead was 0.0 ppm in bore hole to 0.034 ppm in the river. Because no one ingests soil directly, these values are regarded as safe by Medscape (2012). It is expected that concentrations in the soil have direct proportional relationship with that in the water which bathes the soil or it is quantity which is washed from land that enters water environment and vise versa (Duruibe et al., 2007).

USEPA (2007) regarded water containing the following concentrations as clear water: Cadmium (30 ppm), Copper (1500 ppm), Lead (300 ppm), Nickel (420 ppm) and Zinc (2800 ppm). These values and those reported by Duruibe et al. (2007) from Food and Nutrition Board (USA) and Food and Drug Administration Control (NAFDAC in Nigeria) are above those recorded in this investigation. The surface waters collect water from their basins. For instance the river basin collects all its sources from Cameroon, Ikom in Cross River State as well as other villages along its course before the sampling point. Entrance of pollutants into bore hole has limited surface area of potential input. The input of pollutants could come from limited area, a phenomenon which Wikipedia (2012) described as point source of pollution with identifiable sources such as sewage treatment plants, factory or city storm drains. Though the stream and pond have small basins that limit amount of inputs of these metals to small areas, these could have supply from the river during wet season. The bore holes have limited supply, which could come mainly from precipitation. As Schueler (2000) and Burton and Pitt (2007) noted, disposal of personal care products containing heavy metals can increase heavy metals contamination of a water body along its course. Soon et al. (1980) and Higgings and Dasher (1986) pointed out that water contamination can be by many manufacturing processes and by waste water from sewage. Wikipedia (2012) describe metals or pollutants inputs into water from such sources as non-point source because the pollutants come from diffused sources. Pollutants often come in small amounts gathered from large areas in case of river. Sources include agricultural lands, nutrient run off in storm water or from forest (Oguzie, 1996; Ogbeibu and Ezeunara, 2002). The lower concentrations of some metals in the bore holes which are deeper could be due to the fact that the deeper and local soil is poor in these metals.

5. Conclusion

No concentration of metal elements or any metal has been reported as being safe, because long term exposure to low concentration is equally harmful. Though some are essential in life processes, in the cases of Iron, Zinc, Magnesium and Calcium, at moderate concentrations, quantities extremely low can still pose danger especially when exposed for extended period of time (Zhou et al., 2008). Differences existed in concentrations of metals between surface and ground waters. Such differences are likely due the sources from the different water bodies are been fed. However, the concentrations observed in this study are lower than the averages recorded elsewhere as acceptable limit for fish culture, since their limits acceptable for the waters to be used as portable water are not exceeded. Other metals like Mercury, Lead, Silver and Cadmium are not allowed at any concentration. Water from this area could therefore be used as portable water after it may have been screened for other metals and the biotic components not considered in this investigation.

References


Federal Environmental Protection Agency (FEPA) (2003), *Guidelines and Standards for Environmental Pollution Control in Nigeria*, Nigeria


