Geochemical Investigation of Heavy Metals Characterization of Groundwater in Hydrocarbon impacted site in Part of Niger Delta, Nigeria

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Abstract: - Heavy metal pollution is ubiquitous in Groundwater especially in hydrocarbon impacted site in the Niger Delta, due to anthropogenic and possible terrigenous sources. A total of ten boreholes were drilled in the study area to assess the degree of contamination; Six boreholes were drilled in the hydrocarbon impacted site, while four boreholes were drilled in the un-impacted site to serve as control. The study is to evaluate and characterize the heavy metals status in the area (Zn, Pb, V, Ni, Cr, Cd, As, Hg, Co, Mn, and Cu) and their trends in order to interpret the environmental implications to Community inhabitants. Groundwater samples were collected and analysed using atomic absorption spectrophotometer. The results indicated higher concentration of iron in the hydrocarbon impacted site than the un-impacted site. Mn, Pb and Zn are relatively higher in concentration in the hydrocarbon impacted site than the un-impacted site. Cr, Cu and Ni also presented higher concentration in the hydrocarbon impacted site than the un-impacted site. V, As and Hg also presented higher concentrations in the hydrocarbon impacted site than the un-impacted site. Cd and Co also indicated higher concentration in the hydrocarbon impacted site than the un-impacted site. When the hydrocarbon impacted site result was compared with WHO (2006) standard, the analysed values were above WHO (2006) standard, which signifies that the study area has been polluted with heavy metals. Hence, these metals will continue to deteriorate the aquifer if not checked. The effects will be on the inhabitants; therefore proactive measures should be taken to remediate the environment.

Keywords: Geochemical Investigation, Hydrocarbon, Groundwater, Heavy Metals

I. INTRODUCTION

The chemical environment inhabited by humans is full of toxic substances which are introduced to the environment through waste disposal, hydrocarbon exploration and exploitation, flooding, mining and other natural processes. In the process humans inhale or ingest and absorb these chemicals. Heavy metal concentration in humans is difficult to establish and identify their specific symptoms, because in most cases, heavy metal poisoning has a long gestation period, and the effect is recognized only when it has assumed epidemic proportion. Heavy metals causes chronic and acute diseases to inhabitants, as such there is need to study their concentrations in soil and drinking water. These metals are capable of impairing serious defects on human when absorbed. Considering the nature and the cumulative effect of these substances to the environment and the inhabitants. Understand the concentration and distribution of these heavy metals in ground water samples and when compared with the observed field results with the regulatory environmental standard, WHO 2006. The essence is to understand the nature and the source of contamination qualitatively and quantitatively. There has been no geochemical baseline data of the study area with respect to heavy metals concentration. Therefore, this study will unveil the concentration of these metals and their cumulative environmental implications to inhabitants.

II. SITE DESCRIPTION

The study area is part of Yenagoa Local Government Area of Bayelsa State which is situated in Niger Delta Basin. It lies within latitude N05° 08’ 33.6” and longitude E006° 26’ 32.8”. It is at the eastern flank of the east west road, comprising of communities such as: Zarama, Okordia, Akumoni, Ikarama, Kalaba Biseni. It is bounded by Sampou, Agbare and Odoni community on the eastern side, and Akumoni, Okordia and Zaramaon on the northern side. Biseni, Jainkerema on the Southern side, while mbiama and Rumuekpe are located at the western side. These communities are accessible by road. For over two and half decades, this areas have been championing crude oil exploration activities, hence, a dense network of crude oil pipeline and flow stations are found in these areas. Taylor creek shares tributaries with the River Nun which drains the area. Most of the spill flows into these tributaries.

Geology of the Study Area

The study area is prototype of the Niger Delta Sedimentary basin. The stratigraphy of the Niger Delta basin constitutes an advance of Terrestrial deposits into high energy marine environment. At present deposition of the Niger Delta occurs simultaneously under terrestrial fluvialite conditions which interplay between Terrestrial and Marine influence (parralic) condition. (Frankl and Cardry, 1967; Short and Stauble, 1967); identified three basic subsurface stratigraphic units which are the continental Benin Formation. The parralic Agbada Formation and the marine Paleocene Akata Formation. All engineering structures and the hydrogeological attributes are predominant in the Benin Formation. The Benin Formation is overlying conformable by the Oligocene Afam clay and lying under conformable by the...
plistocene Ogwashi-Asaba sandstone. The detailed hydrogeological potentials of Benin Formation have been elaborately documented by (Etu-Efeotor, 1981; Etu-Efeotor and Michalski, 1989; Etu-Efeotor and Odigi, 1983; Udom et al., 1998, Offodile, 1992). The parallic Agbada Formation is the reservoir rock which is capable of retaining and transmitting hydrocarbon. The upper part of the Agbada Formation is the oil window where the hydrocarbon potentials are embedded. The Agbada formation is Eocene in age, and its lateral equivalent of Bendel Ameki Formation. The Akata Formation is the basal unit of the Niger Delta stratigraphic system which is a marine environment. It consists of clay and shale lithology that is considered as the source rock. The Akata Formation is Paleocene and it is rich in calcareous and siliceous micro-organism such as foraminifera, radiolarians, and ostracoid.

III. METHODOLOGY

Ten groundwater Samples were collected from ten boreholes in the study area, and the water was allowed to run for five minutes until a constant pH was obtained. This was to ensure the collection of a representative sample from the aquifer and for the removal of any stagnant or polluted water within the pipe. The samples were collected from the well head in clean air tight plastic bottles. The bottles were filled to the brim and were corked immediately to avoid contact with oxygen. The samples were placed in a cooler maintained at 4°C and transported to an analytical laboratory within twenty-four hours (24 hours) of sample collection.

The samples were subjected to geochemical laboratory analysis for heavy metals (Zn, Pb, V, Ni, Cr, and Cd, As, Hg, Co, Mn and Cu). Heavy metals were analysed with atomic absorption spectrophotometric method.

IV. PRESENTATION OF RESULTS AND DISCUSSION

The result of the Groundwater analysis and data are presented in (Tables: 1 & 2). The qualitative and quantitative discussions and interpretations are given succinctly.

Table 1: Heavy metal Concentration of Groundwater in the impacted site of the study area

<table>
<thead>
<tr>
<th>S/N</th>
<th>Groundwater code</th>
<th>Mn</th>
<th>Zn</th>
<th>Pb</th>
<th>Cr</th>
<th>Cu</th>
<th>Ni</th>
<th>V</th>
<th>Ba</th>
<th>As</th>
<th>Hg</th>
<th>Cd</th>
<th>Co</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>KAL/BHW10/C/02</td>
<td>0.045</td>
<td>0.016</td>
<td>0.130</td>
<td>0.131</td>
<td>0.161</td>
<td>0.051</td>
<td>0.04</td>
<td>0.004</td>
<td>0.003</td>
<td>0.001</td>
<td>0.09</td>
<td>0.045</td>
</tr>
<tr>
<td>2</td>
<td>IKA/BHW2/C/03</td>
<td>0.023</td>
<td>0.016</td>
<td>0.220</td>
<td>0.172</td>
<td>0.181</td>
<td>0.134</td>
<td>0.014</td>
<td>0.075</td>
<td>0.005</td>
<td>0.004</td>
<td>0.083</td>
<td>0.123</td>
</tr>
<tr>
<td>3</td>
<td>IKA/BHW6/C/07</td>
<td>0.013</td>
<td>0.055</td>
<td>0.112</td>
<td>0.081</td>
<td>0.421</td>
<td>0.061</td>
<td>0.142</td>
<td>0.032</td>
<td>0.0040</td>
<td>0.003</td>
<td>0.006</td>
<td>0.131</td>
</tr>
<tr>
<td>4</td>
<td>IKA/BHW7/C/08</td>
<td>0.034</td>
<td>0.044</td>
<td>0.014</td>
<td>0.310</td>
<td>0.270</td>
<td>0.071</td>
<td>0.151</td>
<td>0.003</td>
<td>0.005</td>
<td>0.001</td>
<td>0.341</td>
<td>0.141</td>
</tr>
<tr>
<td>5</td>
<td>IKA/BHW8/C/09</td>
<td>0.023</td>
<td>0.043</td>
<td>0.381</td>
<td>0.410</td>
<td>0.272</td>
<td>0.134</td>
<td>0.141</td>
<td>0.07</td>
<td>0.08</td>
<td>0.009</td>
<td>0.134</td>
<td>0.315</td>
</tr>
<tr>
<td>6</td>
<td>IKA/BHW9/C/10</td>
<td>0.241</td>
<td>0.048</td>
<td>0.128</td>
<td>0.134</td>
<td>0.301</td>
<td>0.071</td>
<td>0.132</td>
<td>0.003</td>
<td>0.002</td>
<td>0.003</td>
<td>0.050</td>
<td>0.003</td>
</tr>
</tbody>
</table>

Table 2: Heavy metal Concentration of Groundwater in the control site of the study area

<table>
<thead>
<tr>
<th>S/N</th>
<th>Groundwater code</th>
<th>Mn</th>
<th>Zn</th>
<th>Pb</th>
<th>Cr</th>
<th>Cu</th>
<th>Ni</th>
<th>V</th>
<th>Ba</th>
<th>As</th>
<th>Hg</th>
<th>Cd</th>
<th>Co</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>KAL/BHW1/U/01</td>
<td>0.028</td>
<td>0.026</td>
<td>0.016</td>
<td>0.03</td>
<td>0.016</td>
<td>0.011</td>
<td>0.003</td>
<td>0.003</td>
<td>0.001</td>
<td>BDL</td>
<td>0.001</td>
<td>0.08</td>
</tr>
<tr>
<td>2</td>
<td>IKA/BHW3/U/04</td>
<td>0.028</td>
<td>0.019</td>
<td>0.008</td>
<td>0.003</td>
<td>0.121</td>
<td>0.007</td>
<td>0.003</td>
<td>0.005</td>
<td>0.0005</td>
<td>&lt;0.001</td>
<td>0.003</td>
<td>0.004</td>
</tr>
<tr>
<td>3</td>
<td>IKA/BHW4/U/05</td>
<td>0.153</td>
<td>0.121</td>
<td>0.010</td>
<td>0.001</td>
<td>0.010</td>
<td>0.011</td>
<td>&lt;0.005</td>
<td>BDL</td>
<td>&lt;0.001</td>
<td>BDL</td>
<td>0.005</td>
<td>0.006</td>
</tr>
<tr>
<td>4</td>
<td>IKA/BHW5/U/06</td>
<td>0.111</td>
<td>0.071</td>
<td>0.090</td>
<td>0.006</td>
<td>0.015</td>
<td>0.004</td>
<td>&lt;0.001</td>
<td>BDL</td>
<td>&lt;0.0001</td>
<td>BDL</td>
<td>0.013</td>
<td>0.015</td>
</tr>
</tbody>
</table>
Concentration of manganese in the hydrocarbon impacted site ranges from 0.013mg/l to 0.241mg/L at the impacted site. Manganese ranges from 0.028mg/l to 0.153mg/l in the un-impacted site (Table 1& 2). The permissible limit of manganese in drinking water is 0.2mg/l. (WHO 2006 standard)

Concentration of manganese in the study area falls within the acceptable limit exception of Borehole 9 which had a value slightly above the permissible limit. A plot of manganese concentration of groundwater in the study area against the standard are shown in Fig 2

Zinc concentration in the hydrocarbon impacted site in the study area ranges from 0.019mg/l to 0.121mg/l and zinc concentration in the un-impacted site ranges from 0.044 to 0.055mg/l (Table 1& 2). The allowable limit of Zinc WHO (2006) standard is 3mg/l. The concentration of Zinc in the study area is within the acceptable limit. High concentration of Zinc in drinking water causes new arteriosclerosis disease and zinc is carcinogenic in nature. Acute ingestion of zinc causes vomiting diarrhea and abdominal pains. However, Zinc is an important catalyst during metabolic activities. It is also an essential element for plants and animals. Deficiency of Zinc adversely affects growth and causes chronic sickness. A Plot of Zinc concentration in the study area against the standards are shown in Fig 3
Lead concentration in the hydrocarbon impacted site ranges from 0.112mg/l to 0.381mg/l and that of un-impacted site lead concentration ranges from 0.010mg/l to 0.016mg/l (Table 1 & 2) the allowable limit of lead in drinking water is 0.03mg/l (WHO 2006). Groundwater samples 2, 6, 7, 8, 9 and 10 have higher concentrations of lead. Whereas, Boreholes 1, 3, 4 and 5, have samples with concentrations below the allowable limit. This suggests that borehole sample 2, 6, 7, 8, 9 and 10 are impacted with crude oil. Higher concentration of lead damages tooth and the central nervous system. Illness known as plumbersim in the central nervous system is induced by lead poisoning. Lead also destroys the IQ of infant babies (Egai et al., 2013). Plot of Lead concentration of all the locations in the study area against standard are shown in Fig 4.

![Pb (mg/l)](image)

**Fig 4: Lead concentration of groundwater against WHO (2006) Standards**

Chromium concentration in the study area ranges from 0.31mg/l to 0.172mg/l in the hydrocarbon impacted site while Chromium concentration ranges from 0.001mg/l to 0.006mg/l in the un-impacted site (Table 1 & 2). Borehole 1, 2, 6 and 9 have concentration values ranging from 0.081mg/l to 0.134mg/l whereas borehole 7 and 8 have concentration values ranging from 0.310mg/l to 0.410mg/l. The allowable limit of chromium is 0.05mg/l (WHO 2006), which is lower than the values in boreholes 10, 6, 7, 8 and 9. Chromium is an essential element in the human diet possibly involved in sugar metabolism. Low level exposure leads to skin irritation; Long term exposure can cause kidney or liver damage. Higher concentration of chromium in an aquatic environment makes eating of fish dangerous (Imasuen and Egai, 2013). Plot of Chromium concentration in groundwater of all the locations in the study area against standard are shown in Fig 5.

![Cr (mg/l)](image)

**Fig 5: Chromium concentration in groundwater against WHO (2006) standard**
Concentration of Copper in the hydrocarbon impacted site in the study area ranges from 0.161mg/l to 0.421mg/l and that of the un-impacted site ranges from 0.01mg/l to 0.121mg/l (Table 1& 2). The allowable limit of copper by WHO (2006) is 1mg/l. Copper concentration in groundwater in the study area is lower than the permissible limit. Higher concentration of copper leads to gastrointestinal disorders. Plot of Copper concentration in groundwater of the study Locations against standard are shown in Fig 6.

The concentration of Nickel in the hydrocarbon impacted site of the study area ranges from 0.011mg/l to 0.134mg/l and that of the impacted site ranges from 0.007mg/l to 0.01mg/l (Table 1 & 2.). The permissible limit of nickel by WHO (2006) is 0.02mg/l. The concentration of nickel in the water samples from borehole 2, 10, 6, 7, 8, and 9 are above this standard. Boreholes 3, 4, and 5 have values lower than the permissible standard. The crude oil activities in the impacted site are probably the main cause of the elevated values of nickel in the study area. Higher concentration of nickel in an aquatic body or soil is possibly carcinogenic. Nickel is a component of motor exhaust of diesel oil, heavy oil and coal. Nickel is also a component of tobacco puff. Plot of Nickel concentration of groundwater in the study Locations against WHO 2006 standard are shown in Fig 7.
Concentration of Vanadium in the hydrocarbon impacted site in the study area ranges from 0.04mg/l to 0.151mg/l and that of the un-impacted site ranges from <0.005mg/l to 0.003mg/l (Table 1& 2). The impacted site registered higher values of vanadium concentration. The source of vanadium is from the oil spill contamination. Vanadium is a potent respiratory irritant. It affects the lungs, liver, kidney, spleen and bones of human (Kamaruzzaman et al., 2008). Therefore, higher concentrations of vanadium are injurious to both aquatic bodies and humans. Plot of Vanadium concentration of groundwater in all the Locations of the study area against WHO (2006) standard are shown in Fig 8.

Concentration of Arsenic in the hydrocarbon impacted site in the study area ranges from 0.002mg/l to 0.08mg/l and that of un-impacted site ranges from <0.001mg/l to 0.005mg/l (Table 1& 2). The allowable limit of arsenic by WHO (2006) standard in drinking water is 0.01mg/l. Borehole 8 recorded high values of arsenic concentration in the study area when compared with the regulating standards. Moreover, the values of arsenic concentration in the impacted site are higher than the un-impacted site. Higher concentrations of Arsenic in the environment if absorbed by human can induce cancer. Arsenic is a deadly heavy metal that does not have a vital use for man (National Research Council of Nigeria, 1997). Plot of arsenic concentration in groundwater in the study area against the WHO (2006) standard are shown in Fig 9.
Concentration of Mercury in the hydrocarbon impacted site in the study area ranges from 0.003mg/l to 0.03mg/l (Table 1&2) and that of the un-impacted site is <0.001> mg/l. However, Borehole 2, 6, 8 and 9 of the impacted site have values higher than that of the un-impacted site. WHO (2006) allowable limit of Mercury is 0.001mg/l. Borehole 2, 6, 8 and 9, had values above WHO (2006) this limits. These boreholes are located in the pipeline and manifold areas in which oil facilities are also located. High concentrations of Mercury in the area are from the crude oil spill. 0.001mg/l of Mercury concentration in aquatic environment reduces plankton growth by half, whereas 0.01mg/l stops any form of plankton growth (Ellis et al., 1989). Plot of Mercury concentration of groundwater in the area are shown in Fig 10

Concentration of Cadmium in the hydrocarbon impacted site ranges from 0.06mg/l to 0.341mg/l and the concentration of Cadmium ranges from 0.001mg/l to 0.013mg/l in the un-impacted site (Table 1&2). The un-impacted site has lower values of cadmium concentration than the impacted site. The permissible limit of cadmium in drinking water by WHO (2006) standard is 0.003mg/l. The values of cadmium in boreholes 2, 6, 7, 8, 9 and 10 at the impacted site are higher than this standard. This implies that the impacted site have cadmium toxicity. Cadmium concentration in the environment particularly in soil may be due to dumped dry cell batteries and crude oil activities in the study area. Higher concentration of cadmium in the environment if absorbed by man is toxic to the kidney. The gestation period of cadmium in the human body is between 10-30 years (National Research Council of Nigeria, 1997). Cadmium causes pains in the body. It attacks bones causing them to become brittle and thin so that they can break easily. Plot of Cadmium concentration in groundwater in the study area against WHO (2006) standard are shown in Fig 11.
Concentration of cobalt in the hydrocarbon impacted site in the study area ranges from 0.003mg/l to 0.315mg/l and that of the un-impacted site Cobalt range from 0.004mg/l to 0.08mg/l (Table 1 & 2). The impacted site has higher values of cobalt concentration. The permissible limit of this parameter by WHO (2006), standard is 1mg/l. The concentration of cobalt at both the impacted site and un-impacted site has lower values than the WHO (2006) standard, hence Cobalt does not constitute any health problem in the area. Plot of Cobalt concentration in groundwater in the study Locations against the standard are shown in Fig 12.

![Fig 12: Cobalt concentration in groundwater against WHO (2006) standard](image)

V. CONCLUSION AND RECOMMENDATION

The study has shown that concentration of heavy metals in groundwater, in the impacted site is higher than (WHO 2006) standard as well as the control site. The higher values of heavy metals indicated oil spill contamination as the main source. These metals are bio accumulative and have the tendency to cause acute and chronic illness to the people through food chain (oral ingestion).

**Recommendation**

Hence, effective remediation such as bioventing and contaminant removal is recommended for the hydrocarbon impacted site in the study area.

REFERENCES


