Article

Heavy metals, risk indices and its environmental effects: A case study of Ogoniland, Niger Delta region of Nigeria

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Abstract

Nigeria has the largest petroleum industries in West African region and the second largest in Africa after Algeria. Nigeria has a total of 159 oil fields and 1481 wells in operation, Explorations in the oil industry in Nigeria have resulted in release of hydrocarbons and associated pollutants including heavy metals into the Niger Delta environment from refine and unrefined petroleum products. Extraction, processing, and transport of crude oil dating back to the 1950s have had a devastating impact on Ogoniland, a territory in the Niger Delta region of Nigeria. Unlike hydrocarbons that can be degraded by microorganisms, heavy metals are recalcitrant to biodegradation, hence this research. Samples were collected from five communities in Ogoniland and these samples were analyzed for heavy metal concentration using inductively coupled plasma-mass spectrometry. The mean of the heavy metals detected are Co (0.912 mg/kg), As (1.04 mg/kg) and Ba (42.39 mg/kg). Heavy metal concentration in these sampled sites exceeded the maximum limit set by Standard Organization of Nigeria. From the results Barium had the highest concentration of heavy metal which is due to the use of barium sulphate to increase the density oil during drilling operations. Barium present in the environment is of public health concern and uptake of water-soluble barium may cause a person to experience vomiting, abdominal cramps, diarrhea, difficulties in breathing, increased or decreased blood pressure, numbness around the face and muscle weakness. Therefore, there is need for stringent implementation of regulations guiding oil exploration industries in the release of heavy metals to the environment as in the case of Ogoniland.

Keywords heavy metal; environmental concerns; Ogoniland; pollution; sediment.

1 Introduction

Environmental pollution either land, air, water and sediment has been of concern to the society, especially in developing countries witnessing tremendous and rapid industrialization as Nigeria (Chikere et al., 2017).
Nigeria has Africa’s largest reserves of oil and gas within its borders and most of these resources exist in the Niger Delta region that comprises of nine states. Oil spills have occurred repeatedly for decades in the Niger Delta and large parts of the land and wetlands are chronically affected by oil spills (Linden and Jonas, 2013). Nigeria has the largest petroleum industries in West African region and the second largest in Africa after Algeria. Nigeria has a total of 159 oil fields and 1481 wells in operation (Ekperusi and Aigbodion, 2015). Explorations in the oil and gas industry in Nigeria has resulted in release of hydrocarbons and associated pollutants including heavy metals into the Niger Delta environment (Obot et al., 2006; UNEP, 2011). Several researchers have found elevated levels of heavy metals in oil and gas facilities (Iwegbue et al., 2006), street dusts (Mmolawa et al., 2011; Wei and Jiang, 2010; Baba et al., 2009; Abdel-Latif and Saleh, 2012; Salmamanzadeh, 2012), agricultural soils (Dinev et al., 2008; Wei and Yang, 2010), solid waste dumps (Ajah et al., 2015) and lake sediments (Li et al., 2013). High concentrations of heavy metals in different parts of the globe have increased the interest for environmentalists and ecotoxicologists in toxicity and environmental degradation (Prajapati, 2012; Al-Farrag et al., 2013; Su et al., 2014; Ackah et al., 2015; Afsaneh et al., 2018). Inhabitants of the ecosystem may be exposed to these elevated heavy metals that have polluted the ecosystem through direct ingestion of contaminated soil, consumption of crops and vegetables grown on the contaminated lands or drinking water that has percolated through such soils (McLaughlin et al., 2000).

The severe pollution scenario of these elevated heavy metals have resulted in the degradation of the environment especially soil, resulting in a substantial decline in both below and above ground biodiversity, affect public health and disrupt life support system for local people. Environmental and public health concerns is of interest due to their carcinogenic, mutagenic, recalcitrant, and other detrimental effects of heavy metals on living organisms (Erdogmus et al., 2015). Several health hazards have been associated with consumption of high doses of heavy metals (Mahmood and Malik, 2014; Jarup, 2003). These health hazards range from mild illnesses such as ulcers, diarrhea, nausea, abdominal pain, gastrointestinal disorders, respiratory disorders, cough, nervous disorder, psychological disturbances to life threatening diseases such as cancers, cardiovascular diseases, asthma, kidney and liver damage, coma and diabetes (Ajah et al., 2015). A thorough search of the scientific literature revealed only one health study conducted in the Niger Delta region, which reported higher rates of respiratory and skin disorders in Eleme, a local government in Ogoniland compared to a less-industrialized Nigerian community (Ana et al., 2009). Extraction, processing, and transport of crude oil dating back to the 1950s have had a devastating impact on Ogoniland, a territory in the Niger Delta region of Nigeria. Ogoniland, immediately east of Port Harcourt, this area consists of four local government areas (LGAs): Eleme, Tai, Gokana, and Khana with a total population of 830 000 (UNEP, 2011). Ogoniland is heavily polluted with petroleum hydrocarbon and heavy metals, at the request of the Federal Government of Nigeria, the United Nations Environment Programme (UNEP) carried out a survey of the nature and extent of oil pollution in Ogoniland. The assessment covered contaminated land, ground and surface water, sediments etc. (Linden and Jonas, 2013). The United Nations Development Programme estimates that 6178 oil spills occurred in Ogoniland between 1976 and 2011 (Kponee et al., 2015). Once oil has contaminated wetlands such as marshes and mangroves, it is often very difficult to remove without causing further damage to these environments (NOAA, 1994, 2002; NRC, 2003; Chan and Baba, 2009), the resulted unmitigated pollution of land, air and water exposes the populace to miasma of health hazards (Ajah et al., 2015). Most heavy metals along side with petroleum hydrocarbon are naturally occurring in the earth crust as trace elements are usually found buried deep in the heart of the earth. However, massive exploitation of natural resources has given rise to a build-up of these toxic elements in the human environment. Many of the toxic as well as non-toxic hydrocarbons evaporate and are degraded by microorganisms quite rapidly (NRC, 2003; ITOPF, 2011b) but heavy metals which are xenobiotics are recalcitrant to biodegradation.
From the above background of literature review, the aim of this report was to know the extent of heavy metal contamination in Ogoniland. The specific objective of this research therefore, was to evaluate the extent of heavy metal pollution using pollution indices such as Contamination Factor (CF), Pollution load index (PLI) and Geoaccumulation index (Igeo).

2 Material and Methods
2.1 Study areas and sampling
Ogoniland is a region covering some 1,000 km$^2$ in the south-east of the Niger Delta basin, It has a population of close to 832,000 (UNEP, 2011). The region is divided administratively into four local government areas: Eleme, Gokana, Khana, and Tai (Fig. 1). Five communities in Ogoniland was sampled, At each location, five sub-samples were collected in a plastic bucket and mixed before being transferred to a glass sampling jar (UNEP, 2011). Only the top 10 cm of the sediment core were used for the samples and care was taken to avoid flushing away the surface floc on top of the more solid sediment. The samples were stored frozen until the analyses were performed, heavy metal analyses was carried out as described by (UNEP, 2011), briefly, For the determination of trace metals in sediments, sediments were finely grounded by agate pestle and mortar. Triplicate samples of 0.25g were oven dried (105°C), ashed (450°C) and digested in concentrated HNO$_3$ (Aristar, VWR) for “pseudo-total” digestion using a microwave (CEM Mars 5) following the adapted USEPA method 3051 (Yafa and Farmer, 2004). Pseudo-total digestion was used since the main interest was in anthropogenic rather than mineral-bound elements. Following digestion the samples were evaporated to near-dryness on a hot plate, added to a 25ml volumetric flask (three washes from beaker were also added) and diluted with dilute nitric acid (2% v/v, VWR, Aristar). This was filtered (Ashless Whatman 45) into a polypropylene centrifuge tube (Fisher) and stored at 4°C prior to analysis with inductively coupled plasma-mass spectrometry (ICP-MS). The following trace elements were detected using ICP-MS analysis: Co, As and Ba.

![Fig. 1 Map of Ogoniland showing sampling sites.](image-url)
2.2 Contamination factor
Contamination factor has been widely used to evaluate the degree of contamination by each element in the sediments (Hakanson, 1980; Chakraborty et al., 2014). It is calculated using the equation \( \text{Cf}_i = \frac{C_i}{C_n} \). Where \( C_i \) and \( C_n \) are the concentrations of the trace elements in the sediment and geochemical background value of the element respectively.

2.3 Pollution load index (PLI)
The Pollution Load Index (PLI) is used to estimate degree of contamination and pollution in coastal and estuarine sediments (Tomlinson et al., 1980). The classification of the sediments of the study locations is based on PLI values. It has been calculated using the following equation: \( \text{PLI} = (\text{CF}_{1} \times \text{CF}_{2} \times \text{CF}_{3} \times \ldots \ldots \text{CF}_{n})^{\frac{1}{n}} \). The Pollution Load Index (PLI) is obtained as Contamination Factors (CF). This CF is the quotient obtained by dividing the concentration of each metals.

2.4 Geoaccumulation index (Igeo)
The Igeo is measured to quantify the degree of contamination in sediments according to seven enrichment classes (Müller, 1969; Forstner and Stoffers, 1990). It has been calculated using \( \text{I}_{\text{geo}} = \log_2 \left( \frac{C_n}{K \times B_n} \right) \), where \( C_n \) and \( B_n \) are the concentration of the trace elements in the sediment and geochemical background of that element. Classification of the sediments of the study sites is based on the Igeo value (Müller, 1979).

2.5 Statistical analysis
Statistical analyses using Pearson correlation matrix (Zhang, 2018; Zhang and Li, 2015) was done to reveal the relationship between metals. Hierarchical cluster analysis was also done using the five sampling sites for better explanation and to comprehend the sampling stations with respect to analyzed heavy metal concentrations.

3 Results and Discussion
Three major heavy metals were found in five sediment samples collected from five communities in Ogoniland. The concentrations of the heavy metals obtained for the samples generally exceeded maximum allowed limits as shown in (Table 1a). NWIKARA-AGU site had the highest concentration of all metals assayed for. From these results, we can say categorically that NWIKARA-AGU sampling site contained high concentrations of Cobolt (0.59 mg/kg), Arsenic (1.99 mg/kg) and Barium (166 mg/kg) as against the maximum allowed limit approved by Nigerian Industrial Standard (NIS)/Standard Organization Of Nigeria (SON, 2007). These metals are associated with petroleum contamination of which Ogoniland is known to be contaminated with petroleum hydrocarbon. The presence of these metals in aquatic environment ensures a selective pressure such that only tolerant fauna and flora can survive in such environment thereby eliminating sensitive ones. The sediments are in contact with petroleum seepage as these areas are prone to petroleum explorations. Heavy metal pollution in the five communities sampled could be attributed to anthropogenic heavy metals enrichment of the oil-rich industrialized state, as well as oil exploration. There are previous reports of elevation of heavy metals as a result of oil development activities in the Niger Delta (Iwubgue et al., 2006; Howard et al., 2006) and there are evidences of heavy metal bioaccumulation (James et al., 2003; Davies et al., 2006; Obire et al., 2003; Ohimain et al., 2004; Chindah et al., 2004).
Table 1a Heavy metal concentrations and pH at various sites.

<table>
<thead>
<tr>
<th>Community/LGA</th>
<th>Cobalt (mg/kg)</th>
<th>Arsenic (mg/kg)</th>
<th>Barium (mg/kg)</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>AKPAJO, ELEME</td>
<td>0.92</td>
<td>0.3</td>
<td>9.8</td>
<td>5.72</td>
</tr>
<tr>
<td>OKULUEBO, ELEME</td>
<td>2.12</td>
<td>1.54</td>
<td>21.9</td>
<td>6.34</td>
</tr>
<tr>
<td>KPITE, TAI</td>
<td>0.72</td>
<td>1.07</td>
<td>13</td>
<td>6.2</td>
</tr>
<tr>
<td>NWIKARA-AGU</td>
<td>0.59</td>
<td>1.99</td>
<td>166</td>
<td>5.12</td>
</tr>
<tr>
<td>GBE, GOKANA</td>
<td>0.21</td>
<td>0.3</td>
<td>1.25</td>
<td>5.26</td>
</tr>
</tbody>
</table>

Table 1b Background knowledge of metals.

<table>
<thead>
<tr>
<th>Elements</th>
<th>Conc. (mg/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Arsenic (As)</td>
<td>0.01</td>
</tr>
<tr>
<td>Barium (Ba)</td>
<td>0.7</td>
</tr>
<tr>
<td>Cobolt (Co)</td>
<td>0.15</td>
</tr>
</tbody>
</table>

Barium was the prominent element amongst other elements and NWIKARA-AGU site had the highest concentration of Ba, it ranged from (1.25 mg/kg to 166mg/kg). From best of our knowledge, this is the first time Barium was detected in sediment in Niger Delta region of Nigeria. In exploration oil from the ground, exploration industries use barium sulphate to increase the density of the fluid used in drilling operations. During the drilling process, the cuttings which come up with the drilling fluid are separated and are disposed off in a pit next to the wellhead. These pits were unlined and, on close observation, it is not uncommon to find a range of contaminants in them, including barium. Based on the results, a risk reduction strategy that involves local containment, or excavation and transport should be carried out on the sites.

Table 2 Contamination factor (CF).

<table>
<thead>
<tr>
<th>Community/LGA</th>
<th>Cobalt (mg/kg)</th>
<th>Arsenic (mg/kg)</th>
<th>Barium (mg/kg)</th>
<th>Contamination factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>AKPAJO, ELEME</td>
<td>6.12</td>
<td>30</td>
<td>14</td>
<td></td>
</tr>
<tr>
<td>OKULUEBO, ELEME</td>
<td>14.13</td>
<td>154</td>
<td>31.29</td>
<td></td>
</tr>
<tr>
<td>KPITE, TAI</td>
<td>4.80</td>
<td>107</td>
<td>18.57</td>
<td></td>
</tr>
<tr>
<td>NWIKARA-AGU, KHANA</td>
<td>3.93</td>
<td>199</td>
<td>237.1</td>
<td></td>
</tr>
<tr>
<td>GBE, GOKANA</td>
<td>1.40</td>
<td>30</td>
<td>1.79</td>
<td></td>
</tr>
</tbody>
</table>

The concentration of sediment contamination was observed by contamination factor (CF) proposed by Hakanson (1980) to express the level of contamination by each metal in sediment. CF<1 refers to low contamination, 1≥CF≥3 means moderate contamination, 3≥CF≥6 means considerable contamination, and CF>6 which means a very high contamination. Table 2 shows the contamination factor of all elements assayed. At site GBE Co and Ba showed moderate contamination CF>1. Co shows considerable contamination (3≥CF≥6) at locations NWIKARA-AGU, KPITE and AKPAJO but showed very high contamination at location OKULUEBO. Arsenic and Barium showed very high contamination (CF>6) at locations AKPAJO, OKULUEBO, KPITE and NWIKARA-AGU. These metals are mainly derived from lecheates from petroleum.
Table 3 Pollution Load Index (PLI).

<table>
<thead>
<tr>
<th>Community/LGA</th>
<th>Cobalt (mg/kg)</th>
<th>Arsenic (mg/kg)</th>
<th>Barium (mg/kg)</th>
<th>PLI</th>
</tr>
</thead>
<tbody>
<tr>
<td>AKPAJO, ELEME</td>
<td>6.12</td>
<td>30</td>
<td>14</td>
<td>13.7</td>
</tr>
<tr>
<td>OKULUEBO, ELEME</td>
<td>14.13</td>
<td>154</td>
<td>31.29</td>
<td>40.8</td>
</tr>
<tr>
<td>KPITE, TAI</td>
<td>4.80</td>
<td>107</td>
<td>18.57</td>
<td>21.2</td>
</tr>
<tr>
<td>NWIKARA-AGU, KHANA</td>
<td>3.93</td>
<td>199</td>
<td>237.1</td>
<td>57.0</td>
</tr>
<tr>
<td>GBE, GOKANA</td>
<td>1.40</td>
<td>30</td>
<td>1.79</td>
<td>4.2</td>
</tr>
</tbody>
</table>

Pollution Load Index (PLI) proposed is a summative indication for the overall level of heavy metal pollution in sediments has been widely employed to evaluate the contamination status (Tomlinson et al., 1980; Ray et al., 2006; Badr et al., 2009). As per the PLI classification a PLI score of zero indicates “no pollution”, PLI score of 1 indicates “baseline levels of Pollutants” and a PLI score more than 1 indicates “deterioration in the sediment quality” (Tomlinson et al., 1980; Chakraborty et al., 2014). Table 3 shows the pollution load index calculated from the five communities, the five sampling sites fall under deterioration in the sediment quality as PLI is more than 1. Heavy metal contamination of these aquatic ecosystems found in Ogoniland as revealed by this research poses a serious health threat and economic survival of the people of Ogoniland. The occupation of Ogoni people are farming and fishing, fish living in polluted waters contain a considerable amount of toxic metals deposited preferably in fish tissues (Jezierska and Witeska, 2006; El-Moselhy et al., 2014; Velusamy et al., 2014; Leung et al., 2014;Baharom and Ishak, 2015).

To know the level of contamination with respect to heavy metals, the values of heavy metals were used to find geoaccumulation index ($I_{geo}$). $I_{geo}$ as defined by Muller (1979) as measure of aquatic sediment quantitatively (Ridgway and Shimmield, 2002). According to $I_{geo}$ classification, extent of pollution can be categorized as: very strongly polluted ($I_{geo} > 5$), strongly to very strongly polluted ($I_{geo}=4–5$), strongly polluted ($I_{geo}=3–4$), moderately to strongly polluted ($I_{geo}=2–3$), moderately polluted ($I_{geo}=1–2$), unpolluted to moderately polluted ($I_{geo}=0–1$) and unpolluted ($I_{geo} < 0$). The results of $I_{geo}$ accumulation index of five different communities in Ogoniland showed that sites OKULUEBO, KPITE and NWIKARA-AGU were very strongly polluted ($I_{geo} > 5$) with As. NWIKARA-AGU site is very strongly polluted ($I_{geo} > 5$) with Ba. Strongly polluted ($I_{geo}=3–4$) with Ba was observed at sites AKPAJO, OKULUEBO and KPITE. Sites AKPAJO and GBE were Strongly polluted ($I_{geo}=3–4$) with As. Site OKULUEBO showed Strongly polluted ($I_{geo}=3–4$) with Co. AKPAJO, KPITE and NWIKARA-AGU were moderately polluted ($I_{geo}=1–2$) with Co. Site GBE were unpolluted ($I_{geo} < 0$) with Co and Ba showing a negative trend as shown in Fig. 2. The level of contamination in these locations is as a result of anthropogenic activities (Martin et al., 2011) such as the use of speed boat which could also leave some levels of heavy metals in the water. Our results are in the same range with the work of Martin et al. (2011). Previous research by Ciji and Nandan (2014), reported the presence of extremely high concentration of metals in water and sediments.
Fig. 2 Igeo pattern of contamination.

Table 4 Pearson correlation matrix for the analyzed metals.

<table>
<thead>
<tr>
<th></th>
<th>Co</th>
<th>As</th>
<th>Ba</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co</td>
<td>Pearson Correlation</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Sig. (1-tailed)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>As</td>
<td>Pearson Correlation</td>
<td>.372</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>Sig. (1-tailed)</td>
<td>.269</td>
<td></td>
</tr>
<tr>
<td>Ba</td>
<td>Pearson Correlation</td>
<td>-.151</td>
<td>.772</td>
</tr>
<tr>
<td></td>
<td>Sig. (1-tailed)</td>
<td>.404</td>
<td>.063</td>
</tr>
</tbody>
</table>

a: listwise N=5.

Fig. 3 Dendrogram showing the cluster of sampling locations.
Multivariate statistical analyses using Pearson correlation matrix revealed that positive relationship exist between As and Ba indicating that these metals travel together in a point source, it also means that as one of the metal is increasing in an ecosystem, the other metal is also increasing. Weak relationship exists between Co and As but there was negative correlation between Co and Ba as shown in Table 4. Salas et al. (2017) reported metal to metal correlation. Hierarchical cluster analysis was done using the five sampling sites for better explanation and to comprehend the sampling stations with respect to analyzed heavy metal concentrations. Using agglomeration schedule statistics, dendrogram plot, centroid clustering and Squared Euclidean distance, a dendrogram was obtained Figure 3. Dendrogram showed two cluster analysis with respect to sampling sites. Cluster 1 includes locations AKPAJO, KPITE, GBE and OKULUEBO. It is observed that low to moderate pollution of metals were observed at these sites. Cluster 2 contains NWIKARAGU site which is an out cluster, this site in this cluster has been influenced by severe anthropogenic activities coupled with oil exploration in this site showing very high pollution of heavy metals studied. Cluster analysis has helped to better classify the sampling sites, according to the observed metal levels.

4 Conclusion
From this study, we have observed that sediments as an indicator to know the loads of heavy metals present in these aquatic environment proved to be loaded with heavy metals, these metals are xenobiotic that is, are not biodegradable by microorganisms, therefore, there is need for bioremediation of these contaminated environment of which the future work of this group would be focusing on.

Acknowledgement
The authors wish to say a big thank you to UNEP for analyzing the heavy metals used for this research; we would not forget to appreciate Professor Fagade O.E. for his tutelage all through the period of the research.

References


Chan HT, Baba S. 2009. Manual on guidelines for rehabilitation of coastal forests damaged by natural hazards in the Asia-Pacific region. ISME & ITTO, Japan

Chikere CB, Christopher CA, Evan MF. 2017. Shift in microbial group during remediation by enhanced natural attenuation (RENA) of a crude oil-impacted soil: a case study of Ikarama Community, Bayelsa, Nigeria. Biotechnology, 7: 152


Erdogmus SF, Korcan SE, Konuk M, Guven K, Mutlu MB. 2015. Aromatic hydrocarbon utilization ability of *Chromohalobacter sp*. Ekologi, 24: 10-16


