Speciation of Some Heavy Metals in Sediments of the Pennington River, Bayelsa State, Nigeria

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Authors’ contributions

This work was carried out in collaboration between all authors. Author LKE designed the study, performed the statistical analysis, wrote the protocol, and wrote the first draft of the manuscript. Author LKE the analyses of the study. Author LKE managed the literature searches. Edited and proved by authors HMJ and SAI. All authors read and approved the final manuscript.

ABSTRACT

The total heavy metal concentrations of some environmentally toxic metals in sediments of the Pennington River System, Bayelsa state, Nigeria was examined. The concentrations of heavy metals in each fraction were determined using a ANALYST 400 Perkin-Elmer AAS. The mean concentrations (mg/kg) for the six metals in dry season sediment samples were: 0.14±0.17(As), 0.39±0.55(Co), 2.43±5.06(Cu), 26.82±22.19(Fe), 0.69±1.10(Pb), and 1.22±1.19(Zn), while the mean metal concentrations (mg/kg) in wet season samples were: 0.11±0.18(As), 0.37±0.6(Co), 2.07±4.35(Cu), 26.65±24.79(Fe), 0.61±1.08(Pb), and 1.11±1.00(Zn) respectively. Speciation study applying the five-stage sequential extraction scheme revealed that As, Co, and Pb in sediment prevails mostly in exchangeable fraction. Cu and Zn were more prevalent in residual fraction, while Fe was found more in residual and Fe/Mn-Oxide fractions. In an attempt to infer anthropogenic input from natural input, comparison with sediment quality guideline (SQGs) and ecotoxicological sense of heavy metal contamination was employed. The concentration of the studied heavy metals in Pennington River System does not pose a threat to the sediment dwelling fauna and anyone who consumes aquatic animals, particularly fish, from the Pennington River. According to SQGs, the studied heavy metals of the Pennington River sediments were under the category of non-polluted.
Keywords: Speciation; Pennington River System; Sediment.

1. INTRODUCTION

Speciation helps in the identifications and quantification of the defined geochemical fractions, forms or phases in which an element exists in the environment \[1,2\]. Speciation in sediment compartment is a significant step to understand the potential environmental risk, distribution, mobility and bioavailability of pollutants. Determining the total content of heavy metals in the sediments may be useful for the characterization of pollution intensity, however, speciation of heavy metals with selective extracting agents gives further information about the fundamental reactions that govern the behaviour of metals in sediment and helps to assess the environmental impact of contaminated soil and sediment \[3,4,5\]. Sequential extraction procedure is used to partition heavy metals in soil and sediments in order to assess the forms of heavy metals in contaminated soils and sediments. It provides information on potential mobility as well as bioavailability and plant uptake of heavy metals \[6,7\]. It also determine the bioavailability of the metal in soil and sediment to other biota within the aquatic ecosystem. Metals dissolved in soil solution, surface and interstitial waters and those adsorbed on the sediment by cation exchange processes are usually readily available to aquatic and benthic organisms as well as to plants. Metals strongly bound to the sediments and complexes with other chemical compounds are of less concern as they most likely unavailable to the biota \[8\]. Sediments contaminated with metals may act as a secondary pollution source for aquatic ecosystem, and study of metal concentration in sediment is useful for the estimation of pollution trends \[5\]. Study on the geochemistry of river sediment in the Pennington River system has not been undertaken by previous workers. The river is under tidal influence and receives effluent from several sources and oil production activities take place off-shore of the environment. In addition, there is uncontrolled domestic sewage disposal; fishing, marine boats are very common of the Pennington River system and anecdotal information suggests that the river receives effluents off-shore where oil production activities take place. This study was carried out to check the speciation of heavy metals (arsenic, cobalt, copper, iron, lead, and zinc) in the surface sediments from Pennington River system, Bayelsa State, Nigeria.

2. MATERIALS AND METHODS

2.1 Study Area

The Pennington River is a natural river geographically located in Bayelsa state, Niger Delta region, Nigeria (Fig. 1). The river lies between the coordinates of latitude 04°01’ North and latitude 05°23’ South and longitude 05°22’ West and 06°45’ East. Pennington River is a distributary and it also flows into the Atlantic Ocean (Bight of Benin).

2.1 Reagents Used and Their Sources

The reagents and chemicals used are of analytical grade. The reagents used are HNO₃ (Riedel-deHaën, Germany), 30% hydrogen peroxide, H₂O₂ and 70% perchloric acid, HClO₄ British Drug House (BDH) Chemicals Ltd, Poole, England. Solutions were prepared using doubly distilled water. All glass wares used (conical flask, measuring cylinder, volumetric flask, and watch glass) were washed with liquid detergent and rinsed thrice followed by oven drying.

2.3 Sampling and Pre-treatment of Sediment Samples

In this study, sediment samples were collected from four stations located along the Pennington River system. Details of these sites are given in Table 1. Sediments were sampled using a bottom grab sampler (Hydro-Bios) and then immediately transferred into plastic bags and refrigerated. In order to get a representative sample for each station, several sub-samples were collected and mixed together. The sediment samples were analyzed for total metal \[9\] and metal speciation \[10\].

2.4 Determination of Metal Speciation in Sediment

For the heavy metal speciation in sediment a five-stage sequential extraction procedure was employed in this study. This sequential extraction was based on the principles of \[10,11\]. This extraction procedure defines the following five metal speciation regular forms: exchangeable, carbonate-bound, Fe/Mn-oxide bound, organic matter/sulfide bound and residual fraction (Table 2).
Table 1. Sites, description of activities and details

<table>
<thead>
<tr>
<th>Sites</th>
<th>Description of activities</th>
<th>Details</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>Fishing, marine boats</td>
<td>Upstream</td>
</tr>
<tr>
<td>B</td>
<td>Fishing, marine boats</td>
<td>Middle reach</td>
</tr>
<tr>
<td>C</td>
<td>Fishing, marine boats</td>
<td>Downstream</td>
</tr>
<tr>
<td>D</td>
<td>Fishing, marine boats</td>
<td>Mouth</td>
</tr>
</tbody>
</table>

Stage 1. Exchangeable fraction: 1g of sediment + 16ml of MgCl₂ at pH = 7 were extracted at room temperature for 1 hour. The mixture of extraction solution and sediment were shaken carefully throughout extraction.

Stage 2. Carbonate bound: Residue of fraction 1 + 16ml of 1M Sodium acetate/acetic acid buffer at pH=5 for 5 hours at room temperature. Continuous shaking was maintained throughout the period.

Stage 3. Fe/Mn-Oxide bound: Residue from fraction 2 + 20 ml of 0.4M NH₂OH·HCl (13.9g NH₂OH·HCl dissolved in 500ml of distilled water) in 25% (v/v) acetic acid at a temperature of 96°C in water bath for 6 hrs.

Stage 4. Organic matter/sulfide bound: Residue from fraction 3 + 3 ml of 0.02M HNO₃ + 5ml of 30% (v/v) hydrogen peroxide, which has been adjusted to pH= 2. Mixture was heated to 85°C in water bath for 2 hours, with occasional shaking and allowed to cool down. Then + 3 ml of 30% H₂O₂ adjusted to pH=2 with HNO₃. Mixture heated again at 85°C for 3 hours with occasional shaking and allowed to cool down. Lastly + 5ml of 3.2M ammonium acetate in 20% (v/v) HNO₃, followed by dilution to a final volume of 20ml with de-ionized water.

Stage 5. Residual or inert fraction: Residue from fraction 4 was oven dried at 105°C. Digestion was carried out with a mixture of 5ml conc. (HNO₃, 70% W/W) + 10 ml of hydrofluoric acid (HF, 40%, W/W) + 10 ml of perchloric acid (HClO₄, 60% w/w in Teflon beaker).

2.5 Instrumentation and Statistical Analysis of Data

In this study, raw data was used in calculating the correlation coefficient using Microsoft Excel 2010. Both descriptive and inferential statistical analyses were used to interpret the data in this study. Pearson correlation analysis was also carried out. The heavy metal concentrations in each fraction were determined by using an ANALYST 400 Perkin-Elmer AAS.

3. RESULTS AND DISCUSSION

The results of the metal speciation in sediment samples in dry season (January, 2011), wet season (September, 2011) of the Pennington River are presented in Table 3. The percentages of the heavy metals in the fractions are represented graphically in Figs. 2-7 for dry and wet season.

Table 2. Summary of sequential Extraction Scheme Used

<table>
<thead>
<tr>
<th>Fraction</th>
<th>Extractant</th>
<th>Time(h)</th>
<th>Temp. °C</th>
<th>Designation</th>
</tr>
</thead>
<tbody>
<tr>
<td>F1</td>
<td>1g of sediment sample +16ml of 1M MgCl₂, pH=7</td>
<td>1</td>
<td>RT</td>
<td>Exchangeable</td>
</tr>
<tr>
<td>F2</td>
<td>16ml of CH₃COONa/CH₃COOH buffer, pH=5</td>
<td>5</td>
<td>RT</td>
<td>Carbonate bound</td>
</tr>
<tr>
<td>F3</td>
<td>20ml of 0.4M NH₂OH. HCl in 25% CH₃COOH</td>
<td>6</td>
<td>96</td>
<td>Fe/Mn-oxide bound</td>
</tr>
<tr>
<td>F4</td>
<td>1.3ml of 0.02M HNO₃+5ml of 30% H₂O₂, pH=2 with HNO₃ 2.3ml of 30% H₂O₂, pH = 2 with HNO₃ 3. 5ml of 3.2M NH₄OAc in 20% HNO₃ followed by dilution to 20ml with de-ionized water</td>
<td>2</td>
<td>85</td>
<td>Organic matter bound</td>
</tr>
<tr>
<td>F5</td>
<td>5ml HNO₃+ 10ml HF +10ml HClO₄</td>
<td>3</td>
<td>85</td>
<td>Residual</td>
</tr>
</tbody>
</table>

*Tessier et al. (1979); **Abu-Kukati, 2001 ***RT = room temperature
3.1 Metal Speciation in Sediments

The data shows that, concentration (mg/kg) of arsenic in sediments ranged from 0.12 - 0.19 with mean value of 0.14±0.17 during the dry season while it ranged from 0.08 - 0.12(0.11±0.18) in wet season. A comparative analysis between arsenic levels in Pennington River and average shale as reported in Table 4 shows that, values of arsenic in this study were low. The result agreed with concentration of arsenic in natural environment [12].

The concentration of cobalt ranged between 0.36 – 0.42 mg/kg with an average of 0.39 ± 0.55 mg/kg during the dryseason while it ranged from 0.36 – 0.39 mg/kg in wet season with an average of 0.37±0.60 mg/kg. The levels were also lower when compared with levels in natural environment [12].

Concentration (range, mean ± standard deviation, mg/kg) for copper was 0.56 - 6.15, (2.43±5.06) in dry season and 0.92-3.74, (2.07±4.35). The levels were also low when compared to levels in natural environment [12].

The values (mg/kg) for iron (range, mean ± std) in dry and wet seasons were (14.60 45.08, 26.82 ±22.19) and (15.40-32.39, 26.65±24.79) respectively. The levels of iron were lower when compared to levels in natural environment [12].

The concentration of Pb ranged from 0.57 – 0.87 mg/kg with a mean (0.69±1.10) mg/kg during the dry season while it ranged from 0.51–0.72 mg/kg in wet season with a mean of 0.61±1.08 mg/kg. The levels were also low when compared to levels in natural environment [12].

Table 3. Seasonal variation of total mean concentrations (mg/kg) in sediment of Pennington River

<table>
<thead>
<tr>
<th>Metals</th>
<th>Range</th>
<th>Mean±std</th>
<th>Range</th>
<th>Mean±std</th>
</tr>
</thead>
<tbody>
<tr>
<td>As</td>
<td>0.12-0.19</td>
<td>0.14±0.17</td>
<td>0.08-0.12</td>
<td>0.11±0.18</td>
</tr>
<tr>
<td>Co</td>
<td>0.36-0.42</td>
<td>0.39±0.35</td>
<td>0.36-0.39</td>
<td>0.37±0.60</td>
</tr>
<tr>
<td>Cu</td>
<td>0.56-6.15</td>
<td>2.43±5.06</td>
<td>0.92-3.74</td>
<td>2.07±4.35</td>
</tr>
<tr>
<td>Fe</td>
<td>14.60-45.08</td>
<td>26.82±22.19</td>
<td>15.40-32.39</td>
<td>26.65±24.79</td>
</tr>
<tr>
<td>Pb</td>
<td>0.57-0.87</td>
<td>0.69±1.10</td>
<td>0.51-0.72</td>
<td>0.61±1.08</td>
</tr>
<tr>
<td>Zn</td>
<td>1.15-1.28</td>
<td>1.22±1.19</td>
<td>0.88-1.32</td>
<td>1.11±1.00</td>
</tr>
</tbody>
</table>

Fig. 1. Map of study area showing sampling sites
Zinc levels in Pennington River sediment samples were 1.15-1.28, (1.22±1.19) mg/kg in dry season and 0.88–1.32, (1.11±1.00) mg/kg for wet season. The result obtained in this study for zinc concentrations agreed with those reported by [13,14] from Diobu River in Port Harcourt, which are of the same geographical Niger Delta region with similar sources of contaminant input.

3.2 Statistical Evaluation of Data

To find an internal structure not accessible at first glance of the results in Table 3, statistical multivariate methods were used to study the data by considering the sediments as objects and the determined parameters as variables, by building a Pearson's correlation matrix (PCM) and the data presented in Table 5. The PCM analysis provided a means of statistically ascertaining the association/correlation of one parameter with another. PCM analysis reveals a positive correlation between the metal ions in both seasons; this could indicate a common source for all the metals, however, very few of the metals are significantly correlated with each other. This behavior could indicate non-point source.

The six heavy metals investigated in sediment samples of the Pennington River system in Bayelsa state, Nigeria was investigated in both dry and wet seasons and results are presented in (Figs. 2-7) as percent fraction of metal species in the five geochemical phases.

Speciation patterns for arsenic in dry and wet seasons are shown in Fig. 2. The results indicate an occurrence of the highest arsenic percentage in exchangeable and carbonate fractions in both dry season and wet seasons. The least percent of arsenic appeared in the Fe/Mn-Oxide and residual fractions. This is an indication that arsenic was biologically available in the river being investigated.

Speciation pattern of cobalt in both seasons is presented in Fig. 3. The figure shows that cobalt had highest accumulation in exchangeable fraction in both dry and wet seasons. It was however low in all the other immobilized fractions. This is an indication that cobalt was biologically available in the river being investigated.

Speciation pattern of copper in both seasons is presented in Fig. 4. The figure shows that copper had highest accumulation in residual fraction in both dry and wet seasons. It was however low in all the other easily mobilized fractions. This shows that there is little or no danger of copper bioavailability in the study area.

Fig. 5 shows the speciation pattern of Fe. The lowest value of iron in the fractions was obtained in exchangeable fraction. The other geochemical fractions that contain low percent of iron are carbonate and organic respectively. The highest value was obtained in the residual fraction in both seasons. This shows that iron cannot be remobilized in the study area.

Table 4. Comparison of heavy metal concentration with some river

<table>
<thead>
<tr>
<th>Rivers</th>
<th>As</th>
<th>Co</th>
<th>Cu</th>
<th>Fe</th>
<th>Pb</th>
<th>Zn</th>
</tr>
</thead>
<tbody>
<tr>
<td>Genesse, USA</td>
<td>18</td>
<td>40</td>
<td>47</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Toyohira, Japan</td>
<td>22</td>
<td>24</td>
<td>152</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Lagos Lagoon</td>
<td>0.60</td>
<td>19.39</td>
<td>0.45</td>
<td>0.73</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Average Shale</td>
<td>13</td>
<td>19</td>
<td>45</td>
<td>4.10</td>
<td>20</td>
<td>95</td>
</tr>
<tr>
<td>This study</td>
<td>0.13</td>
<td>0.38</td>
<td>2.25</td>
<td>26.74</td>
<td>0.65</td>
<td>1.27</td>
</tr>
</tbody>
</table>

Table 5. Correlation coefficient matrix of mean heavy metal concentrations in dry and wet seasons of Pennington River

<table>
<thead>
<tr>
<th></th>
<th>Dry Season</th>
<th></th>
<th>Wet Season</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>As</td>
<td>Co</td>
<td>Cu</td>
</tr>
<tr>
<td>As</td>
<td>1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Co</td>
<td>3.20</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>Cu</td>
<td>0.37</td>
<td>0.90</td>
<td></td>
</tr>
<tr>
<td>Fe</td>
<td>0.19</td>
<td>0.87</td>
<td>0.82</td>
</tr>
<tr>
<td>Pb</td>
<td>0.45</td>
<td>0.88</td>
<td>0.92</td>
</tr>
<tr>
<td>Zn</td>
<td>0.28</td>
<td>0.16</td>
<td>0.48</td>
</tr>
<tr>
<td>As</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Co</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cu</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pb</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Zn</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

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In Fig. 6, lead accumulated most in the exchangeable fraction in both seasons followed by the other fractions. This is an indication that lead was biologically available in the river being investigated. In Fig. 7, zinc accumulated most in the residual fraction in both seasons followed by the other fractions. This means that zinc will not be released easily to the water layers and so will be less bio-available to the organisms in the study area.

Assessment of sediment pollution based on SQGs and ecotoxicological sense of heavy metal contamination. Sediments were classified as non-polluted, moderately polluted and heavily polluted based on SQGs of USEPA [15]. According to SQGs, the heavy metals studied in sediments of the Pennington River were under the category of non-polluted in both dry and wet seasons [16,15]. The ecotoxicological sense of heavy metal contamination in sediments was determined using sediment quality guidelines developed for marine and estuarine ecosystem [17,18,19,20]. These effects are as follow: a) The effect range low (ERL) / effect range median (ERM) b) The threshold effect level (TEL) / probable effect level (PEL). The heavy metals studied in sediments of the Pennington River do not exceed TEL values which can lead to adverse impact on the sediments dwelling fauna (Table 6). The guideline thereby proving that the Pennington River is uncontaminated with (As, Co, Cu, Fe, Pb and Zn).

Table 6. Concentration of heavy metals in Pennington River and its comparison with SQDs

<table>
<thead>
<tr>
<th>Element</th>
<th>SQGs non-polluted(mg/kg)</th>
<th>SQGs moderately polluted(mg/kg)</th>
<th>SQGs heavily polluted(mg/kg)</th>
<th>TEL(mg/kg)</th>
<th>This study(mg/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>As</td>
<td>5.9</td>
<td>0.13</td>
<td></td>
<td></td>
<td>1.17</td>
</tr>
<tr>
<td>Co</td>
<td>0.38</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cu</td>
<td>&lt;25</td>
<td>25-50</td>
<td>&gt;50</td>
<td>18.70</td>
<td>2.25</td>
</tr>
<tr>
<td>Fe</td>
<td>&lt;40</td>
<td>40.60</td>
<td>&gt;60</td>
<td>30.20</td>
<td>0.65</td>
</tr>
<tr>
<td>Pb</td>
<td>&lt;40</td>
<td>40.60</td>
<td>&gt;60</td>
<td>30.20</td>
<td>0.65</td>
</tr>
<tr>
<td>Zn</td>
<td>&lt;90</td>
<td>90-200</td>
<td>&gt;90</td>
<td>124.00</td>
<td>1.17</td>
</tr>
</tbody>
</table>

Fig. 2. Dry and wet seasons speciation pattern of arsenic
Fig. 3. Dry and wet seasons speciation pattern of cobalt

Fig. 4. Dry and wet seasons speciation pattern of copper

Fig. 5. Dry and wet seasons speciation pattern of iron
4. CONCLUSION

Speciation is a powerful and versatile technique for predicting the degree of contamination risk of a river system. In this present study, all heavy metals investigated are relatively stable under normal conditions of Pennington River system. This means that there is a low source of pollution arriving to the Pennington River system. Iron was found to be the highest occurring heavy metal and arsenic was the least occurring heavy metal in this study. Furthermore, there is no heavy metal pollution threat pose to sediments dwelling fauna and anyone who consume aquatic animals, particularly fish from the Pennington River system. To preserve the unpolluted state of the Pennington River system it remains important that allochthonous inputs are devoid of heavy metals.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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