Speciation of Heavy Metals in Sediment of Agbabu Bitumen deposit area, Nigeria

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ABSTRACT: Speciation of heavy metals Cu, Cd, Pb, Ni, Zn, Mn, Fe, Cr and Hg was carried out on sediment of Agbabu with a sequential extraction procedure in the dry and rainy seasons of year 2008. Hg was not detected in all the fractions in the two seasons. In the dry season, all the metals were mostly abundant in Fraction-5; however, Cr (30%) and Mn (23.73%) had high abundance in Fraction-1, Zn (30.97%) was high in Fraction-III, Cu (45.14%) and Fe (31.67%) were also high in Fraction-4. In the rainy season, Cr (35.82%) was mostly abundant in Fraction-1, Zn (36.71%) was high in Fraction-5, Cu (29.28%) was high in Fraction-4 and the remaining metals were mostly abundant in Fraction-V. From the results of the two seasons, the metals had high abundance in Fraction-5 indicating firstly, low mobility and bioavailability, secondly, low degree of pollution by the metals considered and thirdly, the origin of the metals in the environment was likely to be lithogenic. The average potential mobility was calculated for the metals in the two seasons and the following decreasing order was obtained: Cr>Zn>Cu>Mn>Fe>Cd>Ni>Pb>Hg.

Bitumen was first discovered in Nigeria in 1910. The first bitumen well NBC-7 was drilled at Agbabu in Ondo State in the South Western part of Nigeria. Heavy metals are present everywhere in the environment (Adekola, 2002). Today it is generally recognized that the particular behavior of trace metals in the environment is determined by their specific physicochemical forms rather than by their total concentration. Speciation of metals largely determines their bioavailability and toxicity (Tack and Verloo, 1995). Speciation can be defined as identification and quantification of the different species or forms of phases in which elements occur. It is generally recognized that information about the physicochemical forms of the elements is required for understanding their mobility, pathways and bioavailability. Studies on the distribution and speciation of heavy metals in sediments can provide not only information on the degree of pollution, but specially the actual environmental impact, metal bioavailability as well as their origin (Ramirez, 2005).

Heavy metal speciation in sediment impacted with crude oil in the Niger-Delta region of Nigeria has been reported (Iwegbue et al., 2006). It was found that Cd, Pb, Zn, and Ni have high mobility indices. Cd was associated with easily Exchangeable/Adsorbed and Carbonate fractions, Cu and Cr predominantly occur in Organic and Residual fractions. Zn was associated with Carbonate and Fe-Mn oxide fractions (Iwegbue et al., 2006). Olajire et al. (2003) studied the levels and speciation of five heavy metals in soils of industrial Southern Nigeria and found that the highest amount of Cd was found in the Exchangeable fraction and Cu and Zn were significantly associated with the Organic fraction. Some studies have been carried out on the Nigerian bitumen and Agbabu Bitumen deposit such as multi-elemental analysis (Adebiyi et al., 2006), environmental impact assessment of bitumen exploitation on animal resources of Ode – Irele (Lameed and Ogunusi, 2002), compositional analysis of the oil component of the Nigerian bitumen (Oderinde and Olanipekun, 1991), Distribution of Polycyclic Aromatic hydrocarbons in soils and water from the vicinity of Agbabu bitumen field (Olajire et al., 2007), and solvent extraction of vanadium from Nigerian bitumen (Oguntimehin and Ipinmoroti, 2007). The need for this research arose because no study has been reported on the speciation of metals in sediment of Agbabu bitumen deposit environment.

MATERIALS & METHODS
Samples were collected from four sediment locations in the dry season and two sediment locations in the rainy season. Sampling points were geo-located with Geographical Position System (GPS) to ensure consistency. Samples were collected in polythene bags. Dirt and other unwanted substances were removed from the samples and oven dried at 105°C before sieving. All reagents used were of analytical grade. The sequential extraction scheme was followed (Tessier et al., 1979; Abu-Kukati, 2001). Five fractions of the sample solutions were prepared in assessing the effect of changing environment conditions.

Fraction I – Exchangeable fraction: Samples (1g) of sediment were extracted at room temperature for 1hour with 16ml of MgCl₂ solution (1M MgCl₂) at pH 7. Sediment and extraction solution were thoroughly agitated throughout the extraction. This is mainly an adsorption – desorption process. Metals extracted in the exchangeable fraction include weakly
adsorbed metals and can be released by ion-exchange process. Changes in the ionic composition of the water would strongly influence the ionic exchange process of metal ions with the major constituents of the samples like clays, hydrated oxides of iron and manganese (Abu-Kukati, 2001). The extracted metals were then decanted from the residual sediment.

Fraction II – Bound to carbonates: The metals bound to carbonate phase are affected by ion exchange and changes of pH. The residue of Fraction 1 was extracted with 16ml of 1M sodium acetate/acetic acid buffer at pH 5 for 5 hours at room temperature. Significant amount of trace metals can be co-precipitated with carbonates at the appropriate pH. The extracted metal solution was decanted from the residual sediment. The residual sediment was used for the next extraction.

Fraction III – Bound to iron and manganese oxides: The residue from fraction 2 was extracted under mild reducing conditions. 13.9g of hydroxyl amine hydrochloride (NH₂OH.HCl) was dissolved in 500ml of distilled water to prepare 0.4M NH₂OH.HCl. The residue was extracted with 20ml of 0.4M NH₂OH.HCl in 25% (v/v) acetic acid with agitation at 96°C in a water bath for 6hours. Iron and manganese oxides which can be present between particles or coatings on particles are excellent substrates for absorbing trace metals. Under reducing conditions, Fe (III) and Mn (IV) could release adsorbed trace metals. The extracted metal solution was decanted from the residual sediment which was used for the next extraction.

Fraction IV – Bound to organic matter and sulphide: The residue from fraction 3 was oxidized as follows: 3ml of 0.02M HNO₃ and 5ml of 30% (v/v) hydrogen peroxide, which has been adjusted to pH2, were added to the residue from fraction 3. The mixture was heated to 85°C in a water bath for 2hours with occasional agitation and allowed to cool down. Another 3ml of 30% hydrogen peroxide, adjusted to pH2 with HNO₃, was then added. The mixture was heated again at 85°C for 3hrs with occasional agitation and allowed to cool down. Then 5ml of 3.2M ammonium acetate in 20% (v/v) HNO₃ was added, followed by dilution to a final volume of 20ml with de-ionized water. Trace metals may be bound by various forms of organic matter, living organisms and coating on mineral particles through complexation or bioaccumulation. These substances may be degraded by oxidation leading to a release of soluble metals. The extracted metal solution was decanted from the residual sediment which was used for the next extraction.

Fraction V – 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 (HNO₃, 70% w/w), 10ml of hydrofluoric acid (HF, 40% w/w) and 10ml of perchloric acid (HClO₄, 60%w/w) in Teflon beakers. Fraction 5 largely consists of mineral compounds where metals are firmly bonded within crystal structure of the minerals comprising the sediment.

Analysis was carried out with AAS using GBC Avanta PM. Ver 2.02. To validate the procedure, the instrument was programmed and it carried out metal detection by displaying three absorbance readings and what was reported was the average. Blanks were also used for correction of background and other sources of error. Apart from calibration before use, quality checks were also performed on the instrument by checking the absorbance after every ten sample runs.

RESULTS AND DISCUSSION

The results of the sequential extraction of the sediment samples in the dry season (March 2008) rainy season (August 2008) are summarized in Table 1. The percentages of metals in the fractions are represented graphically in Figure 1 for dry and rainy seasons.

Table 1: Seasonal variation of heavy metal fractions in the study area. (F = FRACTION; D = dry season; R = rainy season)

<table>
<thead>
<tr>
<th>F</th>
<th>Cu(%)</th>
<th>Cd(%)</th>
<th>Pb(%)</th>
<th>Ni(%)</th>
<th>Zn(%)</th>
<th>Mn(%)</th>
<th>Fe(%)</th>
<th>Cr(%)</th>
<th>Hg(%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>D</td>
<td>R</td>
<td>D</td>
<td>R</td>
<td>D</td>
<td>R</td>
<td>D</td>
<td>R</td>
<td>D</td>
</tr>
<tr>
<td>F1</td>
<td>0.6</td>
<td>0.0</td>
<td>7.2</td>
<td>2.8</td>
<td>0.3</td>
<td>0.0</td>
<td>2.0</td>
<td>2.6</td>
<td>4.6</td>
</tr>
<tr>
<td>F2</td>
<td>0.0</td>
<td>0.0</td>
<td>11.5</td>
<td>13.4</td>
<td>0.0</td>
<td>0.0</td>
<td>2.4</td>
<td>3.4</td>
<td>9.5</td>
</tr>
<tr>
<td>F3</td>
<td>8.9</td>
<td>5.2</td>
<td>12.6</td>
<td>17.9</td>
<td>3.5</td>
<td>1.5</td>
<td>8.6</td>
<td>9.6</td>
<td>31.0</td>
</tr>
<tr>
<td>F4</td>
<td>45.1</td>
<td>29.3</td>
<td>4.0</td>
<td>4.0</td>
<td>2.9</td>
<td>2.6</td>
<td>5.6</td>
<td>3.5</td>
<td>10.5</td>
</tr>
<tr>
<td>F5</td>
<td>45.4</td>
<td>65.6</td>
<td>64.7</td>
<td>61.9</td>
<td>93.3</td>
<td>95.9</td>
<td>81.3</td>
<td>81.0</td>
<td>44.5</td>
</tr>
</tbody>
</table>

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In the dry season, all the heavy metals were mostly abundant in the Residual or Inert fraction as follows: Cu (45.14%), Cd (64.66%), Pb (93.26%), Ni (81.28%), Zn (44.46%), Mn (42.55%), Fe (48.25%) and Cr (37.85%). However, Cr (30.97%) and Mn (23.73%) were also very abundant in the Exchangeable fraction. Zn (30.97%) was also high in the fraction Bound to Iron and Manganese; Cu (45.14%) and Fe (31.67%) were high in the fraction Bound to Organic matter and sulphides. These indicate that Mn, Cr, Zn, Cu and Fe had higher bioavailability in sediment than other metals such as Cd, Pb, Ni which were mainly available in the Residual or Inert fraction in the dry season. In the rainy season, Cr was mostly abundant in the Exchangeable fraction (35.82%) while the remaining metals were mostly abundant in the Residual or Inert fraction as follows: Cu (65.57%), Cd (61.86%), Pb (95.89%), Ni (80.96%), Zn (41.21%), Mn (69.11%) and Fe (67.53%). Zn (36.71%) was also found to have high abundance in the fraction Bound to Iron and Manganese oxides and Cu (29.28%) in the fraction Bound to organic matter and sulphides in the rainy season. This shows that Cr was more available and mobile, followed by Zn and Cu in the rainy season. Generally, from the results of the two seasons, the metals were mostly abundant in the Residual or Inert fraction implying low mobility and bioavailability. It also indicates probably a low degree of pollution by the metals considered.

The sum of different phases of metals can be used to express the potential mobility of metals. The potential mobility of a metal can be assessed by adding up the results of the Exchangeable phase, Carbonate phase, Fe-Mn oxide phase and organic phase of that metal (Haung et al 2007). The potential mobility of Cr in sediment in the dry season was 62.15% while it increased to 68.48% in the rainy season. The percentage reduction in concentration from March to August in sediment was 14.28%. The high potential mobility of Cr in the environment was confirmed with the percentage reduction in concentration of Cr between March and August. In sediment samples, Zn had very high abundance in the fraction Bound to Iron and Manganese oxides. The abundance was 30.97% in the dry season and 36.71% in the rainy season. This is in agreement with Zerbe et al, 1999. This accounts for high percentage potential mobility of Zn in the dry season (55.54%) and rainy season (58.79%). The percentage reduction in concentration between March and August was 14.26%.

Copper can easily complex with organic matters because of the high formation of organic-Cu compounds (Haung et al 2007). The result of sequential extraction shows that in the sediment samples, Cu in the fraction Bound to Organic matter and Sulphides was very high in the dry season (45.14%) and rainy season (29.28%). Heavy metals Bound to Organic matter and Sulphides are more available than the heavy metals in the residue fraction. Therefore, the potential mobility of Cu in sediment in the dry season was 54.64% and 34.43% in the rainy season. The percentage reduction in concentration in sediment samples between March and August is 58.07% (Table 1). The remaining heavy metals studied in sediment samples (Cd, Pb, Ni, Mn, and Fe) are mostly abundant in the Residual fraction. This agrees with Ramirez et al. (2005) who reported that Cd, Fe, Mn, Ni and Pb were mostly associated with the residual phase. Metals present in the residual fraction are a measure of the degree of environmental pollution. The higher the metals present in this fraction, the lower the degree of pollution (Banat, 2001).

Metals with anthropogenic origin are mainly extracted in the first step of sequential extraction procedures while lithogenic metals are found in the
Metal chemical speciation carried out by sequential extraction of the metals is essential to the metal mobility (Tessier et al., 1979). The order of mobility of the metals considering their abundance in the fractions is: Exchangeable > Bound to carbonate > Bound to iron and Mn oxides > Bound to organic matter and sulphide > Residual (Tesser et al. 1979). Iron and Manganese oxides exist as nodules and cement between particles. These oxides hold trace metals and can be mobilized under reducing and acidic conditions. The organic phase is relatively stable in nature but can be mobilized under strong oxidizing conditions due to degradation of organic matter (Tessier et al., 1979; Haung et al., 2007). From the result of the sequential extraction in all the sediment samples studied, Cr was highly abundant in the samples fraction Exchangeable. The average potential mobility sediment for the two seasons was 65.31%. This shows that Cr was highly mobile and available in the environment and highly toxic. Zn was highly abundant bound to Fe and Mn oxides and the average potential mobility of Zn in the two seasons was 57.16% in sediment. Under reducing and acidic conditions, Zn could easily be mobilized to the environment. Therefore compared with other metals that are mostly abundant in the residue fraction Zn was more available and toxic in the environment. The abundance of Cu in the fraction Bound to organic matter and sulphides in sediment in the dry season was 41.14% while it was 29.28% in the same fraction in the rainy season, thereby making it more mobile than the metals that were mostly abundant in the residual fraction. The average potential mobility of Cu was 44.54% in sediment. Under strong oxidizing conditions, due to degradation of organic matter, Cu becomes very available and toxic in the environment. The remaining metals Cd, Pb, Ni, Mn and Fe were mostly abundant in the residual fraction which shows they were less available and immobile compared with other metals in the environment. More metals are present in this fraction than in the other fractions which showed that the degree of pollution in the environment was low.

Conclusion: Hg was not detected in all the samples tested. The order of average potential mobility of Zn and Cu in sediment samples agrees with the percentage reduction in concentration. However value of the percentage reduction in concentration for Ni in sediment was negative. This shows that the actual behavior of Ni may be controlled not only by its speciation, changes in pH and salinity, but also by unknown factors (Haung et al., 2007). The speciation of heavy metals in Agbabu bitumen deposit area showed that most of the metals considered had the highest abundance in the residual fraction. This indicates that the metals were immobile. Nine metals were considered immobile. Nine metals were considered Hg was not detected at all in all the samples, Cd, Pb, Ni, Mn and Fe were found mostly abundant in the residual fraction of the sequential extraction. This shows that the environment is not likely to be polluted by these metals. Cr was found to be highly abundant in the exchangeable fraction, indicating that it could be easily released to the environment and be of high toxicity in the environment. The average potential mobility of the metals can be arranged in decreasing order for sediment as follows: Cr>Zn>Cu>Mn>Fe>Cd>Ni>Pb>Hg .The average potential mobility of Zn and Cu in sediment samples studied were quite high implying that under favourable conditions they can be released to pollute the environment. The results of the speciation have given the present status of metal pollution and the potential pollutants in Agbabu bitumen area. Research can be carried out further on the speciation of heavy metals in surface water and ground water in the vicinity.

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