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# SPECIATION OF HEAVY METALS IN INTER-TIDAL SEDIMENTS OF THE OKRIKA RIVER SYSTEM, RIVERS STATE, NIGERIA

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**ABSTRACT.** The species and total metal concentrations of some environmentally toxic metals in inter-tidal sediments of the Okrika river system was examined. The determination of the heavy metal loadings, speciation patterns and other chemical parameters has revealed some significant correlation in inter-tidal sediments taken from the Okrika river system as it passes through Okrika. The metal concentrations (mean ± RSD in $\mu g\ g^{-1}$ dry weight) were: Pb, 18.74 ± 0.08; Ni, 46.51 ± 0.70; Cd, 1.05 ± 0.78; Co, 11.41 ± 0.87; Zn, 245.49 ± 0.51; Cu, 66.70 ± 0.49. Chemical variables related to the retention of heavy metals by sediments were also measured and their average levels are % $H_2O$ (52.34), % organic matter (3.93), % $CaCO_3$ (14.67), and % organic nitrogen (0.98). The speciation results revealed a higher environmental risk for cadmium and lead and a lesser degree for zinc due to their higher percentages in the more easily remobilize fractions.

## INTRODUCTION

Speciation is the determination of the species or the physico-chemical forms of an element which together comprise its total concentration in a given sample. Legislation governing the maximum permissible levels of a polluting element in an environmental sample such as river water, biota, sediment or soil refers to total concentration rather than the chemical form of that element. However, this total concentration provides no information concerning the fate of the elements in terms of its interaction with sediments, its ability to cross biological membranes (bioavailability) or its resultant toxicity.

Heavy metals today have a great ecological significance due to their toxicity and accumulative behaviour [1].These elements are not biodegradable and undergo a global eco-biological cycle [2] in which natural waters are the main pathways.

The sediments existing at the bottom of the water column play a major role in the pollution scheme of the river systems by heavy metals [3]. They reflect the current quality of the water system and can be used to detect the presence of contaminants that do not remain soluble after discharge into surface waters. Moreover, sediments act as carriers and possible sources of pollution because heavy metals are not permanently fixed by them and can be released back to the water column by changes in environmental conditions such as pH, redox potential or the presence of organic chelators [3]. Therefore, the analysis of heavy metals in sediments permits us to detect pollution that could escape water analysis, and also provides information about the critical sites of the water system under consideration [4].

The major mechanisms of accumulation of heavy metals in sediments [5] lead to the existence of five categories [6]: (1) adsorptive and exchangeable, (2) bound to carbonate phases,(3) bound to reducible phases (iron and manganese oxides), (4) bound to organic matter and sulphides and (5) detrital or lattice metals. These categories have different behaviours with respect to mobilization under changing environmental conditions [7]. A knowledge of the total content of heavy metals in a sediment does not give a complete picture of the environmental situation, thus it is necessary to determine the species of heavy metals in the sediment to evaluate the eco-toxic potential of the system. Furthermore, there is no literature on heavy metal speciation studies of any of the known river systems in the Niger Delta area of Nigeria.

The aim of this research was therefore to study the heavy metals distribution and ascertain their contamination risk by speciation study in the Okrika River System.

## EXPERIMENTAL

*Study Area.* The Okrika river system is one of the main tributaries of the Bonny river and flows through the town of Okrika (Figure 1). The river is under tidal influence and receives effluent from several sources, including the two oil refineries at Eleme, two fertilizer plants at Onne, a petrochemical industry and several oil and oil related companies, dredging and sand filling for coastal development and uncontrolled domestic sewage and industrial waste water discharges and barge ballasting. In addition, intensive human activities are very well common on the banks of the river.

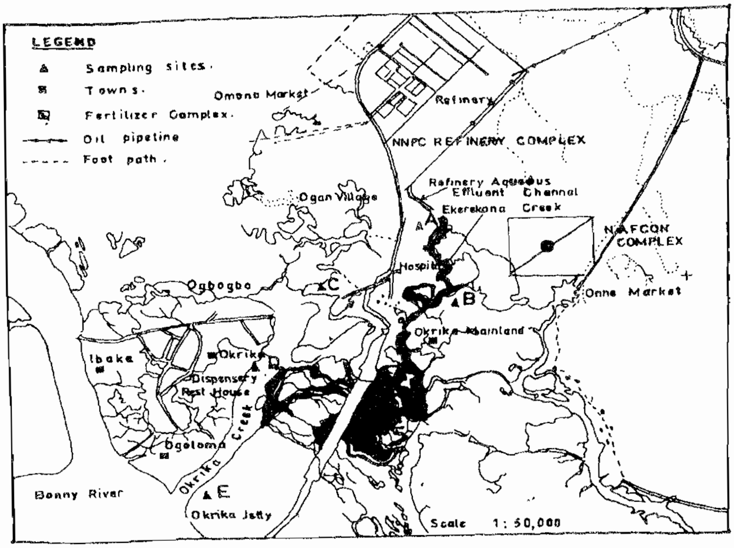

Figure 1. The study area indicating the sampling sites.

Inter-tidal flat sediments were collected during low tide in November 1997 from six representative sites chosen to provide coverage of the different pollution possibilities.

*Analysis of the sediments for chemical variables.* Two replicate of each sample was analyzed for known chemical variables related to the retention of heavy metals by the sediments: water content (WC), organic matter (OM), carbonate ($CaCO_3$), and organic nitrogen (ON), by using standard methods [8].

*Water content.* A suitable container was heated to dryness, cooled in a desiccator and weighed. 10 g of inter-tidal sediment was thin spread in the container and weighed rapidly, and dried in an air-circulation oven at 105 °C to constant weight for 3 h. The percent WC was calculated as the change in weight after cooling.

*Organic matter.* OM was determined by ashing 0.5 g of sediment in a Gallenkamp Muffle Furnace size 3 at 500 °C for 1 h. The loss in weight of the residue gave the OM in the sample.

*Carbonate.* A 0.5 g finely divided sediment was placed in 25 mL of distilled water. The solution was titrated with 0.01 M HCl using methyl red indicator. The carbonate content was calculated as the $CaCO_3$ total alkalinity.

*Organic nitrogen.* ON was determined by the semi-micro-Kjeldahl method. 0.5 g of sample was digested by the addition of 10 mL digestion reagent (prepared by dissolving 134 g $K_2SO_4$ in 650 mL water and 200 mL conc. $H_2SO_4$, followed by adding with stirring a solution prepared by dissolving 2 g red mercuric oxide, HgO, in 25 mL 3 M $H_2SO_4$. The combined solution was diluted to 1.0 L with distilled water) until the solution becomes clear and further digested for 30 min. The digested sample was quantitatively transferred into the micro-Kjeldahl distillation apparatus. Then 10 mL of hydroxide- thiosulphate reagent (prepared by dissolving 500 g NaOH and 25 g $Na_2S_2O_3.5H_2O$ in water and diluted to 1.0 L ) was added and the solution distilled into a 10 mL 0.02 M $H_2SO_4$ solution. The ON was determined and calculated by the phenate method.

*Heavy metal determination and speciation.* The speciation scheme as reported by Tessier *et al.* [9] was used. A 5.0 g of inter-tidal flat sediments which has been previously dried, homogenized and sieved with 2 mm sieve were extracted sequentially as follows:

*Fraction 1.* The finely divided sediment was extracted with 40 mL of 1.0 M $MgCl_2$ solution at a pH 7.0 using a Stuart Flask Shaker. This fraction gave the adsorptive and exchangeable metals.

*Fraction 2.* The residual from step 1 was then extracted with 40ml of 1.0 M sodium acetate (adjusted to pH 5 with glacial acetic acid) for 5 h using the shaking device. This faction gave the metals bound to carbonates.

*Fraction 3.* The residue from step 2 was leached with 100 mL of 0.04 M $NH_2OH.HCl$ in 25% (v/v) acetic acid for 6 hours and the solution mixed occasionally. This fraction gave metals bound to Fe-Mn oxides.

*Fraction 4.* The residue from step 3 was mixed with 15 mL of 0.02 M $HNO_3$ and 25 mL of 30% $H_2O_2$ and heated for two hours at 85 °C with intermittent agitation. Then another 15 mL portions of the 30% $H_2O_2$ solution was added and the mixture adjusted to pH 2 with conc. $HNO_3$ at 85 °C for 20 h with intermittent agitation. After cooling, 25 mL of 3.2 M $NH_4Ac$ in 20% (v/v) acetic acid was added to the mixture and agitated continuously at room temperature for 30 min. This fraction gave the metals bound to organic matter.

*Fraction 5.* The residue from step 4 was dried and digested with a mixture containing 100 mL of 40% HF and 150 mL of 60% $HClO_4$, the mixture was evaporated almost to dryness and then 2 mL of 60% $HClO_4$ was added and evaporated until white fumes emerged. The residue was dissolved in 100 mL of 3.0 M HCl. This fraction gave the residual metals which are of detrital and lattice origin.

*Centrifugation.* After each step, the fractions were centrifuged at 3000 rpm for 10min. The supernatant was withdrawn and aliquot of it were analysed for heavy metals.

*Method of determining the heavy metals.* The heavy metal concentrations in each fraction were determined by using a Varian-Techron AA-6 atomic absorption spectrophotometer with multi-element hallow cathode lamp system. All determinations were carried out at 25 °C after deaeration with nitrogen for 10 min. No further sample treatment was necessary, but to avoid the problems derived from the different analytical matrix of the extracts, the standard addition method was applied to check for possible matrix effects. All reagents used were of analytical grade and demineralized water was used throughout

The final results were corrected according to the water content of each sediment sample. Total concentrations were obtained by adding the sediments of each speciation category, and all samples were analysed in duplicate.

## RESULTS AND DISCUSSION

Table 1 shows the results corresponding to the total metal concentrations in the inter-tidal flat sediments from each sampling station as well as other known chemical variables related to the retention of heavy metals by sediments. Table 1 was studied by the linear regression analysis of the data to find associations between the variables in order to find an internal structure not accessible at first glance by considering the sediments as objects and the determined parameters as variables. The correlation matrix with the significant values highlighted are presented in Table 2. The linear regression data was obtained by calculating the Pearson's correlation coefficient, r, with a computer program PROC CORR of SAS.

Table 1. Mean total concentrations of parameters in the inter-tidal flat sediments from the Okirika River System.

| | Sampling stations | | | | | | |
|---|---|---|---|---|---|---|---|
| Parameters | A | B | C | D | E | Mean | RSD |
| Pb | 30.24 | 18.81 | 8.88 | 22.33 | 13.61 | 18.77 | 0.08 |
| Ni | 85.82 | 67.49 | 49.87 | 23.73 | 5.66 | 46.51 | 0.70 |
| Cd | 2.24 | 0.85 | 1.34 | 0.60 | 0.22 | 1.05 | 0.78 |
| Co | 12.98 | 27.31 | 10.07 | 4.80 | 1.91 | 11.41 | 0.87 |
| Zn | 429.18 | 198.91 | 303.37 | 113.43 | 182.65 | 245.81 | 0.51 |
| Cu | 92.95 | 92.95 | 80.14 | 49.41 | 18.05 | 66.70 | 0.49 |
| WC | 73.81 | 76.99 | 65.56 | 59.65 | 38.02 | 14.46 | 0.23 |
| OM | 5.11 | 5.80 | 5.17 | 4.90 | 2.60 | 4.72 | 0.26 |
| $CaCO_3$ | 14.22 | 25.49 | 24.26 | 6.13 | 17.89 | 17.60 | 0.45 |
| ON | 1.70 | 0.57 | 0.36 | 1.19 | 1.19 | 1.16 | 0.60 |

All results are dry weight basis except water content. All metals are in $\mu g\ g^{-1}$ and other chemical parameters in %.

Table 2. Pearson's correlation matrix of the analysed parameters.

| | Pb | Ni | Cd | Co | Zn | Cu | WC | $CaCO_3$ | OM | ON |
|---|---|---|---|---|---|---|---|---|---|---|
| Pb | 1.000 | 0.517 | 0.526 | 0.177 | 0.343 | 0.329 | 0.517 | -0.566 | 0.289 | 0.431 |
| Ni | | 1.000 | 0.870 | 0.727 | 0.754 | 0.951 | 0.973 | 0.298 | 0.767 | -0.313 |
| Cd | | | 1.000 | 0.297 | 0.928 | 0.764 | 0.756 | 0.051 | 0.536 | -0.079 |
| Co | | | | 1.000 | 0.193 | 0.794 | 0.825 | 0.590 | 0.743 | -0.560 |
| Zn | | | | | 1.000 | 0.600 | 0.583 | 0.230 | 0.259 | 0.070 |
| Cu | | | | | | 1.000 | 0.969 | 0.387 | 0.908 | -0.589 |
| WC | | | | | | | 1.000 | 0.280 | 0.867 | -0.422 |
| $CaCO_3$ | | | | | | | | 1.000 | 0.194 | -0.537 |
| OM | | | | | | | | | 1.000 | -0.736 |
| ON | | | | | | | | | | 1.000 |

$n = 5, \alpha = 0.05$, if $r \geq 0.754$, then value is significant.

All the metals have positive coefficients and to indicate which of the many pair relationships are "significant" in the statistical sense, the critical multiple correlation coefficient, R, was obtained from the table of significant values. The critical value of R with $n = 5$, $\alpha = 0.05$ is 0.754. By extracting the values $r \geq R$ from Table 2, a reduction of the dimensionality of the data matrix which resulted in revealing the number of significant relationships between the parameters became clear (see Table 3).

Table 3. Number of significant Relationships between parameters obtained by the linear regression analysis, R.

| Couples | Significant correlation values |
|---|---|
| Ni - Cd | 0.870 |
| Ni - Zn | 0.754 |
| Ni - Cu | 0.951 |
| Ni - WC | 0.973 |
| Ni - OM | 0.767 |
| Cd - Zn | 0.928 |
| Cd - Cu | 0.764 |
| Cd - WC | 0.756 |
| Co - Cu | 0.794 |
| Co - WC | 0.825 |
| Co - OM | 0.743 |
| Cu - WC | 0.969 |
| Cu - OM | 0.908 |
| WC -OM | 0.867 |

$R = 0.754$ at $\alpha = 0.05$.

Stronger associations occur between the couples Ni - Cu ($r = 0.951$), Cd - Zn ($r = 0.928$) and Ni - Cd ($r = 0.870$). Other significant correlations include Co - Cu ($r = 0.794$), WC-OM ($r = 0.867$), as well as those existing between Cu, Co, and Ni with organic matter and that between Cu, Ni and Co with water content.

The above associations can be explained in terms of a common source or by chemical similarity [10]. Thus, the positive correlations found between all metals could indicate a common source. The correlation of OM with water seems logical because organic particulates are characterized with high water retention capacity. Also a similar behaviour for Cu, Ni and to a lesser degree Co, with regard to water and OM. Pb is not significantly correlated with any other metal or parameter. This differential behaviour is confirmed by its negative correlation with total carbonate, in an opposite way to the rest of the examined metals.

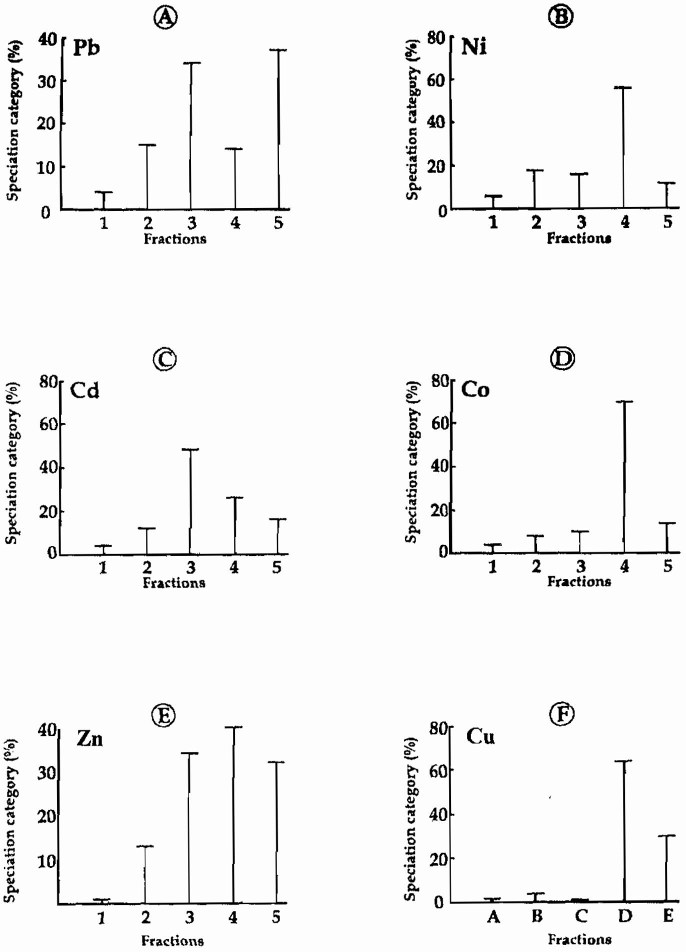

Figure 2. Speciation categories of each metal (A-F).

*Speciation of heavy metals*. The behaviour of each metal based on their, speciation categories can be pointed out by considering Figure 2 (A-F). Figure 2A represents the speciation category of lead. The figure show that the higher percentage corresponds to fractions 3 and 5 which are "bound to reducible phases" and "inert" fractions. The most remarkable feature of the speciation pattern of Ni (Figure 2B) is that most of the metal are found mainly in the bound to "organic matter and sulphides" fraction. Cadmium speciation pattern shows that the metal is mainly bound to the reducible phases. In some cases, the low cadmium levels do not allow its determination, but the mean results of the 5 samples seem to confirm the trend indicated. Cobalt speciation category is represented in Figure 2D. This metal has a stronger association with the bound to organic matter (OM) fraction. For zinc, with the exception of fraction 1, the metal is mainly present in high percentage in fractions 3, 4 and 5. The most remarkable feature of copper is its strong association in all samples with the "bound to organic matter and sulphides fraction (Figure 2F). The trend is typical of this metal in sediments [6] and waters [11].

The speciation patterns of the trace metals in the inter-tidal flat sediments based on the different sampling sites of the study area are presented in Figure 3. This figure presents the percentage distribution of the metal species among the different sampling sites. With respect to sampling sites A to E of fraction1, there is generally a more marked similarity between the species of Ni and Co with the highest amount appearing in site E. No special pattern was observed for Pb, Cd, Zn and Cu, however, Cu presents an approximately equal amount of adsorptive and exchangeable species for sampling sites D and E.

Metals bound to carbonate phases are exhibited in fraction 2. In this fraction, the highest levels are found in sampling sites E for Pb, Co and Cu while Ni, Cd and Zn exhibits their highest level in site D. The only noticeable observation in fraction 2 is that the lowest species of all the metals studied except Co appeared in sampling site C. The speciation pattern for fractions 3 and 4 has some remarkable similarity in that, this species of metal featured prominently in a number of sampling sites except those of site E for Cd and site D for Co. The higher percentage of species for fraction 3 were found in site E for Pb, Ni and Co while Cd, Zn and Cu showed no specific pattern. The most remarkable general trend observed in fraction 5 is that, all the metals investigated except Cd appear in their least amount in sampling site E. The differences observed in the speciation pattern based on sampling sites may be attributable to geological composition.

The environmental impact of the five speciation categories depends upon the ease of remobilization. The first three fractions which can release their metal loads by lowering the pH ("adsorptive and exchangeable", "bound to carbonate", or redox potential i.e. " bound to reducible phases") are the most dangerous.

Figure 3 shows that the metals analysed have different polluting potentials. Cd and Pb are the more dangerous, since both appear in the first fractions in percentages of 67.82 and 52.90%, respectively. Zn has a similar distribution, thus confirming its environmental similarity with Cd. On the other hand, Cu appears mainly in the "bound to organic matter and sulphides" fraction, whereas Ni and Co show a behaviour intermediate between Zn and Cu, having a more marked similarity with the last. In general, the speciation patterns found in the sediments, follow the trends shown by the same metals in sediment [7].

The metals present in the "inert phase" can be taken as a guide to show the degree of contamination of the fluvial system; the greater the percentage of metal present in the category, the smaller the pollution of the zone, because this "inert phase" corresponds to detrital or lattice-bound metals which cannot be remobilized - at least under "normal" polluting circumstances.

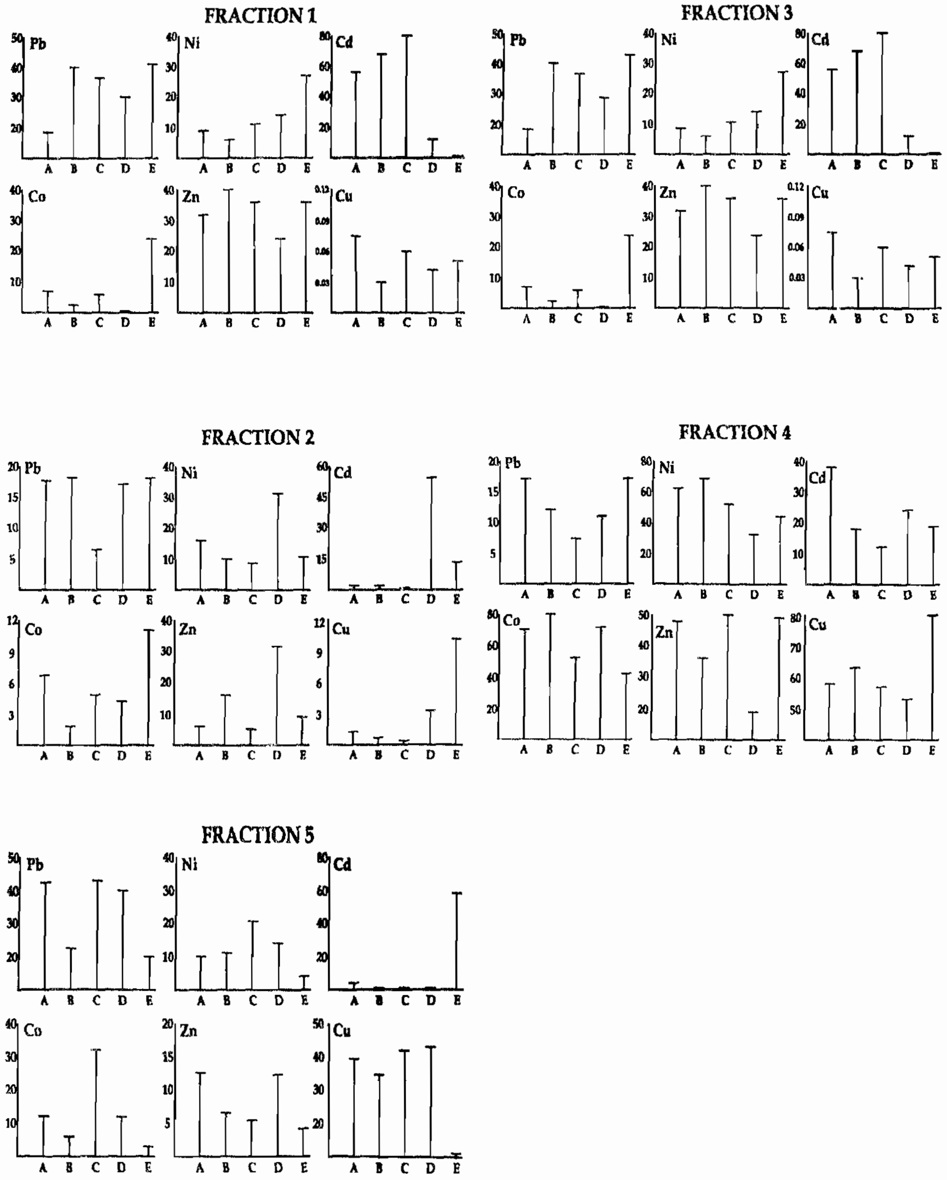

Figure 3. Speciation patters (fraction 1-5) based on sampling sites.

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