Assessment of Cd and Cr Bioavailability in Sediment of River Challawa, Nigeria

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ABSTRACT

Sediment quality assessment are a scientific tools that synthesize information regarding the relationships between the sediment concentrations of heavy metals and any biological effects resulting from exposure to these heavy metals. A field study was conducted to determine the physico-chemical parameters and level of Cd and Cr bioavailability of the river sediment of Challawa. The study revealed that the physiochemical parameters of river Challawa such as pH and organic matter favours bioavailability of Cd and Cr. The distribution pattern of Cr chromium in different fractions was in the order; Residual > Carbonate bound > Fe-Mn oxide bound > Organic bound > Exchangeable in the study and control areas. Chromium was associated mainly (65 – 93.3%) with the residual fraction in all the samples and relatively small amount of chromium occur in the non-residual fractions. The Cd association with different sediment fraction followed the order: Residual bound > Exchangeable > Carbonate bound > Fe-Mn oxide bound > Organic bound. In the residual fractions, 26.68% was associated with exchangeable. Also, despite the high levels of Cr, the very low percentages of the metal in the non-residual fraction indicate their limited environmental mobility. Cd is associated more with exchangeable and carbonate fractions, an indication of potential bioavailability of the metals. The potential risk to river water contamination was highest downstream (Site C) for Cd based on the calculated contamination factor. Based on this study, Cd posed the highest risk to Challawa river water contamination.

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1. INTRODUCTION

River sediments are important sinks for various pollutants like pesticides and heavy metals and also play a significant role in the remobilization of contaminants in aquatic systems under favorable conditions and in interactions between water and sediment (Ikem et al., 2003).

The release of trace metals from sediment into the water body and consequently to fish will depend on the speciation and other factors such as sediment pH and the physical and chemical characteristics of the aquatic system (Morgan and Stuum, 1991).

River Challawa is an important river in Kano state. The river is used for various human activities including washing, fishing, farming and drinking. The domestic water supply for the area comes from this Challawa River. Some peasant farmers along the course of the river also use the water from the river to water their food crops especially vegetables during the dry season. This river receives untreated municipal waste and waste water from the Challawa Industrial areas.

Most of the works on River Challawa concentrate on total metal concentration in water (Bichi, 2001), sediment (Akan et al., 2007), farmland food crops along the bank (Abdullahi et al., 2008; Awode et al., 2008). There are no literatures yet on the speciation of heavy metals in bottom sediment of River Challawa. This study would attempt to determine the pathway of heavy metals in the bottom sediment of River Challawa.

It is therefore necessary to identify and quantify the forms in which a metal is present in sediment to gain a more precise understanding of the potential and actual impacts of elevated levels of metals.

Therefore this study aims at investigate the speciation and bioavailability of selected heavy metals, Cd and Cr in sediments of river Challawa because of their toxicity effect on aquatic life and man through the food chain.

2. MATERIALS AND METHODS

2.1 SAMPLING

Ten sampling points were chosen as the study area (points A to J) while five sampling points (points 1 to 5) as control areas along the Challawa River as shown on figure 1 between May and June 2006 during the dry season. In choosing the sampling points, preference was given to such factors such as point of effluent discharge into the river. A canoe was used as sampling craft and at each point the canoe was stopped for samples to be collected. Samples of the bottom sediment were collected using a core sampler at each point. Sediment samples collected were wrapped with polythene bags and all the samples kept on ice and subsequently transported to the laboratory where they were frozen in a deep freezer.
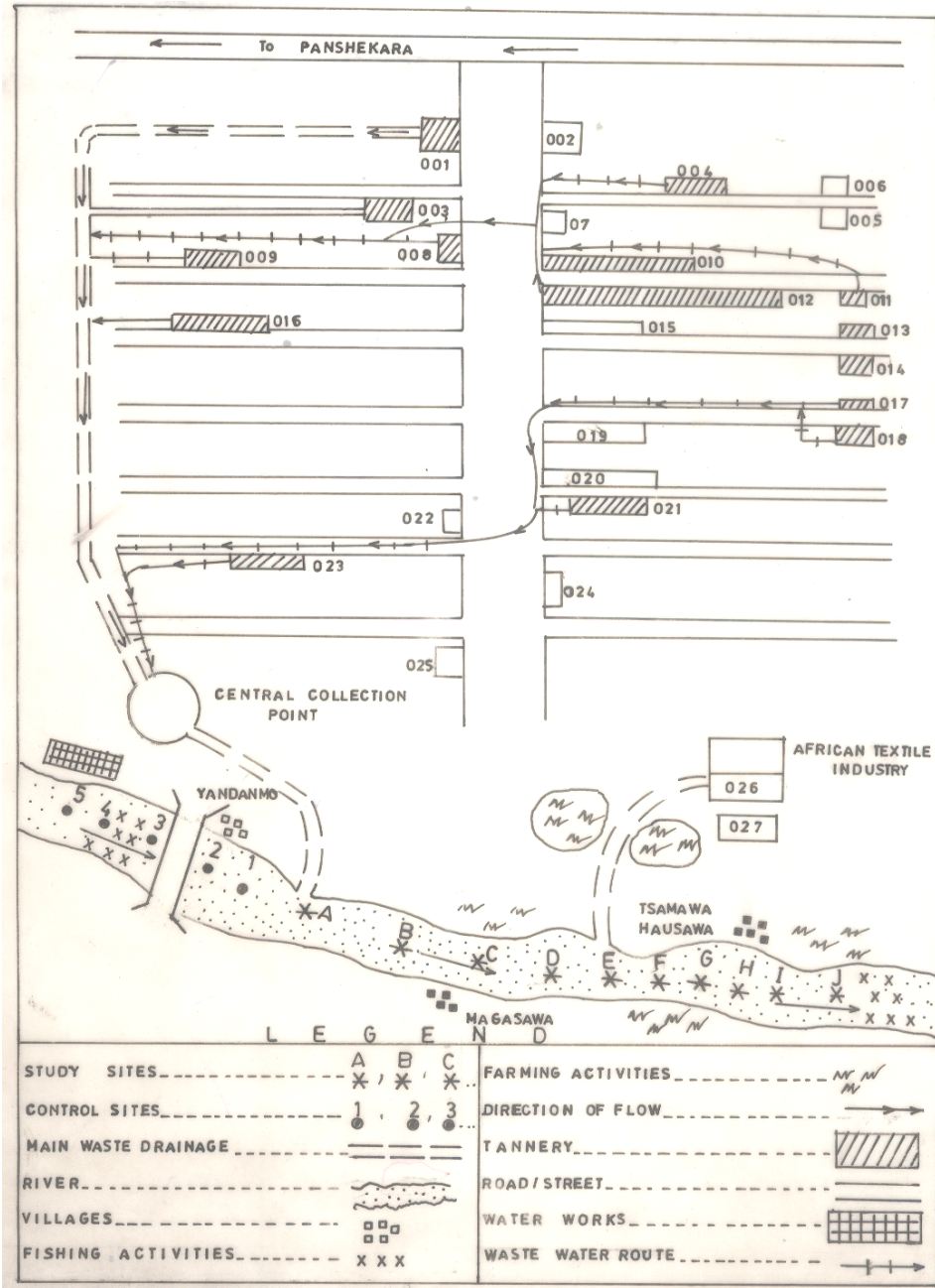
Fig. 1. Sketch map of challawa industrial estate showing the sampling sites

2.2 SAMPLE PREPARATION

Sediment samples for metal analysis were allowed to defrost and then allowed to air-dry. Dry sediments were grinded into fine powder and homogenized using a clean mortar and pestle.

They were then stored in desiccators to attain constant weight before being stored in air-tight plastic bottles. Dry sediment samples were sieved with 200µm sieve before being used for sediment analysis. All metallic determination from sediment samples was based on the fine particles obtained.

2.3 QUALITY CONTROL

Glasswares, crucibles and plastic containers were washed with liquid soaps, rinsed with distilled water and soaked in 10% HNO_3 for 24hrs; cleaned with distilled – deionized water and in such a manner that no contamination occurred (Adnan et al., 2003).

2.4 PHYSICOCHEMICAL PARAMETERS

The pH of sediment samples was measured with sediment: water ratio 1:2 using Crison MicropH 2000, pH meter as described by Herdershot *et al.* (1993). Organic matter was determined by the method of Walkley and Black (1934). Also, Chloride (Cl^-), Sulphate – Sulphur (SO_4^{2-}-S) Nitrate – Nitrogen (NO_3^--N), Nitrite – Nitrogen (NO_2^--N), Phosphate – Phosphorus, PO_4^{3-}-P were determined by methods described by Allen *et al.* (1974).

2.5 SEQUENTIAL EXTRACTION AND SAMPLE ANALYSES

Sequential extraction was carried out on the principle on selective extraction proposed by Shrivastava and Banerjee (2004). Three sub-samples with 1g each from the study and control area were subjected to sequential extraction separately. The extraction was aimed at differentiating fractions in five stages as follows:

Exchangeable phase:
Each sample was shaken at room temp. with 16mL of 1M $Mg(NO_3)_2$ at pH 7.0 for 1 hour, centrifuged and supernatant decanted and made up to 40ml with double distilled water prior to analysis.

Oxidisable phase (Bound to organic matter):
Residue from (1) + 10mL of 8.8 $molL^{-1}$ H_2O_2 + 6mL of $0.02molL^{-1}$ HNO_3 was shaken for 5 + 1 hour at 98^0C. 10ml of $3.5molL^{-1}$ CH_3COONH_4 was added as an extracting agent, centrifuged and supernatant made up to 40ml with distilled water prior to analysis.

Acid soluble phase (Bound to carbonates):
25ml of $0.05ML^{-1}$ Na_2 EDTA was added to the residue from (2) shaken for 6hrs and centrifuged. The supernatant was decanted and made up to 40ml with distilled water prior to analysis.

Reducible phase (Bound to Fe/Mn oxide and hydroxides):
Residue from (3) + 17.5ml $NH_2OH.HCl$ + 17.5ml CH_3COONH_4 ($3.5ml^{-1}$) supernatant descanted and made up to 40ml with distilled water prior to analysis.

Residual Fraction:
Residual from (4) was digested by using HCl–HNO_3/HF (0.35:12 with sediment/solution ratio) in acid digestion Teflon cup. It was dry ash for 2 hours and evaporated to dryness. The residue was made up to 40ml with distilled water prior to analysis.

After each successive extraction, the samples were centrifuged at 4500rpm for 15 minutes. The supernatants were removed with pipette and filtered with Whatman No 42 filter paper. The residue was wasted with deionized water followed by vigorous handshaking and then followed by 15 minutes of centrifugation before next extraction. The volume of rinse water used was kept to a minimum to avoid excessive solubilization of solid materials.

All determination of Cd and Cu in the sediment samples was done using Atomic Absorption Spectrophotometer (AA-650, Double Beam Shimadzu).

3. RESULTS AND DISCUSSION

3.1 PHYSICOCHEMICAL PARAMETERS

The results of the physico-chemical parameters for study and control areas are presented in Table 1 and 2. In the study area, organic matter content varied from 7 – 10.55% while that of control area ranged from 7.10 – 8.35%. The difference in the sediment organic matter between the study and control areas may be attributed to the tannery effluent discharge into the river. Tannery effluents are discharged raw into the Challawa River and contains high organic matter due to animal hide product in it. It may also be seen from Tables that organic matter content return to values similar to those of control area as from sampling points F to J. This shows that deposition of animal hide occurs mainly from the point of tannery effluent discharge to sampling point E. The decrease in organic matter content with the distance from the point of entry of tannery effluent may also be due to possible biodegradation of organic matter by microorganism in the sediment, an indication of self-cleaning effect of the river.

In the study area, the pH of the sediment samples varied from 5.0 – 6.65. The low pH at sampling points A to D observed might be due to discharges of acidic waste in the tannery effluents from pickling process which prepares the hides by providing an acidic environment. There is no much considerable variation in the pH values for sampling points 1 to 5 as shown in Table 2. The sampling point 1 has the lowest value, which might be due to the proximity of that point to the point of entry of the tannery waste into the river. The pH values obtained in the study area revealed that the sediment samples were slightly acidic. This is similar to the pH range of 4.0 – 7.0 reported by Lee et al. (2003) in their study of the implications to water quality, heavy metals in bed and suspended sediments of Anyang River, Korea. The pH range found in this investigation falls within the limits of 4.0 – 7.00 (WHO, 2005) for the survival of fish in the aquatic environment. The slightly acidic medium of the sediment of River could indicate possible mobility of the metals to other environments since metals are known to be more soluble in acidic medium than in alkaline medium (Chimuka et al., 2003).

The chloride content of the sediment samples as shown in Table 1 and 2 respectively ranged from 0.400 – 2.415 mgkg^{-1} for the study area and 0.150 – 0.350 mgkg^{-1} for the control area. The variations in the chloride content of the sediment in the study and control areas may be attributed to the tannery effluent discharged into the river. Sampling points A to F showed a higher chloride content because of their proximity to the point of discharge into the river since the tannery waste is known to contain high chloride content (Yisa, 2004). The decrease in the chloride content from points G to J might be due to formation of complexes with heavy metals downstream. The range of chloride content in this study are lower than the ranges of 3.5 – 15.5 mgkg^{-1} reported by Odokuma and Abah (2003) in a study of sediment of New Calabar River.

Table 1. Mean (±SD) of physicochemical parameters of study area sediment samples

Site	Parameter								
	pH	OM (%)	$CaCO_3$ ($mgkg^{-1}$)	NO_3^--N ($mgkg^{-1}$)	NO_2^--N ($mgkg^{-1}$)	$PO_4^{3-}-P$ ($mgkg^{-1}$)	$SO_4^{2-}-S$ ($mgkg^{-1}$)	Cl^- ($mgkg^{-1}$)	NH_3-N ($mgkg^{-1}$)
A	5.25±0.25	10.25±0.25	14.25±0.25	0.650±0.100	0.500±0.001	5.02±0.28	12.00±0.20	0.725±0.125	0.170±0.020
B	5.50±0.00	10.15±0.39	14.15±0.35	0.400±0.001	0.600±0.000	6.60±0.30	10.80±0.20	0.450±0.050	0.400±0250
C	5.55±0.00	10.55±0.00	13.75±0.25	0.900±0.000	0.400±0.010	4.50±0.20	11.65±0.25	0.400±0.100	0.850±0.012
D	5.00±0.00	8.90±0.00	10.10±0.10	0.700±0.000	0.400±0.000	6.15±0.25	12.60±0.20	0.525±0.015	0.260±0.040
E	5.00±0.25	9.40±0.00	10.25±0.25	0.700±0.000	0.500±0.001	7.35±0.15	8.95±0.150	0.450±0.050	0.510±0.030
F	5.75±0.00	8.05±0.05	10.85±0.15	0.500±0.001	0.400±0.001	3.50±0.20	14.30±0.30	2.415±0.085	0.250±0.040
G	5.75±0.00	8.10±0.10	10.25±0.25	0.200±0.000	0.600±0.000	4.40±0.10	17.20±0.30	1.500±0.001	0.350±0.040
H	5.00±0.00	7.70±0.20	10.90±0.10	0.600±0.001	0.400±0.000	5.92±0.12	19.70±0.30	1.900±0.100	0.310±0.015
I	5.50±0.00	7.00±0.00	10.30±0.30	0.100±0.001	0.600±0.000	4.21±0.29	10.70±0.20	0.500±0.100	0.220±0.021
J	6.60±0.00	7.25±0.25	10.20±0.20	0.200±0.001	0.300±0.010	2.41±0.29	15.55±0.25	0.690±0.110	0.021±0.007

OM: Organic Matter; SD: Standard Deviation

Table 2. Mean (±SD) of physicochemical parameters of control area sediment samples

Site	Parameter								
	pH (H$_2$O)	OM (%)	Alkalinity (mgkg^{-1})	NO$_3^-$-N (mgkg^{-1})	NO$_2^-$- N (mgkg^{-1})	PO$_4^{3-}$-P (mgkg^{-1})	SO$_4^{2-}$-S (mgkg^{-1})	Cl$^-$ (mgkg^{-1})	NH$_3$-N (mgkg^{-1})
1	5.75±0.75	7.90±0.10	10.40±0.60	0.500±0.000	0.600±0.001	10.30±0.30	4.35±0.15	0.325±0.002	0.820±0.090
2	6.00±0.00	8.35±0.15	10.35±0.35	0.400±0.001	0.000±0.000	14.35±0.15	6.55±0.15	0.275±0.007	0.150±0.003
3	5.25±0.25	7.65±0.15	10.50±0.50	0.600±0.002	0.200±0.001	11.05±0.15	5.35±0.25	0.150±0.005	0.087±0.002
4	5.75±0.25	7.40±0.29	10.50±0.50	0.100±0.000	0.030±0.002	9.55±0.45	5.00±0.20	0.350±0.005	0.140±0.004
5	6.00±0.00	7.10±0.10	10.30±0.30	0.400±0.10	0.505±0.00	8.00±0.30	4.50±0.20	0.275±0.075	0.016±0.004

OM: Organic Matter; SD: Standard Deviation

Alkalinity measured in mgkg^{-1} CaCO$_3$ was in the range of 10.10 – 14.75 mgkg^{-1} for the study area while that of the control area ranged from 10.30 – 10.50 mgkg^{-1}. There is a difference in the alkalinity between sediments samples of study and control areas. This could be attributed to the discharge by tannery effluents that are generally known to be alkaline as reported by Yisa (2004) in the study of impact of tannery operations on Challawa River. There is no significant variation in alkalinity between sampling points 1 – 5 in the control area while in the study area, alkalinity decreases downstream from points A to F. This could imply the possible reaction of the acidic sediment with the CaCO$_3$.

The content of NO$_3^-$ – N, NO$_2^-$ – N and NH$_3$ – N in the sediment of River Challawa are shown in Tables 1 and 2. The content ranged from 0.10 to 0.90 mgkg^{-1}, 0.30 – 0.60 mgkg^{-1} and 0.021 – 0.850 mgkg^{-1} for the NO$_3^-$ – N, NO$_2^-$ – N and NH$_3$ – N, respectively in the study area. The control area has NO$_3^-$ – N in the sediment in the range of 0.10 – 0.60 mgkg^{-1} NO$_2^-$-N, 0.00 – 0.60 mgkg^{-1} and NH$_3$ – N is 0.016 – 0.820 mgkg^{-1}. There is no significant difference between the values in the study and control areas. This implies that there is no significant contribution the tannery effluent is making to the level of those parameters. Such parameters might have passed into the sediments from fertilizer applied on farms from the banks of the river Challawa. Generally, the values of nitrate and nitrite obtained in this study are lower than 1 mgkg^{-1}, since high levels (> 1 mgkg^{-1}) of nitrate and nitrite are not good for aquatic life (Adeyemo *et al*., 2008).

In the study area, the sulphate - sulphur content ranged from 8.95 - 17.20 mgkg^{-1} while the sulphate - sulphur sediment samples from the control area ranged from 4.35 – 6.55 mgkg^{-1}. There is a significant variation between the sulphate -sulphur level in the study and control areas. This could be due to the discharge of tannery effluents untreated into the river. There is no significant variation in the sulphate -sulphur content between sampling points 1 to 5 because the sources of the sulphate -sulphur include agricultural run-off which contains sulphate from applied fertilizers and pesticides.

The level of PO$_4^{3-}$ - P in the sediment samples ranged from 2.41 – 7.35 mgkg^{-1} in the study area while in the control area, the PO$_4^{3-}$ - P ranged from 8.00 – 14.35 mgkg^{-1}. The phosphate level in the control area is very much greater than the level of the phosphate in the study area. This could be as a result of the amount of the phosphate contained in the agricultural run-offs is higher in the control area because the number of farmlands on the banks of the river is higher in the control area that the study area.

3.2 CORRELATION AMONG PHYSICOCHEMICAL PARAMETERS

Correlation analysis amongst sediment physic-chemical parameters in the study area as shown on Table 3 revealed the presence of positive correlation ($p < 0.01$) between PO$_4^{3-}$-P and Cl$^-$. Similarly, and negative correlation ($p < 0.05$) was also revealed between PO$_4^{3-}$-P and NO$_3^-$-N, clay and NO$_2^-$-N. Significant positive or negative correlation could therefore indicate a greater influence of one factor on another.

Table 3. Correlation matrix among physicochemical parameters of the sediment

Parameters	OM	Cl^-	$CaCO_3$	NH_3-N	NO_3^--N	NO_2^--N	SO_4^{2-}-S	PO_4^{3-}-P	pH	Sand	Silt	Clay
OM	1.000											
Cl^-	-0.081	1.000										
$CaCO_3$	0.333	0.142	1.000									
NH_3-N	0.370	0.115	0.170	1.000								
NO_3^--N	0.171	-0.250	-0.077	0.245	1.000							
NO_2^--N	0.251	0.116	-0.397	0.183	-0.079	1.000						
SO_4^{2-}-S	0.469	-0.267	0.224	0.009	0.039	-0.395	1.000					
PO_4^{3-}-P	-0.101	0.703**	0.246	0.091	-0.577*	-0.085	-0.169	1.000				
pH	-0.398	-0.107	-0.115	-0.190	0.090	-0.061	-0.515*	-0.107	1.000			
Sand	-0.120	0.052	-0.290	-0.082	-0.179	0.145	0.070	-0.081	-0.361	1.000		
Silt	0.238	0.094	-0.082	-0.088	-0.128	0.319	-0.015	-0.003	-0.031	-0.504	1.000	
Clay	-0.190	-0.243	-0.454	-0.231	0.141	-0.622*	0.111	-0.100	0.508	-0.630*	0.073	1.000

*Significant at p   0.05; ** Significant at p   0.01

Table 4. Correlation analysis among fractions of Cr and Cd in sediment

Parameters	$Cr_{Ex.}$	Cr_{CB}	Cr_{Fe-MnO}	Cr_{OB}	Cr_{RED}	$Cd_{Ex.}$	Cd_{CB}	Cd_{Fe-MnO}	Cd_{OB}	Cd_{RED}
Cr_{EX}	1									
Cr_{CB}	-0.818[**]	1								
Cr_{Fe-MnO}	-0.518	0.408	1							
Cr_{OB}	0.528	-0.373	0.381	1						
Cr_{RED}	-0.102	-0.269	0.268	-0.057	1					
Cd_{EX}	-0.156	0.215	-0.254	-0.345	0.069	1				
Cd_{CB}	-0.180	0.349	0.175	0.104	-0.075	0.409	1			
Cd_{Fe-MnO}	-0.337	0.494	0.514	0.262	-0.136	0.323	0.628	1		
Cd_{OB}	-0.369	0.313	-0.042	-0.279	0.024	0.013	0.450	0.322	1	
Cd_{RED}	0.433	-0.645[*]	-0.321	0.025	0.131	-0.350	-0.922[**]	-0.756[*]	-0.547	1

**Correlation is significant at the 0.01 level (2-tailed); *Correlation is significant at the 0.05 level (2-tailed).
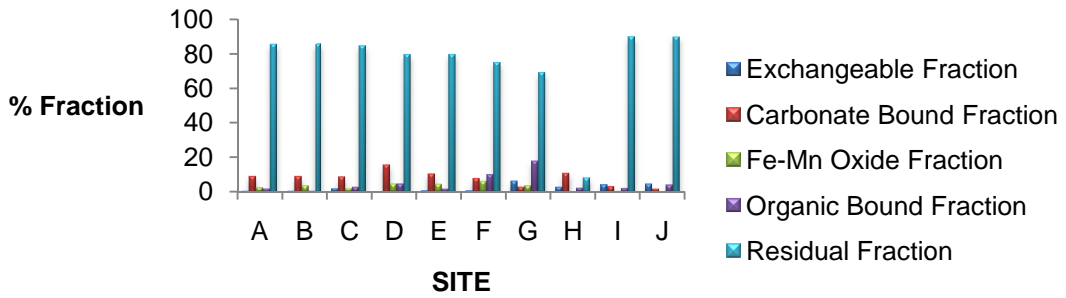*EX.: Exchangeable Fraction; CB: Carbonate Bound; OB: Organic Bound; RED: Residual Fraction*

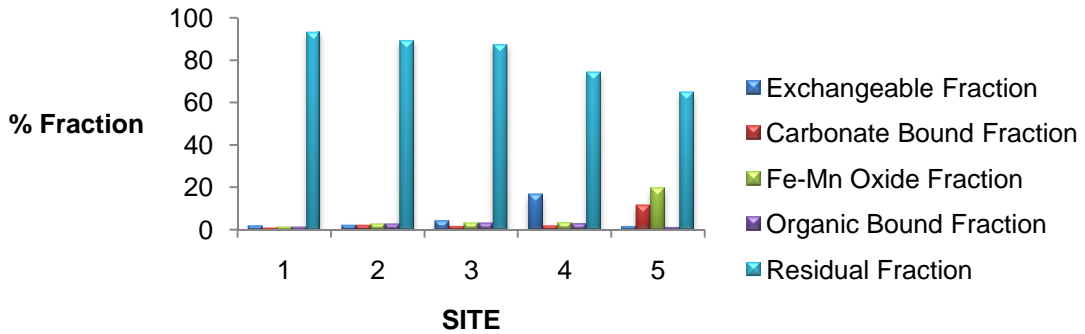**Fig. 2a. Percentage fractions of Cr in sediment across the study area**

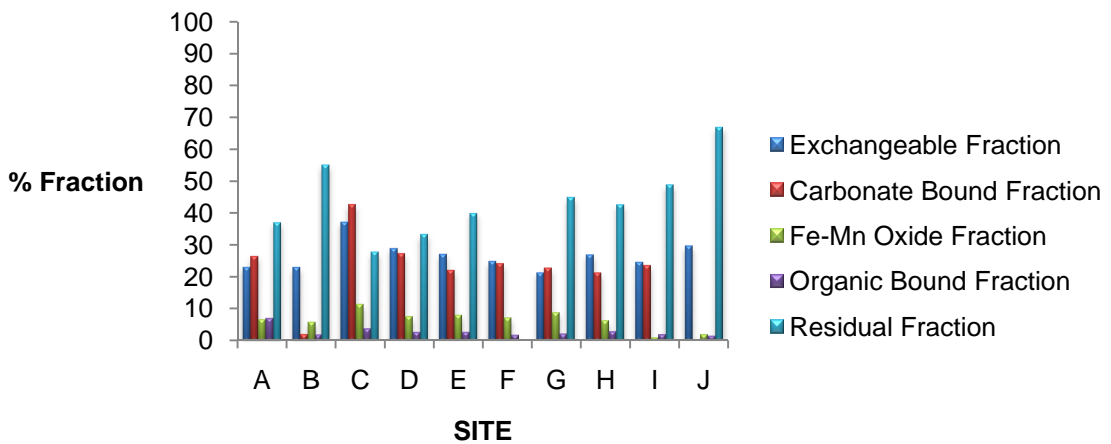**Fig. 2b. Percentage fractions of Cr in sediment across the control area**

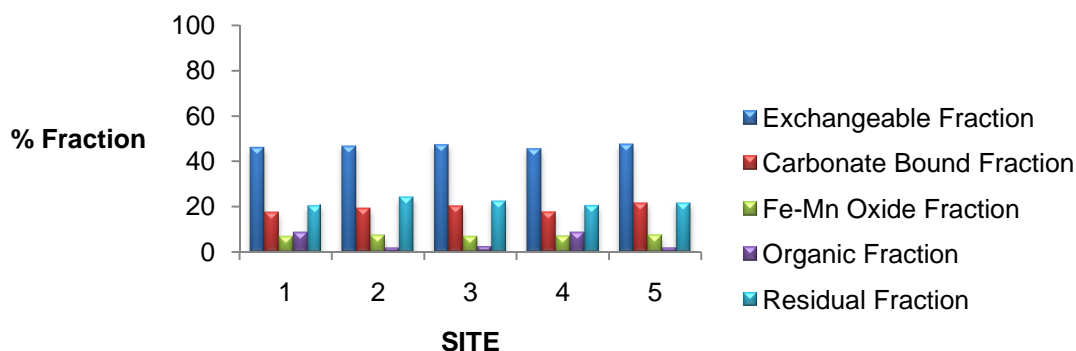**Fig. 3a. Percentage fractions of Cd in sediment across the study area**

Fig. 3b. Percentage fractions of Cd in sediment across the control area

3.3 SEQUENTIAL EXTRACTION

The sequential extraction scheme adopted in this study, analysed distribution pattern of metals in this study in the five geochemical phases of the sediments of River Challawa. The extraction scheme is useful in assessing the mobility and bioavailability of heavy metals in river sediment. The distribution pattern of Cr chromium in different fractions as presented in Figure 2a and 2b was in the order; Residual > Carbonate bound > Fe-Mn oxide bound > Organic bound > Exchangeable in the study and control areas. Chromium was associated mainly (65 – 93.3%) with the residual fraction in all the samples and relatively small amount of chromium occur in the non-residual fractions. Studies of Stone and Maslek (1996) have shown similar results.

The Cd association with different sediment fraction as presented in Figure 3a and 3b followed the order: Residual bound > Exchangeable > Carbonate bound > Fe-Mn oxide bound > Organic bound. In the residual fractions, 26.68% was associated with exchangeable. This was in agreement with the findings of Ramos et al. (1994). The smaller percentage of Cd in the organic fractions as noted in this study is commonly found in the river sediments (Forstner and Whittman, 1979). Speciation data in this study indicated that Cd has the greatest overall affinity in the exchangeable fractions while other metals showed much less affinity. Metals extracted in these fractions are adsorbed on solid matrices by relatively weak electrostatic interaction and can be released by ion-exchange.

This indicates the highest mobility of Cd. 21.25% of Cd was associated with carbonate fraction which can be released under acidic conditions. Also, inspite of the high levels of Cr, the very low percentages of the metal in the non-residual fraction indicates their limited environmental mobility. The result suggests that Cd is associated more with exchangeable and carbonate fractions. An indication of potential bioavailability of the metals, since metals present in the exchangeable is usually readily available for plant or organism uptake (Xian, 1989).

3.4 CORRELATION AMONG METAL FRACTIONS

As shown on Table 4 above, correlation analysis revealed negative correlation between Cr_{Ex}: Cr_{CB} (r = -0.888, p < 0.01), Cr_{Fe-MnO}, Cr_{RED}, Cd_{Ex}, Cd_{CB}, Cd_{Fe-MnO} and Cd_{OB}; Cr_{CB}: Cr_{OB}, Cr_{RED} and Cd_{RED} (r = -0.645, p < 0.05); Cr_{Fe-MnO}: Cd_{EX}, Cd_{OB} and Cd_{RED}; Cr_{OB}: Cr_{RED}, Cd_{EX}, and Cd_{OB}; Cr_{RED}: Cd_{OB} and Cd_{Fe-MnO}; Cd_{EX}: Cd_{RED}; Cd_{CB}: Cd_{RED} (r = -0.922, p < 0.01); Cd_{Fe-MnO}: Cd_{RED} (r = -0.756, p < 0.05) and Cd_{OB}: Cd_{RED}. This strongly suggests these fractions do not contribute to the heavy metals concentrations in the study area. Positive correlations were shown among other fractions, an indication of contribution of these fractions the concentration of one another.

3.5 CONTAMINATION FACTOR

Contamination factor as shown on Table 5 revealed the individual contamination factor of Cr and Cd in the Challawa sediments analysed. The individual contamination factors (ICF) for the various sampling sites were calculated from the result of the fractionation study dividing the sum of the first four extractions (i.e. the exchangeable, carbonate bound, Fe-Mn oxide forms and the oxidizable forms) by the residual fraction for each site (Ikem et al., 2003). The ICF reflects the risk of contamination of a water body by a pollutant. From the results, with exception of Site B and Site J, all Sites from the river had higher contamination factor for Cd with the highest at Site C. The high trend for Site C may be attributed to the increased movement of contaminants downstream. For Cr highest contamination was obtained at Site H. Compare to Ikem et al. (2003), highest contamination was obtained in this study for Cd. This high levels of the mobilizable fractions (i.e. exchangeable, carbonate bound, Fe-MnO and organic matter) in the sediments indicates potential risk to water contamination by sediment.

Table 5. Contamination factor of Cr and Cd in Challawa sediments

SITE	Individual Contamination Factor (C_f)	
	Cr	**Cd**
A	0.17	1.72
B	0.17	0.60
C	0.19	3.42
D	0.32	2.00
E	0.22	1.51
F	0.34	1.30
G	0.45	1.23
H	1.97	1.35
I	0.12	1.05
J	0.12	0.50

4. CONCLUSION

The result of the samples collected showed appreciable amount of Cd in the exchangeable which is the first fraction to be extracted and hence the most soluble. For the sequential

extraction procedure used in this study, mobility and biological availability are assumed to decrease in the order of the metal extraction sequence of this basis the apparent mobility and potential bioavailability of the metals for the sediment in the study area are Cd > Cr. Based on the calculated individual contamination factors, Cd posed the highest risk to river water contamination. Due to the potential toxicity of these metals, there is need that the industrial waste be sorted and separated to facilitate safe and appropriate treatment and disposal.

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