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Total and Extractable Toxic Metal in Water and Sediments of River Kaduna Within Kaduna Metropolis

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Abstract: Geochemical analysis of some heavy metals in water, sediment and their speciation in the sediment samples were carried out in river Kaduna within Kaduna metropolis to determined the distribution and association of heavy metals namely As, Cd, Co, Cr and Pb. The method adopted for the analysis of these metals is Atomic Absorption Spectrometer (A.A.S.). The results for the study revealed that the metal levels in the water from the study areas range from 0.013 – 0.420, 0.002 – 0.880, 0.011– 1.330, 0.010 – 0.990 and 0.020 – 0.850 mg/L for As, Cd, Co, Cr and Pb respectively, while in the sediment samples from the same location, the levels of the same metals ranged from 7.250 – 9.850, 2.200 – 5.550, 14.550 – 27.970, 10.550 – 25.890 and 39.650 – 55.650 mg/g for As, Cd, Co, Cr and Pb respectively. Water and sediment samples contained higher concentrations of the toxic metal determined in the study sites as compared to the toxic metals from control areas indicating the presence of contaminants particles in the area A five-step sequential extraction protocol of toxic metals "As, Cd, Co, Cr and Pb" in sediments from River Kaduna within Kaduna metropolis indicated that Cr, Pb, and Cd contribute significant quantities in the exchangeable and acid extractable fractions (mobile phase), making them easily bio available while As and Co, residual fractions contributed the maximum, which is inert form and hence the environmental effect may not be significant. Detection of these heavy metals especially Cd and Co at higher concentrations in sediment samples calls for sustained monitoring since transfer of metals across the food chain and accumulation are most probable with resultant health problems.

Keywords: Association, Distribution, River Kaduna, Sediments, Speciation, Toxic Metal, Water

1. Introduction

The natural entry route of toxic metals into aquatic environment is through weathering of the earth crust. In addition to geological weathering, human activities have also introduced large quantities of metals to localized area of the sea, in some cases upsetting the natural steady state balance (Li and Mahler *1992*). Metals such as cadmium, chromium, cobalt, iron, nickel, lead and arsenic exhibit aquatic toxicity when present above recommended standard in that they can contaminate surface and ground water bodies, soil, plant, aquatic life and man, through bioaccumulation. The process of absorption and accumulation of metals in plants is complicated, usually defined by the behaviour of the element, soil characteristics and the properties of the biological

reagents. Hence regular investigations of these processes have to be a part of the environmental monitoring (Bradford *et al 1996*), (Katyal and Vlek *1985*).

Metal partitioning among sedimentary organic and mineral components as well as the physicochemical mechanisms of trace metals enrichment both remain as important research areas. In sediment, trace metals can be present in a number of chemical forms, and generally exhibit different physical and chemical behaviour in terms of chemical interaction, mobility, biological availability and potential toxicity (Odoh *et al 2011*). It is 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 in sediments and to evaluate processes of downstream transport, deposition and releases under changing environmental conditions. The major mechanisms

of accumulation of trace metals in sediment lead to the existence of five categories; exchangeable, bound to carbonate, bound to reducible phases (iron and manganese), and bound to organic matter and residues Singh *et al* (*2005*). These categories have different behaviours with respect to remobilization under changing environmental conditions. The fractions introduced by anthropogenic activity include the adsorptive, exchangeable and bound to carbonate fractions. These are considered to be weakly bounded metals, which may equilibrate with the aqueous phase and thus become more rapidly bio – available (Pardo *et al 1990*). Due to rapid expansion of state and industries within Kaduna state more waste products have been discharged from municipalities, industries and spilled into water ways. Much concern has been focused on the investigation of the total metal contents in sediments. The result from the determination of trace metals in sediments reflects the impacts of industrial activities and urban development (Fang 2005). Trace metals are not fixed permanently in the sediment and may be recycled via biological and chemical agents both within the sedimentary compartment and water column. In general, the environmental risk arising from metal contamination in river sediments cannot be assessed only on the basis of total contents but needs to consider also the forms in which they are associated with sediment (Odoh *et al 2014*). Today it is generally recognized that the particular behaviour of trace metals in the environment is determined mostly by their specific physicochemical fractionation and speciation or chemical form rather than by their total concentration (Tack and Verloo 1995), and therefore, speciation studies increasingly gain importance (Liu *et al 2007*), (Zakir and Shikazono *2003*). There are a wide variety of sequential extraction procedures available in literature based on a different sequence of extractants and / or different operating conditions (Zakir and Shikazono 2003). Among those, the 4 step SM & T (Formerly BCR scheme, modified by Rauret *et al*. 1999) and the 5 – step (Tessier *et al*. *1979*) schemes are most applied. In the entire Hall scheme Hall *et al* (1996), the oxide/reducible phase is divided into metals associated with amorphous Fe oxyhydroxide and crystalline oxides of Fe. However, in sequential extraction procedures, four to eight extractants are usually employed in an order in which the earlier ones are the least aggressive and the most specific, and subsequent extractants are progressively more destructive and less specific. It is generally assumed that the availability of the metals to the living organisms follows a decreasing order from the first step towards the last step in a sequential extraction scheme.

River Kaduna within Kaduna metropolis receives significant amount of waste from surrounding industrial, commercial and residential area. River Kaduna is one of the biggest rivers in Northern part of the country and the enrichment of toxic metal in some fraction especially in mobile fraction will be emphasized to assessing the pollution status of the farm lands and fish farm around and along the river bank within the Kaduna metropolis, the extent to which the crop plants and fishes grown on these farmlands were

exposed to toxic metals, and hence, the safety levels of the fish and plant leaves and crops produced for human consumption. The present study was evaluating the toxic metal level in the river and the geochemical speciation of Cd, Cu, As, Pb, and Zn in sediments taken from River Kaduna which has been mainly affected or associated by industrialization, urbanization and technogenic impact/ anthropogenic activities as the industrial sector is a major contributor to environmental pollution. Therefore, the main objective of this work was the assessment of toxic metal status, distribution and speciation in sediments from river Kaduna in Kaduna metropolis.

2. Materials and Methods

2.1. Study Area

Kaduna State, north central Nigeria, is politically classified as belonging to the now 'North - West' zone of the current six (6) Geo - political zones of Nigeria. It is populated by about 59 to 63 different ethnic groups if not more with the exactitude of the number requiring further verification through a genuine field work (Hayab, 2014). The Hausa and Fulani are the dominant ethnic groups followed by at least 60 others. It was from the old Northern Region that in the year 1967 gave birth to six states in the north, leaving Kaduna as the capital of North-Central State, whose name was changed to Kaduna State in 1976. Most of the industries in Kaduna state are sited in Kaduna south. Kaduna south industrial areas are bounded by residential areas of Kakuri, Makera, and Nassarawa. Another important neighbouring is Unguwar Television. These areas provide residential accommodation for about 80% of the low income industrial workers. The industrial area in Kaduna south is about seven kilometres from the city centre but all the industrial effluent is discharged into the river Kaduna and river Kaduna tributaries within Kaduna Metropolis. Kudenda industrial area is located at the edge of the city but lies close to some residential areas of Nassarawa, Unguwar Muazu and Tudun Wada which are located at the opposite the industrial area, the two industrial area in Kaduna are located close to each other and they discharging the waste and effluent into river Kaduna.

2.2. Reagents Used

The reagents used were of analytical grades and they include: HNO_3, HCl, H_2O_2, NaOH pellets, NaCl and anionic trimethylhyroxyammonium chloride resin all the reagents from (British Drug House (BDH) Chemicals Ltd, Poole, England). Solutions were prepared using doubly distilled water.

2.3. Pre-treatment and Sterilization of Apparatus

All glass wares used (Erlenmeyer flask, conical flask, beakers, measuring cylinder, volumetric flask, and watch glass) were washed with liquid detergent and rinsed thrice with distilled water followed by oven drying. Polyethylene sample bottles and Teflon beakers were washed with liquid

detergent and rinsed with distilled water prior to sample collection (Ogunfowokan and Fakankun 1998), (Ogunfowokan *et al* 2008)

2.4. Sample Collection and Pre-treatment

Samplings were taken from five different sites (Tabel 1 – 5) along the river in Kaduna metropolis and in each of the sample site, ten sampling points were taken and label as KDA, KDB, KDC, KDD, KDE, KDF, KDG, KDH, KDI, KDJ, while control were collected from area where industrial, agricultural and other human activities were absent and is label as KAA. The water samples were collected in 2 L treated polythene containers. Before filling, the containers were rinsed thrice with the water sample to be collected at the sampling sites. Samples were adjusted to pH 2 to prevent further microbial degradation. Similarly, sediment samples were collected in polythene bags. The collected sediment samples were air-dried, large unwanted particles were hand-picked and the rest were ground with agate mortar and pestle to powdery form.

2.5. Speciation Analysis of Heavy Metals in the Sediments

The procedure of Tessier *et al* (*1985*) and Tessier *et al* (*1975*) were used for the speciation study. Thus, the sediment samples were subjected to a five stage sequential procedures to extract and partition Cd, Co, Pb, As, and Cr, into exchangeable, bound to carbonate, bound to Mn oxides, bond to amorphous Fe-oxide, bound to crystalline Fe-oxide, and bound to residual fractions. One gram of each sediment sample was weighed and extractions were made through steps (F1 - F5) by centrifugation and filtration at 10,000 rpm placing the sample in polyethylene centrifuge tubes. Distilled water was used to wash the residues following subsequent extraction in order to ensure selective dissolutions and to prevent possible interphase mixing between the extractants. All samples were run in duplicates.

1. Exchangeable phase: Sample was shaken at room temperature with 16 ml of 1 M $Mg(NO_3)_2$ at pH 7.0 for 1hr, centrifuged and supernatant decanted and made up to 40 ml with double distilled de–ionized water.

2. Oxidisiable phase (bound to organic matter): Residue from 1 + 10 ml H_2O_2 8.8M + 6ml HNO_3 0.02 M, was shaken for 5+ 1 hrs at 98°C. 10 ml CH_3COONH_4 3.5 M was added as an extracting agent, centrifuged and supernatant made up to 40ml with distilled water prior to analysis.

3. Acid soluble phase (bound to carbonates): 25 ml of 0.05M Na_2EDTA 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.

4. Reducible phase (bound to Fe–Mn Oxides): Residue from 3 + 17.5ml $NH_2OH.HCl$ 0.1M +17.T5M CH_3COONH_4 3.5M, shaken for 1hr, centrifuged, the supernatant decanted and made up to 40ml with distilled water prior to analysis.

5. Residual phase (bound to silicates and detrital materials): Residue from 4 was digested by using $HCl–HNO_3/HF$ (0.35:12w/v soil solution ratio) in acid digestion, Teflon cup. It was drying ashed for 2hrs and evaporated to dryness. The residue was diluted to 40ml with distilled water prior to analysis.

3. Results

A. Levels of Heavy Metals in the Water and sediment Samples

Results of the levels (mg/L) of total heavy metals (As, Cd, Co, Cr and Pb) in the water samples from the study areas are shown in Tables (1 and 2). The metal levels in the water from the study areas range from 0.013 – 0.420, 0.002 – 0.880, 0.011– 1.330, 0.010 – 0.990 and 0.020 – 0.850 mg/L for As, Cd, Co, Cr and Pb respectively. Each site showed that Cd level was the least while Pb level was the highest (Table 3), while in the sediment samples from the same location, the levels of the same metals ranged from 7.250 – 9.850, 2.200 – 5.550, 14.550 – 27.970, 10.550 – 25.890 and 39.650 – 55.650 mg/g for As, Cd, Co, Cr and Pb respectively.

Table 1. *Level of Toxic Metal (mg/L) in the water samples from river Kaduna.*

Metals	As	Cd	Co	Cr	Pb
Site A					
MEAN.	0.023	0.003	0.528	0.023	0.037
STD	0.007	0.001	0.369	0.009	0.008
MIN	0.013	0.002	0.100	0.010	0.020
MAX	0.036	0.004	0.980	0.041	0.048
Site B					
MEAN.	0.236	0.466	0.427	0.478	0.408
STD	0.073	0.182	0.367	0.324	0.086
MIN	0.130	0.250	0.080	0.040	0.280
MAX	0.360	0.870	0.980	0.900	0.540
Site C					
MEAN.	0.243	0.058	0.677	0.510	0.486
STD	0.041	0.028	0.226	0.368	0.138
MIN	0.200	0.020	0.320	0.120	0.330
MAX	0.320	0.090	0.960	0.950	0.850
Site D					
MEAN.	0.227	0.533	0.902	0.597	0.494
STD	0.084	0.249	0.211	0.369	0.139
MIN	0.028	0.220	0.650	0.120	0.330

Metals	As	Cd	Co	Cr	Pb
MAX	0.320	0.880	1.330	0.990	0.850
Site E					
MEAN.	0.214	0.015	0.026	0.496	0.067
STD	0.103	0.004	0.014	0.220	0.015
MIN	0.110	0.011	0.011	0.133	0.045
MAX	0.420	0.021	0.056	0.788	0.092
All Samples					
MEAN	0.189	0.215	0.512	0.421	0.299
STD	0.108	0.271	0.392	0.347	0.225
MIN	0.013	0.002	0.011	0.010	0.020
MAX	0.420	0.880	1.330	0.990	0.850
Control site					
MEAN.	0.004	N.D	N.D	N.D	0.011
STD	0.004	N.D	N.D	N.D	0.004
MIN	0.001	N.D	N.D	N.D	0.005
MAX	0.011	N.D	N.D	N.D	0.017

N.D = Not Detected

Table 2. Level of Toxic Metal (mg/g) in sediment from river Kaduna.

Metals	As	Cd	Co	Cr	Pb
Site A					
MEAN.	8.323	3.705	21.872	14.872	50.159
STD	0.858	1.265	3.525	2.897	4.872
MIN	7.250	2.200	17.870	10.550	39.650
MAX	9.750	5.550	26.750	19.560	55.650
Site B					
MEAN	8.223	4.543	21.396	15.166	50.994
STD	0.885	0.904	3.883	2.270	4.095
MIN	7.250	3.270	16.550	11.780	43.660
MAX	9.770	5.550	27.970	18.550	55.650
Site C					
MEAN	8.309	3.918	19.879	15.226	50.260
STD	0.867	1.158	3.269	2.404	4.891
MIN	7.250	2.540	15.650	11.780	39.650
MAX	9.750	5.550	25.540	19.560	55.650
Site D					
MEAN	8.454	4.549	20.066	14.935	49.785
STD	0.983	0.895	4.183	2.827	4.345
MIN	7.250	3.330	14.550	11.550	43.560
MAX	9.850	5.550	26.750	19.540	54.550
Site E					
MEAN	8.311	4.145	20.309	16.169	49.648
STD	0.870	1.148	3.361	4.198	5.322
MIN	7.250	2.540	15.650	11.780	39.650
MAX	9.770	5.550	25.540	25.890	55.650
All sediment samples					
MEAN	8.324	4.172	20.704	15.274	50.169
STD	0.860	1.093	3.596	2.912	4.553
MIN	7.250	2.200	14.550	10.550	39.650
MAX	9.850	5.550	27.970	25.890	55.650
Control					
MEAN	1.911	0.445	2.109	1.869	4.848
STD	0.859	0.167	0.499	0.397	0.741
MIN	0.770	0.120	1.550	1.540	3.650
MAX	3.720	0.650	2.880	2.890	5.650

Table 3. Summary Level of Toxic Metal (mg/L) in Water samples from sites and in control from river Kaduna.

Toxic metals	Water		Control	
	Mean±S.D	Range	Mean±S.D	Range
As	0.189±0.108	0.013–0.420	0.004±0.001	0.001–0.011
Cd	0.215±0.271	0.002–0.880	N.D	N.D
Co	0.512±0.382	0.011–1.330	N.D	N.D
Cr	0.421±0.347	0.010–0.990	N.D	N.D
Pb	0.299±0.225	0.020–0.850	0.011±0.004	0.005–0.017

Table 4. *Summary Level of Toxic Metal (mg/g) in Sediment samples and in control sites from river Kaduna.*

Toxic metals	Sediment		Control	
	Mean±S.D	Range	Mean±S.D	Range
As	8.324±0.860	7.250–9.850	1.911±0.859	0.770–3.720
Cd	4.172±1.093	2.200–5.550	0.445±0.167	0.120–0.650
Co	20.704±3.596	14.550–27.970	2.109±0.499	1.550–2.880
Cr	15.274±2.912	10.550–25.890	1.869±0.397	1.540–2.890
Pb	50.169±4.553	39.650–55.650	4.848±0.741	3.650–5.650

Table 5. *Enrichment Factor in the Sediment and Water samples in the Study areas.*

Metals	Sediment	Water
As	4.356	47.250
Cd	9.375	21.500
Co	9.817	51.200
Cr	8.172	42.000
Pb	10.348	27.181

Table 6. *Elemental correlation between Sediment and Water samples.*

Metals	
As/As	0.007
Cd/Cd	0.267
Co/Co	− 0.184
Cr/Cr	0.163
Pb/Pb	− 0.058

Table 7. *Mean ±SD chemical speciation of As (mg/Kg) dry weight in sediments.*

SITES	Exchangeable	Oxidisible	Acid Soluble	Reducible	Residual	Σextracted metals	Nonresidual	Residual	Mobile Phase
KDA	4.36±3.36	17.81±6.73	31.25±6.72	115.29±6.73	N.D	165.74±20.99	97.04	2.96	19.80
KDB	N.D	17.81±3.36	34.61±6.73	135.45±3.37	17.81±3.36	211.68±5.83	91.67	8.33	16.67
KDC	17.81±3.36	41.34±6.73	15.05±0.01	121.45±6.73	14.45±3.37	206.10±13.45	93.44	6.56	15.05
KDD	18.93±3.88	34.61±6.73	19.96±3.96	175.79±6.72	5.48±1.94	249.77±8.48	98.21	1.79	14.77
KDE	4.36±3.06	48.06±6.72	17.81±2.36	125.37±6.72	14.45±3.37	205.05±3.36	93.44	6.56	9.84
KDF	7.72±6.73	68.23±6.73	12.75±6.04	103.25±4.44	7.72±3.36	195.67±7.25	96.55	3.45	9.49
KDG	14.45±3.37	81.67±6.72	34.61±6.73	81.67±6.72	21.17±6.72	229.57±3.36	91.18	8.82	20.59
KDH	4.36±3.06	31.25±6.72	27.89±1.36	98.48±6.72	7.72±3.36	165.70±10.08	95.92	4.08	18.37
KDI	8.45±5.68	14.45±6.73	41.34±6.73	68.23±3.36	14.45±3.37	142.91±5.67	90.52	9.48	33.67
KDJ	34.42±11.99	138.17±10.42	27.84±6.64	192.34±6.73	34.45±3.37	424.21±16.61	92.10	7.90	14.24

Table 8. *Mean ±SD chemical speciation of Cd (mg/Kg) dry weight in sediments.*

SITES	Exchangeable	Oxidisible	Acid Soluble	Reducible	Residual	Σextracted metals	Nonresidual	Residual	Mobile Phase
KDA	10.68±6.45	10.68±3.23	6.38±4.93	10.68±6.45	13.90±6.45	57.31±3.72	72.74	27.26	31.83
KDB	13.90±6.45	13.90±6.45	10.68±3.23	10.68±3.23	13.90±3.23	68.07±8.53	77.78	22.22	38.89
KDC	14.98±1.86	10.68±3.23	10.68±3.23	10.68±3.23	15.69±13.04	62.69±13.04	44.95	55.05	24.72
KDD	13.90±3.23	13.90±3.23	13.90±6.45	17.30±0.01	17.75±3.40	81.59±15.61	76.6	23.4	36.04
KDE	13.90±6.45	13.90±6.45	13.90±3.23	13.90±3.23	17.13±3.23	77.73±22.58	76.18	23.82	38.09
KDF	9.60±4.92	9.60±4.92	13.90±3.23	10.68±3.23	13.90±3.55	62.69±6.40	75.51	24.49	40.81
KDG	10.68±0.68	10.68±3.23	10.68±6.45	10.68±6.45	13.90±6.45	61.61±6.45	75.01	24.99	37.50
KDH	10.68±3.23	13.90±3.23	10.68±3.23	13.90±3.23	18.20±1.86	72.36±8.11	72.42	27.58	31.05
KDI	ND	4.23±3.23	6.05±0.01	8.68±3.23	10.90±6.45	35.80±11.63	61.72	38.28	19.53
KDJ	10.68±3.23	13.90±6.45	13.90±3.23	10.68±6.45	17.13±3.23	71.29±3.23	73.68	26.32	36.84

Table 9. *Mean ±SD chemical speciation of Co (mg/Kg) dry weight in sediments.*

SITES	Exchangeable	Oxidisible	Acid Soluble	Reducible	Residual	Σextracted metals	Nonresidual	Residual	Mobile Phase
KDA	N.D	N.D	41.82±3.34	166.19±9.52	259.42±9.99	446.42±20.12	44.13	55.87	9.14
KDB	N.D	N.D	N.D	4.82±0.96	8.88±0.67	12.70±0.99	32.65	67.35	ND
KDC	N.D	N.D	N.D	5.98±0.14	11.18±0.47	16.16±0.33	32.85	67.15	N.D
KDD	16.61±61	5.05±0.01	N.D	N.D	25.03±17.31	53.69±0.68	45.00	55.00	35.73
KDE	N.D	N.D	12.57±4.13	N.D	25.08±3.33	45.65±0.88	32.45	67.55	32.45
KDF	4.4±0.33	N.D	N.D	N.D	15.42±0.78	18.82±0.48	19.08	80.92	19.08
KDG	N.D	9.00±0.01	17.41±6.67	N.D	50.90±15.00	66.31±8.33	37.38	62.62	25.13
KDH	N.D	N.D	77.63±4.08	12.00±0.05	90.96±8.16	179.46±1.70	46.36	53.64	39.88
KDI	N.D	21.14±11.38	9.00±0.01	40.53±4.94	40.89±15.59	99.56±0.69	65.51	34.49	8.93
KDJ	N.D	N.D	6.31±1.50	9.91±1.00	67.67±4.42	81.88±4.65	17.58	82.42	6.56

Table 10. Mean ±SD chemical speciation of Cr (mg/Kg) dry weight in sediments.

SITES	Exchangeable	Oxidisible	Acid Soluble	Reducible	Residual	Σextracted metals	Nonresidual	Residual	Mobile Phase
KDA	9.57±4.08	75.08±9.29	23.04±4.08	66.71±4.09	203.45±18.37	372.85±9.09	45.70	54.30	8.21
KDB	25.49±8.16	54.06±4.08	33.65±8.17	17.33±4.09	227.53±1.48	354.06±2.39	35.84	64.16	16.18
KDC	N.D	37.73±8.17	17.33±4.09	13.24±4.09	189.67±4.09	258.98±12.25	26.23	73.77	6.56
KDD	17.33±8.17	21.41±8.17	33.65±4.08	N.D	54.06±24.83	133.44±24.82	56.67	43.33	40.00
KDE	N.D	31.48±0.65	31.16±0.08	31.08±0.58	113.90±4.33	205.64±4.08	44.55	55.45	14.81
KDF	8.24±8.17	87.12±0.25	83.04±8.16	46.39±8.17	246.59±4.49	467.39±8.93	47.34	52.66	19.14
KDG	21.41±4.08	173.79±44.02	74.47±16.33	41.82±8.17	205.08±8.63	513.57±8.47	60.11	39.89	18.35
KDH	5.08±4.08	152.02±8.16	98.96±8.16	82.63±4.08	29.57±8.16	365.26±16.32	92.14	7.86	28.09
KDI	58.14±4.08	51.31±2.38	10.68±0.01	39.71±6.13	85.29±1.78	245.13±0.26	64.90	35.10	27.83
KDJ	9.16±4.08	39.51±11.96	29.57±8.16	41.48±0.85	182.48±4.29	298.20±15.92	38.94	61.06	12.36

Table 11. Mean ±SD chemical speciation of Pb (mg/Kg) dry weight in sediments.

SITES	Exchangeable	Oxidisible	Acid Soluble	Reducible	Residual	Σextracted metals	Non residual	Residual	Mobile Phase
KDA	161.00±20.00	42.68±2.29	N.D	132.67±12.58	246.27±12.93	579.62±12.62	57.61	42.39	27.65
KDB	N.D	46.57±8.87	44.20±5.72	61.47±17.61	124.33±10.41	272.57±33.00	54.75	45.25	15.85
KDC	N.D	N.D	N.D	21.25±4.49	20.65±0.01	41.90±4.49	50.75	49.25	N.D
KDD	161.00±2.05	146.30±12.89	43.42±3.76	81.00±0.05	124.64±3.16	552.36±8.94	77.58	22.42	36.71
KDE	74.36±7.65	57.04±3.60	47.69±16.11	54.33±10.41	141.20±17.45	379.62±23.15	62.07	37.93	32.48
KDF	13.11±6.13	N.D	13.13±3.27	N.D	13.53±3.42	38.77±3.83	65.92	34.08	65.92
KDG	81.00±4.00	219.33±10.07	139.90±18.43	45.87±4.24	266.00±13.23	759.10±6.78	64.15	35.85	29.75
KDH	N.D	41.03±4.96	45.30±6.08	54.80±7.27	78.27±7.51	217.40±9.21	64.13	35.87	20.57
KDI	51.04±10.04	106.00±5.00	79.15±0.40	162.99±2.70	162.99±2.70	447.18±14.90	62.95	37.05	29.32
KDJ	N.D	81.30±4.56	108.90±2.70	220.50±10.00	221.50±10.01	570.47±14.10	60.66	39.34	19.25

Table 12. Mean ±SD chemical speciation of metals (mg/Kg) dry weight in the control site.

SITES	Exchangeable	Oxidisible	Acid Soluble	Reducible	Residual	Σextracted metals	Nonresidual	Residual	Mobile Phase
Cd	1.05±3.23	N.D	N.D	N.D	4.90±1.75	5.95±13.65	17.65	82.35	17.65
Co	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D
As	3.72±3.36	1.36±6.73	7.08±3.37	13.61±3.36	32.81±6.73	58.58±3.37	76.77	23.23	18.44
Pb	N.D	4.34±5.42	1.68±5.03	2.06±0.01	9.96±2.86	21.04±6.25	52.66	47.34	7.98
Cr	N.D	3.24±2.13	3.49±2.08	4.65±3.20	22.48±1.80	33.86±6.81	33.61	66.39	10.31

Note: N.D = Not Detected

4. Discussion

In both samples (water and sediment) from the study areas (Kaduna metropolis), the concentrations of the heavy metals were high especially Pb, Co, Cr and As. This is an indication that these heavy metals are contaminant in the water and sediments samples studied in the river Kaduna within Kaduna metropolis which was also reflected in the low level of these heavy metals obtained from the control sites in comparison with those obtained from the study sites. Also, the degrees of heavy metals pollution in water and sediment samples which were determined by its enrichment factors were also high (Table 5). The toxic metal content of water and sediment samples from the study areas have been found to enrich by a factor of 47.250, 21.500, 51.200, 42.000 and 27.181 for As, Cd, Co, Cr and Pb in water sample, while in the sediment samples have been found to enrich by a factor of 4.356, 9.375, 9.817, 8.172 and 10.348 for As, Cd, Co, Cr and Pb respectively. This could be attributed to the industrial waste and effluent discharge into the river from nearby industries, application of organic and inorganic manures, and chemical additive on the farm land including atmospheric deposition of metal/metalloid-bearing particles. Virtually all the metals determined in the water samples have concentration lower than the level in the sediment samples. This may be attributed to the fact that not all metals in the sediments are soluble in the water. Again apart from heavy metals added as a result of the natural soil geochemical composition of an aquatic environment, both solubilised and non-solubilised toxic metals and other contaminants can be transferred into the aquatic system by runoffs from contaminated soil sites, industrial sites and agricultural farmlands, and through atmospheric deposition which can be retained in the sediments. The types of contaminants brought into the aquatic ecosystem are largely influenced by the kind of anthropogenic activities embarked upon within the surrounding areas. This may bring out the different in level of heavy metals in the sediment and water samples from the

same source (Odoh *et al* 2014).

The relationship between heavy metals concentration in the water and sediment samples from the same source was determined using Pearson correlation coefficient (Table 6). The following results were obtained; 0.007, 0.267, – 0.184, 0.163 and – 0.058 for As, Cd, Co, Cr and Pb respectively these results indicated that Cd and Cr in water and sediment samples correlated positively. The negative correlation recorded for Co and Pb in the water and sediment samples indicated that as the concentration of Co and Pb in sediment increases, the rate of its in water decreases, the rate of dissolution of metal in water could be affected by other environmental factors such as PH, exchange and binding capacities might have contributed to their low transfer rates between the sediment and water sample (Alloway and Ayres, *1997*).

B. Distribution of Heavy Metals in the Operationally Defined Geochemical Fractions

The sequential extraction scheme is useful in assessing the mobility and bioavailability of heavy metals in the sediments. The results of the sequential extraction of As, Cd, Co, Cr and Pb in sediments samples of study sites were presented in Tables (7–11). All the metals studied were found in all the operationally defined geochemical fractions. The result of the speciation analysis of the metals is given in Table (7–11) and Table 12 represents the control result.

Arsenic: The results of the sequential extraction of Arsenic in the sample of sediments are shown in Table 3. High percentage of arsenic was observed in the reducible phase in all the sediment samples studied. This may be due to the precipitation of amorphous hydrous oxides of arsenic during ageing of the sediments (Stumm and Morgan *1981*). The order of availability of this metal in different fractions followed the pattern:

Reducible > Oxidisible > Acid soluble > Residual > Exchangeable

The concentration obtained in this study was consistent with the background concentration for uncontaminated sediments (5–500 mg/g, 90.52 to 98.12% of the extractable metal was found in the non–residual fraction. The potential mobility and bioavailability amongst the sediments followed the pattern:

KDI > KDG > KDA > KDH > KDB > KDC > KDD > KDG > KDE > KDF.

Cadmium: The results of the sequential extraction of Cd are presented in Table 7. Total extractable cadmium was found to be above the critical permissible concentration of 3.00 mg/Kg set by the European Commission (Xian *1989*). It was also found to be above levels naturally obtainable in uncontaminated sediments and soils. As revealed from the study area, metal scraps, used batteries, mechanic workshops etc were being dumped from industrial and residential areas which might have contributed to the large concentration of the metal in the sediment samples. The mobile phase contained 19.5 to 40.81% of the total extractable fraction of the metal which indicate that this metal will be readily bio available to the environment. The availability of this metal in

the sequentially extracted fractions follows the order,

Residual > Exchangeable = Oxidisible = Reducible > Acid Soluble.

The potential mobility and bioavailability of this metal in the sediment samples of the study areas were found to be in the order;

KDF > KDB > KDE > KDG > KDJ >KDD > KDA > KDH > KDC >KDI.

The presence of appreciable percentage of the total extractable fraction in the mobile phase suggested that Cd in this sediment was potentially more bio available for plant uptake and other aquatic organism's uptake (Xian *1989*). The above trend may be attributable to element are dumped on daily basis in addition to cadmium containing waste batteries dumped from the nearby industries, residential areas and other activities such as mechanic workshops near and along the river bank.

Cobalt: The concentration is the five fractions for the sediment samples of the ten studied sites are presented in Table 8. The level of cobalt in all the sediment samples studied were below the toxic limit of 140.00 mg/kg (EU, *1986*) with the exception of KDH and KDA sediment samples. Sediment samples of KDD, KDE, KDD and KDG have reasonable percentage of the total extractable fraction in the mobile phase. Thus, cobalt in these sediment samples were more bio available than in other sediments.

The potential bioavailability of the metal was in the following order;

Residual >Oxidisable > Reducible >Acid solubl > Exchangeable.

Among the non–residual fraction cobalt was mostly associated with the reducible fraction in KDH and KDR samples. This implies that it will only be released under extreme conditions for the plant uptake and other aquatic organisms. The metal was also found to concentrate in the last four fractions in all the sediments which is consistent with the findings of similar works (Gupta and Chen *1975*). More than 50% of the total extracted fractions in all the sediments were present in the residual fraction with the exception of KDC sediment. Moreover, significant amount of cobalt was associated with the oxidisible fraction. The major association of cobalt with organic fraction in these sediments may be due to high formation constant of organic cobalt complexes (Hickey and Kittrick *1984*).

Chromium: The extractable fractions of Cr in most of the sediments samples were above the EC (*1986*) threshold limit. The result also indicated that the non- residual fraction of the metal to be >35% in almost all the sediments except site KDC. The mobile phase contained between 7 to 40%, indicating that the metal will be readily bio available to the environment. The potential availability of this metal in different fractions were

Residual > Oxidisable > Acid soluble > Reducible > Exchangeable.

Similarly, the order of mobility and bioavailability of the metal amongst the sediments were

KDD >KDH > KDR > KDF > KDG > KDB > KDE >

KDJ > KDA > KDC.

Among the non–residual fractions, the reducible fraction for KDE and KDJ contained the highest amount of Cr in all the sediments. These may be partially due to high stability constants of chromium oxides. However, some researchers, Kabata– Pendias and Pendias (1984), (Kuo *et al 1983*), found Cr to be associated with reducible fraction.

Lead: Table 11 contained the results of the sequential extraction of lead in the sediment samples. More than 50% of this metal was found to be in the non–residual fraction while 15.85 to 65.92% of the total extractable fraction contributes to the mobile phase (exchangeable and acid soluble). This indicates that the potential availability of this metal in the extracted fractions was

Residual > Reducible > Oxidisible > Acid extractable > Exchangeable

The order of mobility among the sediment was

KDF > KDD > KDE > KDG > KDI > KDA > KDH >KDJ >KDB > KDC.

Only KDF, KDH, KDC and KDB sediment samples did not exceed the toxic limit of 300.00 mg/kg by European commission, and other researchers have reported similar results (Staclens *et al 2000*). Based on the mobile fraction, none of the sediment samples is at risk for lead contamination but it will be readily bio available for plant and aquatic organisms uptake.

The extractable fractions of all the metals (As, Cd, Co, Cr and Pb) for the control site are shown in Table 6. The total extracted fractions for all the metals were below the EC, (*1986*) limit and the natural background concentration for uncontaminated soil. More than 50.00% of Pb and As were present in the non- residual fraction out of which 7.98 and 18.44% were the mobile fractions. Arsenic was found to be the most bio available metal having 18.44% of the metal ion in the mobile phase, followed by cadmium with 17.65%, chromium (10.31%), Pb (7.98%) and lastly, Co (0.00%). The availability of these materials in different fractions was:

As: Residual > Reducible > Acid soluble > Exchangeable> Oxidisible.

Cd: Residual > Exchangeable > Oxidisible = Acid soluble = Reducible.

Co: Residual = Reducible = Acid soluble = Oxidisible = Exchangeable.

Cr: Residual > Reducible > Acid soluble > Oxidisible > Exchangeable.

Pb: Residual > Oxidisible > Reducible > Acid soluble > Exchangeable.

The differences in the distribution patterns can be attributed to possible mobilization of the metals. The greater percentage of chromium (66.39%) in the residual fraction probably reflects the greater tendency of chromium to become unavailable once it is in the environment (soils), (Gupta and Chen *1975*) and others reported similar results.

5. Conclusion

Water and sediment samples show higher concentrations of the toxic metal determined as compared to the toxic metals from control areas indicating the presence of contaminants particles in the area. Excess of these heavy metals in the water and sediment, from the sample sites, as opposed to the average levels of toxic metals in control sample account for incorporation of industrial, commercial and agricultural activities in the studied areas. Among all the metals analyzed, Co was the highest and As was the lowest in absolute concentration in the water sample while Pb was the highest and Cd was the lowest in the sediment sample of the study area. Cr, Pb, and Cd contribute significant quantities in the exchangeable and acid extractable fractions (mobile phase), making them easily bio available. In the case of As and Co, residual fractions contributed the maximum, which is inert form and hence the environmental effect may not be significant. The distribution of the metal concentration of the water and sediment samples in the study area indicated that the area has been affected by anthropogenic activity, in particular the industries, farm land, leading to a high accumulation of toxic metals in the water and sediment from river Kaduna within Kaduna metropolis as compared with the water and sediment from control areas.

The study also showed that the sediment samples contained these toxic metals in various concentrations in different chemical form as a result of effluents discharging into the river from industrial and other human activities, and this was not unexpected since sediment has been described as reservoir of pollutants where they concentrate according to the level of pollutant (Alloway and Ayres 1997), (Becker *et al, 2000*). Detection of these heavy metals especially Cd and Co at higher concentrations in sediment samples calls for sustained monitoring since transfer of metals across the food chain and accumulation are most probable with resultant health problems.

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