

Environmental Effect of Dredging and Geochemical Fractionation of Heavy METALS in Sediments Removed from River

Ogbu Victor, Osu Charles Ikenna*, Iwuoha Godson Ndubuisi

Department of Pure and Industrial Chemistry, Faculty of Science, University of Port Harcourt, Port Harcourt, Nigeria

Email address:

charsike@yahoo.com (O. C. Ikenna)

*Corresponding author

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Abstract: Geochemical fractionation of six heavy metals; Zn, Pb, Cd, Cu, Cr, and Ni in soil from two dredging sites at Chokocho and Umuechem communities in Etche Local Government Area of Rivers State, Nigeria, which is characterized by domestic, oil exploration and other industrial activities. The heavy metal concentration determined were 26.30 ± 0.38 mg/kg, Pb; 10.60 ± 0.04 mg/kg, Cd; 486.00 ± 1.20 mg/kg, Zn; 35.50 ± 0.30 mg/kg, Cr; 43.50 ± 0.40 mg/kg, Ni and 37.70 ± 0.10 mg/kg, Cu for Chokocho site. For Umuechem site, the concentration of the metals revealed were 18.40 ± 0.10 mg/kg, Pb; 6.80 ± 0.70 mg/kg, Cd; 437.00 ± 0.60 mg/kg, Zn; 29.30 ± 0.20 mg/kg, Cr; 36.40 ± 0.10 mg/kg, Ni; and 28.30 ± 0.20 mg/kg, Cu. Results from umuechem site was greater than Chokocho site. Heavy metal fractionation using conventional method was adopted for sequential extraction which was accomplished in five steps. Results revealed that Cd and Pb were dispersed more at exchangeable phase in the sample; Cu and Zn were the least bioavailable. Cd, Pb, and Cr show health risks because of high percent in the exchangeable or dissolved fraction. The results of the analysis also revealed that the bioavailability and mobility of the heavy metals were in order; $Cd > Pb > Cr > Ni > Zn > Cu$.

Keywords: Dredging, Geochemical Fraction, Contamination, Pollution

1. Introduction

Dredging is a worldwide excavation activity that involves removing sediment from a sea, river, or lakebed and depositing it at a new location. Uses are vast and include construction of ports, waterways, dykes, and other marine infrastructure, land reclamation, flood and storm protection, extraction of mineral resources to provide material for the construction industry (e.g. for road construction), and in environmental remediation of contaminated sediments [1, 2, 3, 4]. Dredging can also be described as the process of removing part of the seabed or its overlying sediments with the aim of deepening the area commonly for the purpose of navigation or associated with construction projects. Dredging is an excavation activity usually carried out underwater, in shallow seas or freshwater areas with the purpose of gathering up bottom sediments and widening. This technique is often used to keep waterways navigable and creates an

anti-sludge pathway for boats. It is also used as a way to replenish sand on some public beaches, where sand has been lost because of coastal erosion. Fishing dredges are used as a technique for catching certain species of edible clams and crabs. A variety of harmful substances, including heavy metals can be effectively locked into the seabed sediments. The dredging and disposal processes can release these contaminants into the water column, making them available to be taken up by animals and plants. These contaminants can often be of historic origin and from distant sources. The dredging and disposal processes can release these contaminants into the water column, making them available to be taken up by animals and plants, with the potential to cause contamination and/or poisoning.

Some portion of the total quantity of pollutant present in soil is potentially available for uptake by organisms. This

concept is referred to as the biological availability (or bioavailability) of a chemical [5, 6]. Bioavailable fraction is defined as the fraction of the total amount of a chemical present in a specific environment within a given time span, is either available or can be made available for uptake by organisms or plants, or by ingestion of food [7, 8] have defined 'bioavailable fraction' as the extent to which a chemical can be absorbed by a living organism and reach the systemic circulation. Metal bioavailability in soil is largely dependent on the partition of the metals between the solid and solution phases.

Release of contaminants associated with dredging can occur in particulate, dissolved or volatile fractions, each characterized by differing transport exposure pathways [9]. When sediments contaminated with heavy metals are dredged, their interactions with iron chemistry may temporarily prevent the partial dispersion of their dissolved form. Concentration of the contaminants exhibit great variations in their distribution due to variation in the dredging operations and dilution by turbulent diffusion in the water column [10]. The degree of contamination of sediments clearly plays a very important role in determining the significance of any mobilization of contaminants from those sediments. The majority of metals were bound to particulate matter such as clay minerals, Fe and Mn oxides/hydroxides, carbonate, organic substances [11]. Bioavailability with respect to dredge related bioavailability is mainly site specific and dependant on the degree of contamination, the amount of suspended sediment, the duration of the disturbance and the organism [12].

Most sequential extraction procedures follow similar fractional degradation with little variation. [13] Extracted the exchangeable and carbonate-bound fractions in a single step versus the two steps used in the Tessier procedure. Sequential Extraction Procedures with greater fractions include the procedure developed by [14] which included EDTA extractable, moderately reducible, and strongly reducible fractions for a total of seven; and that by [15] which consisted of nine fractions designed to test waste amended and agriculturally polluted sediments.

The theory behind sequential extraction procedures is that the most mobile metals are removed in the first fraction and continue in order of decreasing of mobility. All sequential extraction procedures facilitate fractionation. [16] named these fractions exchangeable, carbonate bound, Fe and Mn oxide bound, organic matter bound, and residual. These are also often referred to in the literature as exchangeable, weakly absorbed, hydrous-oxide bound, organic bound, and lattice material components, respectively. [13] extracted the exchangeable and carbonate-bound fractions in a single step versus the two steps used in the Tessier procedure. This paper investigates the environmental effect of dredging and geochemical fractionation of heavy metals in sediments removed from river by dredger.

2. Material and Methods

2.1. Sample Collection and Preparation

The soil samples were collected in March/April, 2017 from two different sampling points at 0 to 60 cm depth using soil auger in Etche Rivers State, Nigeria. The samples were air dried and grounded to fairly uniform size and sieved with 2 mm sieve. The samples were stored in a clean polyethene bag and labeled A1 and A2 respectively. Where A1 and A2 represents Chokocho sand dump and Umuechem sand dump respectively all in Etche L.G.A of Rivers State, Nigeria.

2.2. Single Extraction

The single extraction method was adopted after [17]. 5 g sample was extracted with 50 ml water and 0.05M EDTA (pH 7.0), respectively in a shaker for one hour at 25 °C and centrifuged. The supernatants were carefully transferred to plastic bottles and analyzed for metal contents using Flame Atomic Absorption Spectrometry (FAAS). UNICAM SOLAAR 32.

2.3. Heavy Metal Fractionation

The conventional method developed by [16] was followed for the sequential extraction. The sequential extraction process was accomplished in five steps.

Extractions were carried out on 1.0 g aliquots of soil and involved the five following steps [16, 18, 19]:

- (1) F1. Exchangeable fraction: the sample was placed in contact with a high ionic strength solution, in order to release the so-called exchangeable fraction of metal traces by altering the sorption-desorption superficial processes. In this step 8 ml of 1 N MgCl_2 were added to the sample and the suspension was shaken for 1 h.
- (2) F2. Fraction bound to carbonates: the fraction of metal traces bound to carbonates, present in the sample, may be selectively labialized by varying the pH of the sample itself with a slightly acidic extraction solution. 8 ml of 1 M of CH_3COONa , plus CH_3COOH (pH 5) were added to the residue obtained from the first extraction, and the suspension was shaken for 5 h.
- (3) F3. Fraction bound to iron and manganese oxides: this fraction may be labilised in anoxic reducing conditions. Therefore, 20 ml of 0.04 M $\text{NH}_2\text{OH}/\text{HCl}$ in 25% CH_3COOH were added to the residue and the suspension was shaken for 6 h at the temperature of 96 °C.
- (4) F4. Fraction bound to organic matter and to sulphides: this fraction can be released by treating the sample with an oxidising agent. 3 ml of 0.02 N HNO_3 and 5 ml of 30% H_2O_2 were added to the residue obtained from the third extraction, and the suspension was shaken for 5 h at the temperature of 85 °C. After cooling, 5 ml of 3.2 M $\text{CH}_3\text{COONH}_4$ were added to the suspension, which was diluted to 20 ml with HPW and shaken for 30 min.
- (5) F5. Residual fraction: it is the metal fraction present as scatter within the crystal lattice of the rocks and

minerals that constitute the soil. It was calculated from the difference between the concentration of total metal and the sum of the first four fractions.

3. Results and Discussion

Table 1. Concentration of total heavy metals (mg kg⁻¹) in sediments from Etche dredging sites.

Metals	A1	A2
Pb	18.40 ± 0.10	26.30 ± 0.30
Cd	6.80 ± 0.70	10.60 ± 0.04
Zn	437.00 ± 0.60	486.00 ± 1.20
Cr	29.30 ± 0.20	35.50 ± 0.30
Ni	36.40 ± 0.10	43.50 ± 0.40
Cu	28.30 ± 0.20	37.70 ± 0.10

Results = mean ± S.D of three determinations

The results of concentration of metals in soil samples were presented in table 1. The total concentration of heavy metals studied ranged between 18.40 ± 0.10 to 26.30 ± 0.30, 6.80 ± 0.70 to 10.60 ± 0.04, 437.00 ± 2.10 to 486.00 ± 1.20, 29.30 ± 0.20 to 35.50 ± 0.30, 36.40 ± 0.10 to 43.50 ± 0.40 and 28.30 ± 0.20 to 37.70 ± 0.10 for lead, cadmium, zinc, chromium, Nickel and copper respectively. The concentration pattern was observed as: Zn > Ni > Cu > Cr > Pb > Cd. A2 had the highest concentration of metals (26.30 ± 0.30, Pb; 10.60 ± 0.04, Cd; 486.00 ± 1.20, Zn 35.50 ± 0.30, Cr, 43.50 ± 0.40 Ni and 37.70 ± 0.10 Cu) compared to A1 (18.40 ± 0.10, Pb; 6.80 ± 0.70, Cd; 437.00 ± 2.10, Zn; 29.30 ± 0.20, Cr; 36.40 ± 0.10, Ni and 28.30 ± 0.20, Cu). The high level of Pb in these samples indicates the disposal of Pb batteries; chemicals from industrial and domestic waste were discharged into the river.

Table 2. Concentration of heavy metal extracted from sediments by water and EDTA single extraction.

Metals	A1		A2	
	Water extractable (mg kg ⁻¹)	EDTA extractable (mg kg ⁻¹)	Water extractable (mg kg ⁻¹)	EDTA extractable (mg kg ⁻¹)
Pb	2.40 ± 0.03	5.20 ± 0.03	3.69 ± 0.03	7.05 ± 0.01
Cd	0.90 ± 0.08	2.85 ± 0.04	1.45 ± 0.01	4.40 ± 0.05
Zn	1.80 ± 0.01	22.40 ± 0.01	3.10 ± 0.03	30.40 ± 0.04
Cr	0.80 ± 0.002	2.60 ± 0.09	1.90 ± 0.01	4.30 ± 0.01
Ni	6.70 ± 0.10	14.80 ± 0.02	3.80 ± 0.02	15.40 ± 0.08
Cu	1.40 ± 0.02	4.60 ± 0.01	2.01 ± 0.07	6.70 ± 0.07

Results = mean ± S.D of three determinations

Table 3. Percent of total heavy metal extracted from sediments by water and EDTA single extraction.

Metals	A1		A2	
	Water extractable	EDTA extractable	Water extractable	EDTA extractable
Pb	13.04	28.26	14.03	18.54
Cd	13.24	41.91	13.68	41.51
Zn	0.41	5.13	0.64	6.26
Cr	2.73	8.87	5.35	12.11
Ni	18.41	40.66	8.74	35.40
Cu	4.95	16.25	5.33	17.77

Water and EDTA extractable metals and their percentage extractable metals were presented in table 3. Water extractable phase contains most mobile and bio-available metals [20, 35], whereas EDTA is capable of extracting metals in non-silicate bound phase. The percentage of water extractable fraction of metals was less with the range of 13.04 to 14.03 %, Pb; 13.24 to 13.68 %, Cd; 0.41 to 0.64 %, Zn; 2.73 to 5.35 %, Cr; 18.41 to 8.74, Ni and 4.93 to 5.33 %, Cu. EDTA extracts higher

percentage of metals from soils compared to water and ranged from 28.26 to 18.54 %, 41.51 to 41.91 %, 5.13 to 6.26 %, 8.87 to 12.11 %, 40.66 to 35.40 % and 16.25 to 17.77 % for Pb, Cd, Zn, Cr, Ni and Cu respectively. [5, 20, 21] reported that water is less capable in extraction of metals, but the presence of chelating agents (such as soluble organic species) increases the metals extractability and their bioavailability. Results of present study are similar to results obtained by [20] and [21].

Table 4. Fractionation of heavy metals (mg. Kg⁻¹) in different geochemical fractions of Soil from Etche dredging sites A1.

	Pb	Cd	Zn	Cu	Cr	Ni
F1	8.430	4.600	26.490	1.690	8.300	24.500
F2	1.100	2.000	94.300	3.010	4.100	2.100
F3	5.200	0.140	166.800	5.600	14.360	8.200
F4	3.200	ND	104.600	14.400	0.640	1.200
F5	0.500	0.060	34.810	3.600	1.900	0.400
SUM	18.400	6.800	437.000	28.300	29.320	36.400

Results = mean ± S.D of three determinations.

Table 5. Fractionation of heavy metals (%) in different geochemical fraction of Soil from Etche dredging sites A1.

	Pb	Cd	Zn	Cu	Cr	Ni
F1	45.82	67.65	6.06	5.97	28.31	67.31
F2	5.98	29.41	21.58	10.64	13.98	5.77
F3	28.26	2.06	38.20	19.79	48.98	22.53
F4	17.39	-	23.94	50.88	2.18	3.30
F5	2.72	0.88	7.97	12.72	6.48	1.10
SUM	100.17	100	97.75	100	99.93	100.01

Table 6. Fractionation of heavy metals (mg. Kg⁻¹) in different geochemical fractions of Soil from Etche dredging sites A2.

	Pb	Cd	Zn	Cu	Cr	Ni
F1	12.400	6.300	32.400	2.700	9.600	27.000
F2	2.100	3.600	110.500	4.300	5.400	3.600
F3	7.400	0.090	180.700	8.300	16.100	9.400
F4	4.000	ND	120.300	16.600	1.800	2.100
F5	0.400	0.610	42.100	5.800	2.600	1.400
SUM	26.300	10.600	486.000	37.700	35.500	43.500

Results = mean ± S.D of three determination

Table 7. Fractionation of heavy metals (%) in different geochemical fractions of Soil from Etche dredging sites A2.

	Pb	Cd	Zn	Cu	Cr	Ni
F1	47.15	59.43	6.67	7.16	27.04	62.07
F2	7.98	33.96	22.74	11.41	15.21	8.28
F3	28.14	0.85	37.18	22.02	45.35	21.61
F4	15.21	-	24.75	44.03	5.07	4.83
F5	1.52	5.75	8.66	15.38	7.32	3.22
SUM	100	99.99	100	100	99.99	100.07

Geo-Chemical partitioning of heavy metals were presented in table 5 and 7, which provides information on the partitioning of metals into different sediment fractions and can be useful in the understanding of mobility and bioavailability [5]. The study of the distribution of the metals revealed that all the metals are associated with different phase. Zn and Cr are mostly abundant bound to Iron and Manganese oxides with results ranging from 38.20 to 37.18 % and 48.98 to 45.35 % respectively (table 5 and 7). The percent fractions for other metals ranged from 2.72 to 45.82 %, Pb; 0.88 to 67.65 %, Cd; 6.06 to 38.20 %, Zn; 5.97 to 50.88, Cu; 2.18 to 48.98 %, Cr and 1.10 to 67.31 %, Ni for sample A1 and 1.52 to 47.15 %, Pb; 0.85 to 59.43 %, Cd; 6.67 to 37.18 %, Zn; 7.16 to 44.03 % Cu; 5.07 to 45.35 %, Cr; and 3.22 to 62.07 %, Ni for sample A2 This is in agreement with [23, 24, 35]. Fe-Mn oxide minerals have relatively large area and surface site density [24]. The Fe-Mn oxide, the reducible phase of the soil under oxidizing conditions is a significant sink for the heavy metals. The association of higher concentration of metals with this fraction is caused by adsorption of these metals by the Fe-Mn mineral surface [25].

The results of sequential extraction in this study revealed that copper is mostly (50.88 to 44.03 %) abundantly bound to organic matters. Other metals have percent fraction that ranged from 15.21 to 17.39 %, Pb; 24.75 to 23.94 %, Zn; 2.18 to 5.07 %, Cr; 3.30 to 4.83 %, Ni and Zero percent for Cd. Copper can easily complex with organic matters because of high formation of organic-Cu compounds [26]. Heavy metals with high abundance in the phase bound to Organic matter are more available than heavy metals in the residual fraction. The organic phase is relatively stable in nature but

can be mobilized under strong oxidizing conditions due to degradation of organic matter [16, 26]. Organic matter plays an important role in the distribution and dispersion of metals by mechanisms of chelating and cation exchange. In this phase a reaction between a metal ion and an organic ligand leading to a species which can either precipitate directly or be adsorbed on soil materials. Carboxyl, phenolic, hydroxyl and carbonyl functional groups are assumed to be primarily responsible for metal binding [23, 5, 20, 27]. Metal humic complexes are reversible, and metals can be desorbed by salting out or by hydrogen ion competition. The organic fraction of metals is not considered very mobile or available because of its association with high molecular weight stable humic substances.

Cd and Pb are distributed more at the exchangeable phase in the entire sample with the fractions that ranges from; 59.43 to 67.65 %, Cd and 45.82 to 47.15 %, Pb. Other metals have a lower percent of exchangeable phase which ranged from 6.67 to 6.06 %, Zn; 5.97 to 7.16 %, Cu; 27.04 to 28.31 %, Cr and 62.07 to 67.31 % Ni (table 5 to 7). High levels in the exchangeable, acid soluble and easily reducible fractions may indicate pollution from anthropogenic origin [23, 5, 28, 29]. Heavy metals in the exchangeable fraction held by electrostatic adsorption represent the most mobile and readily available for biological uptake in the environment, thus this fraction can be regarded as a pollution indicator [30]. The concentration of metals in this phase indicates the environmental impact. In this study, the Zn and Cu associated with this fraction are the least. Therefore, we conclude that the exchangeable fraction of Zn and Cu is least bioavailable and on the other hand Pb, Cd and Cr show

health risks because of high percent in the exchangeable or dissolved fraction.

These heavy metals, as shown in table 5 and 7 had the lowest abundance in the Residual fraction which ranged as follows: 1.52 to 2.72 %, Pb; 0.88 to 5.75 %, Cd; 7.97 to 8.06 %, Zn; 12.72 to 15.38 %, Cu; 6.48 to 7.32 %, Cr and 1.10 to 3.72 %, Ni. This is in agreement with [5, 23]. 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 and vice versa [33]. In this study it was found that the percentage of these metals present in the residual fraction is the lowest which indicate that the samples are highly polluted with the metals. It also concerned with the most stable and least bioavailable of all the chemical fractions of the soil and sediments, since it is believed that metals are occluded within the crystal lattice of silicates and well crystallized oxide minerals [31, 20]. The residual phase represents metal largely embedded in the crystal lattice of the soil fraction and should not be available for remobilization except under very harsh considerations. The residual fraction is a major carrier of metals in most environmental systems. The relatively small amount of heavy metals in this fraction indicates their high mobility and therefore high environmental contamination risk to rivers and dredged soils in Niger Delta region of Nigeria. The speciation pattern of the carbonate fraction suggests greater environmental risks of Cd with fraction ranging from 33.96 to 29.41 %. The distribution of metals in the samples studied area generally followed the order below for the various metals;

F1: Cd > Ni > Pb > Cr > Zn > Cu
 F2: Cd > Zn > Cr > Cu > Pb > Ni
 F3: Cr > Zn > Pb > Ni > Cu > Cd
 F4: Cu > Zn > Pb > Ni > Cr > Cd
 F5: Cu > Zn > Cr > Pb > Ni > Cd

Table 8. Mobility factor (%) and pH for the metals studied.

Metals	A1	A2
Pb	97.45	98.48
Cd	99.12	94.24
Zn	89.78	91.34
Cr	87.28	84.62
Ni	93.45	92.67
Cu	98.91	96.85
pH	5.60	6.50

Mobility of Pb, Cd, Zn, Cu, Cr and Ni in the studied samples were assessed on the basis of absolute and relative content of fraction weakly bound to soil components [32, 5, 23]. 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 [26]. The results showed that most fractions of all the investigated heavy metals were found in the potentially available form. The mobility factor gave values that ranged from 98.48 to 97.45 %, Pb; 99.12 to 94.24 %, Cd; 91.34 to 89.78 %, Zn; 87.28 to 84.62 %, Cr, 98.91 to 96.85 %, Cu and 93.45 to 92.67 % (table 8), which signified high stability and

as a result of relatively high liability and biological availability of the metals in the samples. The results of this study suggest that the mobility and availability of the metals are in the following order: Cd > Pb > Cu > Ni > Zn > Cu. This potential availability of the heavy metals indicates that metals have contamination risk in Etche rivers were sand are dredged for use in building which can contaminate water supplies and transferred to food chain.

4. Conclusion

The distribution of the metals in the various fractions confirmed differences in mobility of the metals studied, Cd appeared to be the most readily solubilized, thus making the metal the most potentially bioavailable. This may posed a threat as Cd is transferred into the food chain from soil contaminated by Cd. his potential availability of the heavy metals indicates that metals have contamination risk in Etche rivers were sand are dredged for use in building which can contaminate water supplies and transferred to food chain.

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