TOTAL CONCENTRATION, SPECIATION AND RISK ASSESSMENT OF HEAVY METALS (Mn AND Ni) IN SEDIMENTS AND WATER FROM HUNKI OX-BOW LAKE, NASARAWA STATE, NIGERIA

*1U. A. Augustine, 2T.A. Tor-Anyiin, 2R. Sha'Ato and 2R. A. Wuana

1*Department of Chemistry, Faculty of Science, Federal University, Lafia, Nigeria

2Department of Chemistry, College of Physical Sciences, Joseph Sarwuan Tarka University,

Makurdi, Nigeria

*Corresponding Author: abelloves@yahoo.com, uche.augustine@science.fulafia.edu.ng

ABSTRACT

This study aimed at geochemical risk assessment and determination of the total concentration and speciation of Mn and Ni in water and different sediments' particle sizes from Hunki Ox-bow Lake in Awe L.G.A of Nasarawa State, Nigeria, using Atomic Absorption Spectrophotometer during the dry and wet seasons. The mean concentration of Mn in whole (raw) sediment samples was higher than that of Ni irrespective of seasons. However, Ni was higher in water. Baseline levels of Mn and Ni in water samples (mg/L) were: Mn (0.129) and Ni (0.209) which revealed that Ni in water was higher than the WHO (2017) guidelines for drinking water quality. The baseline levels of Mn and Ni in sediment samples (mg/kg) were: Mn (75.085) and Ni (26.143) which showed that Ni was higher than interim sediment quality guidelines – low of 21 mg/kg but that of Mn was not specified. Results of the Tessier five-step sequential extraction procedure indicated that Mn dominated mostly the exchangeable fraction, while Ni dominated the residual fraction of the sediments more than other sequential extraction fractions in both seasons. This study revealed that Mn was more of ecological risk (more available to aquatic ecosystem) than Ni as affirmed by ecological risk indices evaluated.

KEYWORDS: Risk assessment, sediments, speciation, total concentration, water, Nasarawa State

INTRODUCTION

Heavy Metals, HM, can be broadly classified into two categories: essential and non-essential heavy metals. Essential HM like Cu, Mn, Ni, Fe, Co, and Zn are those required by organisms (plants and animals) for carrying out fundamental processes such as growth, metabolism, and development of different organs [1]. Non-essential heavy metals like Cd, Pb and Hg are not

required by organisms, even in trace amounts, for any of the metabolic processes. Essential or non-essential HM can cause serious adverse health effects on exposure at elevated amounts. Non-essential heavy metal ions are chemically similar to their essential metal counterparts and can have similar interactions with the proteins and pathways that regulate essential metal ions, although generally disrupting, rather than enabling these systems. Heavy metals are taken into the body by inhalation, ingestion and dermal routes [1]. These can be accumulated and stored in both soft and hard tissues of the body. Metals disrupt metabolic processes by altering a number of homeostatic processes including antioxidant balance, binding to free sulfhydryl groups, competing for binding sites on a vast array of enzymes, receptors and transport proteins. Nearly one-third of proteins require metals, with approximately 47% of enzymes in need of metals, and 41% requiring metals at their catalytic centers. Iron, copper, manganese, nickel and zinc are essential heavy metals and as such cells have mechanisms to acquire these nutrients from their extracellular environment. However, many of the transporters for these metals are hijacked by non-essential toxic heavy metals such as Cd, Pb, and Hg.

The human population is readily exposed to Mn (an essential HM) through soil erosion, resulting in the presence of Mn in food, air and waterways [2]. In its natural form in the environment, Mn exists usually as oxides, carbonates, and silicates, with Mn dioxide being the most commonly found natural form [2]. Manganese can bioaccumulate to a higher degree in the brain [2]. Cases of excess Mn exposure can arise from the environment, in both urban (steeling, mining, Methylcyclopentadienyl Manganese Tricarbonyl, MMT, in the air from gas combustion, etc.) and rural (agricultural runoff with pesticides and fertilizers) settings. Additionally, neonates (newborn baby) given Mn-supplemented total parenteral nutrition are also at risk for Mn intoxication, due to their undeveloped biliary system that does not allow for proper excretion [2]. A similar risk of Mn toxicity occurs in the patient population suffering from liver dysfunction or Fe deficiency. Severe Mn poisoning can result in an irreversible condition known as 'manganism,' a disorder that resembles the neurodegenerative movement disorder Parkinson's Disease (PD) in both symptomatology and shared cellular mechanisms in the same general brain region [2].

The chemical form of nickel (an essential HM) determines the route by which nickel enter the cells. Soluble nickel for example, nickel carbonyl is fat soluble and can freely cross cell membranes, most probably by diffusion or through calcium channels.

Some authors in fact suggested absorption of nickel by trans-membrane diffusion, whilst others proposed absorption of Ni(II) via Ca(II) channels [3]. The (+2) oxidation state "Ni(II)" is the most common form of nickel in biosystems.

Chemical and physical forces (e.g., erosion, leaching, and precipitation) constantly redistribute nickel between land, water, and air. Depending on the soil type and pH, nickel is highly mobile in soil. Based on laboratory studies, nickel probably does not accumulate in fish and there is little evidence for the bio-magnification of nickel in the food chain. Occupational exposure occurs in mining, alloy production, electroplating, refining and welding [3]. Epidemiological studies revealed an increased risk of respiratory tract and nasal cancers in miners and workers in nickel refineries [3]. Nickel can enter body via inhalation, ingestion and dermal absorption. The amount of nickel absorbed by the gastrointestinal tract depends on the type of nickel species in the food, the content and the absorptive capacity. Normally, only 1-2 % of ingested nickel is absorbed [3].

The main transport protein of nickel in blood is albumin, although a nickel containing (α2-macroglobulin), called nickeloplasmin, also transports nickel. Following exposure to nickel carbonyl, the highest concentrations of nickel appear in the lung, brain, kidney, liver, and adrenals. The biological half-life of nickel oxide in the lung depends, in part, on particle size and ranged from (11-21) months in animal studies. Nickel is not a cumulative metal; it is excreted well via urine and feces [3]. The urinary excretion of nickel is rapid and the elimination appears to follow first order kinetics without evidence of dose-dependent excretion of nickel. Following absorption, the kidney is the primary route of elimination. Excretion of nickel also occurs in the saliva and sweat, which may contribute significantly to the elimination of nickel in hot environments [3].

Based on the data obtained, two mechanisms for nickel-induced oxidative DNA damage have been proposed: (*i*) all the nickel compounds used induced indirect damage through inflammation, and (*ii*) Ni_3S_2 also showed direct oxidative DNA damage through H_2O_2 formation [3]. This double action may explain the relatively high carcinogenic risk of Ni_3S_2. This implies that a high content of nickel and its clearance from tissue is directly proportional to nickel carcinogenic activity [3].

Most analytical measurements deal with the total content of specific element in an analyzed sample (such as lead, mercury or cadmium as examples of toxic elements, or cobalt, selenium or magnesium as examples of essential elements).

The accumulations of heavy metals in sediments from both natural and anthropogenic sources occur in the same way, thus making it hard to identify and determine the origin of heavy metals present in the sediments [4]. Furthermore, the total concentration of metals often does not accurately represent their characteristics and toxicity. In order to overcome the above mentioned obstacles it is helpful to evaluate the individual fractions of the metals to fully understand their origin and potential environmental effects [5]. And this has to do with speciation analysis.

The speciation of an element is the determination of the individual physicochemical forms of that element which together make up its total concentration in a sample [6]. Many studies have been done on heavy metals speciation in aquatic sediments [5 - 9]. The aim of this study was to assess the total concentration and speciation of Mn and Ni in water and sediments from Hunki Ox-bow Lake.

The objectives of this research were to establish the baseline total levels of Mn and Ni in water and sediments, bearing in mind the seasonal variation, to assess the chemical speciation, to analyze sediments particle sizes and to assess the geochemical risk indices of Mn and Ni in sediments from Hunki Ox-bow Lake. Determination of total and individual fractions of Mn and Ni in water and sediments from the Lake will serve as a guide to assist in various remediation processes and also to create awareness about their exposure to the aquatic ecosystem. No speciation study on Mn and Ni has been done on Hunki Ox-bow Lake to the best of our knowledge.

MATERIALS AND METHODS

Chemicals and Apparatus

The reagents used were of analytical grades obtained from Sigma-Aldrich, Germany and M & B LTD, England. Some of the apparatus used for this research include: Oyster pH/Electrical Conductivity meter (Model: 34135A), a handheld Pometer pH meter (Model: PH-009 (III), Noki lab centrifuge (TG-16) Bioevopeak hot plate and stirrer (Model: MGS-M8), an atomic absorption spectrophotometer (ELICO PVT LTD, Model:SL168) and Decent mechanical sieve shaker (Model: DSS200).

Description of the Study Area

The Hunki Ox-bow Lake (Longitude 8° 20' E and Latitude 9° 38' N) is located 30 km from Awe town, Headquarter of Awe Local Government Area and 130 km from Lafia, the Capital of Nasarawa State, Nigeria. The lake is like an Ox-bow, shaped in two arms with each of them measuring 6-7 km long and 70 km wide (Figure 1) [10].
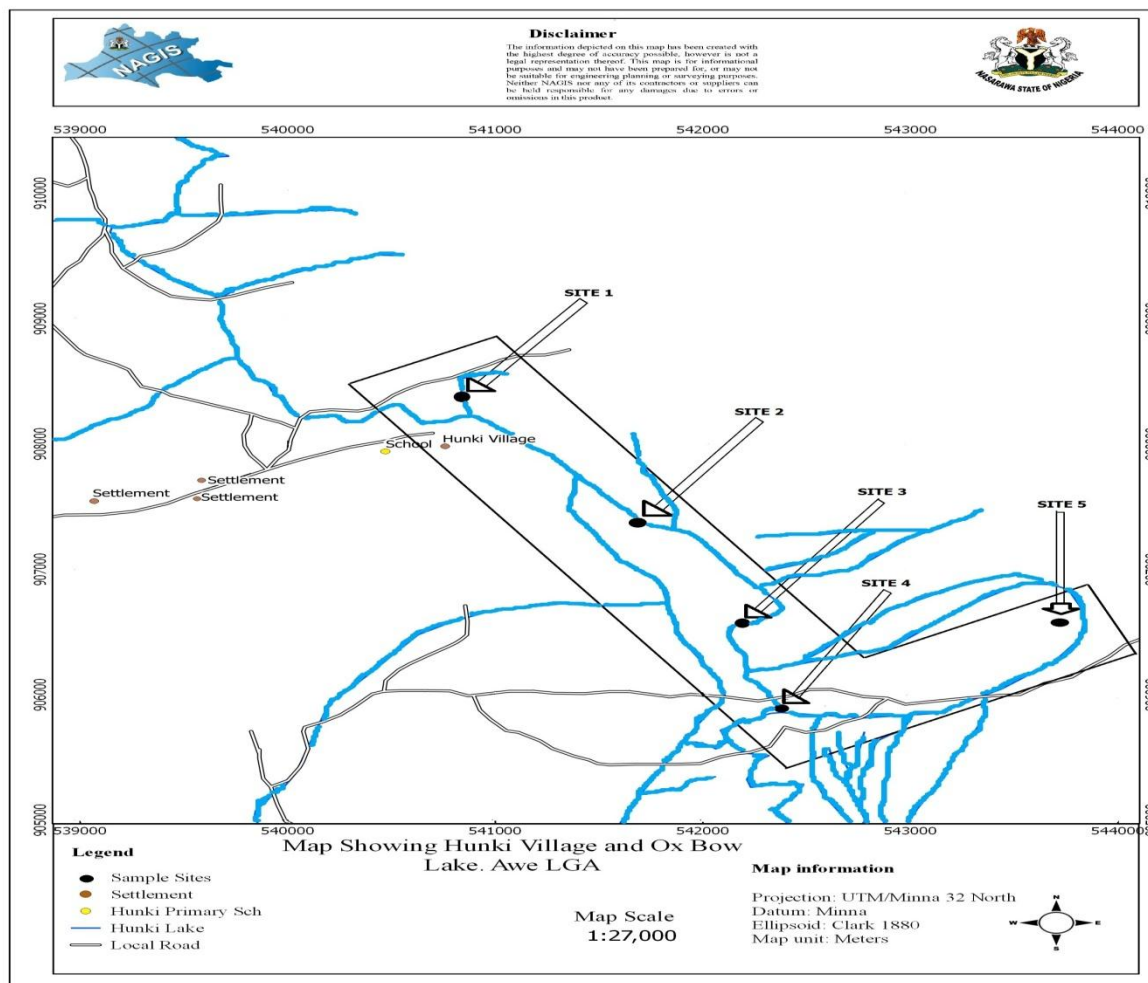

Figure 1: Map of Hunki Ox-bow Lake Showing the Sample Sites

Sampling Design, Sample Collection and Pretreatment

Five sampling sites at approximately 1 km intervals were mapped out along the Hunki Ox-bow Lake. Sediment sampling was carried out in dry and wet seasons from the five (5) sites using a stainless Eckman grab and placed in a pre-cleaned polythene bag. At each site, five samples of surface sediment (5 – 10 cm depth) were taken along transect across the lake (Figure 1).

Composite samples were prepared on the spot by mixing equal amounts of five replicates from the same site. Samples from each of the five sites were placed in each polythene bag. The wet sediments (60.0 g each) was continuously stirred for 12 hours in order to homogenize the samples, and transferred into a mechanical shaker with set of standard sieves arranged from the largest to the lowest mesh size [11]. Based on the particle size, sediment samples were generally classified into five groups as follows: clay (<2 μm); silt (4–74 μm); fine sand (74–500 μm); medium sand (500–2,000 μm) and coarse sand (>2,000 μm) [12]. These were air-dried, ground with clean laboratory mortar and pestle, and stored in separate polythene bags until analysis. Some of the sediments samples from each sample site were not sieved but air-dried, ground and unwanted materials removed. This represented the whole or raw sediments [13].

Water samples were also collected (same spot and time as sediments) from the five sampling sites of approximately 1 km intervals at the depth of 30 cm below the surface using 2 litre High Density Polyethylene (HDPE) bottles with screw caps which were acid washed and rinsed with deionized water prior to the sampling. The samples were preserved at pH <2 in situ with concentrated nitric acid [14].

Sediments particle size analysis

The sediment particle sizes were analyzed by a method used by Adiyiah and Kelderman [15].

Determination of Total Mn and Ni Levels in Sediments and Water

A 1.0 g sample of each ground whole (raw) sediment and the five particle sizes of sediment samples: clay (<2 μm); silt (4–74 μm); fine sand (74–500 μm); medium sand (500–2,000 μm) and coarse sand (>2,000 μm) was weighed into a conical flask and 10 mL concentrated HNO_3 added. The mixture was boiled at a constant temperature for about 45min. After cooling, 5mL of 70% $HClO_4$ was added and the mixture further boiled to release white fumes. This was allowed to cool and, 20 mL deionized water was added and heated until a clear solution was obtained. The mixture was filtered through a whatman filter paper No. 42, transferred quantitatively to a 50mL volumetric flask and made up to the mark with deionized water. The total metal concentration was determined using an Atomic Absorption Spectrometer (AAS) [16].

A 100 mL sample of water was placed in a conical flask and digested with 5 mL of concentrated nitric acid, HNO_3 on a hot plate at 95 ºC until a clear solution was obtained. The wall of the conical flask was washed down with deionized water and then filtered.

The filtrate was then transferred into a 100 mL volumetric flask, diluted to mark with deionized water. The total metals concentration was determined using an Atomic Absorption Spectrometer (AAS) [14].

Sequential Extraction Procedure

A five-step Sequential Extraction Procedure (SEP) proposed by Tessier *et al*. [5] was used to extract Mn and Ni contained in the sediment particle fractions.

Quality Control

The reliability of experimental results was obtained by replicate analysis of water and sediment samples. For metal analysis, standard solutions (1000 mg mL^{-1}) were used for calibration and standardization of instrument. Intermediate solutions were prepared by carefully dilution of stock standard solution (1000 mg mL^{-1}) with freshly prepared doubly distilled deionized water using micropipette.

Each analytical process/batch consisting of method blank and standard solutions were analyzed after every 10 samples to check instrument performance. An internal check on the sequential extraction method was performed by comparing the total amount of metal extracted by different reagents using sequential extraction procedure with the results of the pseudo total metal (total levels) concentration of different particle sizes of sediments [17]. The recovery of the sequential extraction procedure was evaluated as follows:

$$\% \ Recovery = \frac{C_{EF} + C_{MC} + C_{IM} + C_{OM} + C_{RF}}{C_{Pseudototal}} \times 100 \qquad (1)$$

where:

C_{EF} = Concentration of heavy metals bound to exchangeable fraction of sediments,
C_{MC} = Concentration of heavy metals bound to carbonate fraction of sediments,
C_{IM} = Concentration of heavy metals bound to Fe – Mn oxides fraction of sediments,
C_{OM} = Concentration of heavy metals bound to organic matter fraction of sediments,
C_{RF} = Concentration of heavy metals bound to residual fraction of sediments,
$C_{Pseudototal}$ = Concentration of total levels of heavy metals in different particle sizes of the sediments (clay, silt, fine sand, medium sand and coarse sand).

Statistical Treatment of Data

All statistical analyses were conducted using Statistical Package for Social Science, SPSS 26.0 for Windows as used by Tao *et al*. [13]. A two-way Analysis of Variance (ANOVA) was employed to test differences among various data sets.

The pearson correlation matrix was conducted according to the data distribution. Descriptive statistics which include range, mean and standard deviation were also performed.

Risk Assessments by Bioavailability Index (BI), Mobility Factor (MF) and Geo-Accumulation Index (I-geo)

Geochemical risk assessment indices used for the evaluation of sediments level of contamination were Bioavailability Index (BI), Mobility Factor (MF) and Geo-Accumulation Index (I-geo). The calculation of BI was based on the fractions of heavy metals as given by Tessier *et al.* [5] and the equation is as follows:

$$BI = \frac{[\text{Exchangeable (F1)} + \text{Bound to Carbonates (F2)} + \text{Bound to Fe–Mn Oxides (F3)}]}{[\text{Bound to Organic Matter (F4)} + \text{Residual (F5)}]} \quad (2)$$

Bioavailability index (BI) has been widely used to calculate the accumulation extent in living organism and evaluate the potential harm of heavy metals [18].

In a five-stage sequential extraction scheme, Salbu and co-workers [19], employed fraction 1 (F1) and fraction 2 (F2) of Tessier *et al.* [5] to represent the easily remobilizable fractions. Based on their proposal, the mobility factor of metals may be obtained using the following equation:

$$MF = \frac{F1+F2}{F1+F2+F3+F4+F5} \times 100 \quad (3)$$

Where, F1 = adsorptive and exchangeable fraction; F2 = carbonate fraction; F3 = Fe-Mn oxide fraction; F4 = organic fraction and F5 = residual fraction.

The fate of metal ions in sediment of the overlying water column is dependent on its MF. Salbu and co-workers [19] revealed that MF of metals provides an indication of the bioavailability or non-bioavailability of the metal.

Geo-accumulation index (I-geo) is a quantitative indicator proposed by Muller [20] that estimates the heavy metal pollution status of sediment in water. This method directly reflects the degree of enrichment of heavy metals in sediment and the equation is given below.

$$I_{geo} = log_2 \left[\frac{C_n}{1.5 \, B_n} \right] \tag{4}$$

Where C_n is the measured concentration of the sediment from a water body, B_n is the geochemical background value of a particular heavy metal, and 1.5 is the coefficient of variation that may be caused by earth movement and rock formation or other lithogenic effects. He distinguished seven classes of I-geo which include: I-geo < 0 (Class 0 for practically unpolluted, PU, samples); 0 < I-geo < 1(Class 1 for practically unpolluted to moderately polluted, MP, samples); 1 < I-geo < 2 (Class 2 for moderately polluted, MP, samples); 2 < I-geo < 3 (Class 3 for moderately polluted, MP, to heavily Polluted, HP, samples); 3 < I-geo < 4 (Class 4 for heavily polluted, HP, samples); 4 < I-geo < 5 (Class 5 for heavily polluted to very heavily (extremely) polluted, VHP, samples); I-geo > 5 (Class 6 for very heavily (extremely)polluted, VHP, samples).

RESULTS AND DISCUSSION

Distribution of Particle Sizes of the Sediment Samples for Dry and Wet Seasons

The percentage mean of the distribution of particle sizes of the sediment samples for dry and wet seasons are given in Figure 2. The sediment samples of sample sites one (1) to five (5) had higher contents of the finer sizes than the larger ones. This evidenced the higher concentration of Mn and Ni in finer sediment particles with larger surface area than the larger ones with smaller surface area. The results were in line with works done by Lin et *al*. [12] and Xuming *et al.* [7].
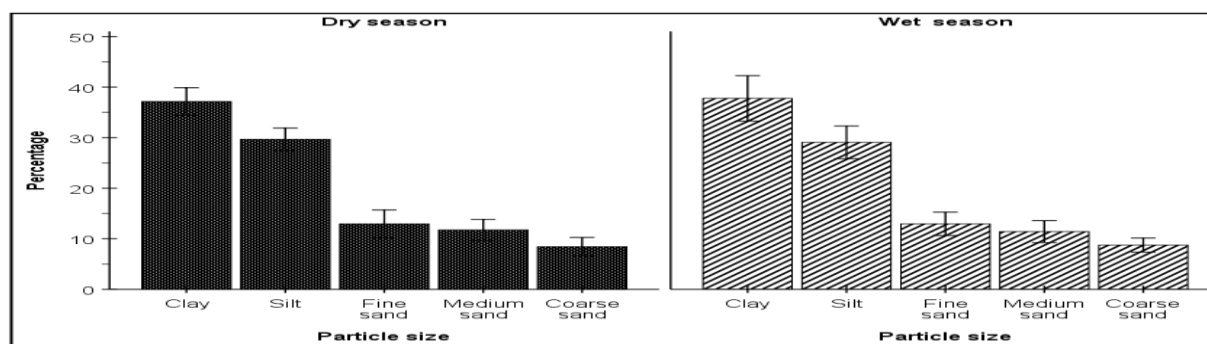

Figure 2: Distribution of Particle Sizes of the Sediment Samples for Dry and Wet Seasons (%)

Total Mn and Ni Concentration Levels in Sediments and Water

It can be depicted from Table 1 that total levels of the heavy metals (Mn and Ni) in sediments were higher than those of the water samples. This was in agreement with the fact that sediments

may act as large sinks or reservoirs of contamination [8]. Manganese was only detected in water sample of site one of dry season with 0.070 mg/L, and was below WHO, Guidelines for Drinking Water Quality (GDWQ) of 0.4 mg/L [21] and hence may not affect humans with disease such as manganism characterized by a Parkinson-like syndrome. Nickel in water samples were all Below the Detection Limits, (BDL), in all the sample sites in dry season, and therefore may not have any harmful effects on the aquatic organisms. However, in wet season Mn and Ni were detected in all the water samples of all sites. The levels of manganese in all the water samples were all below WHO, GDWQ of 0.4 mg/L [21], and may not cause manganism. Nickel levels in water samples, except site 4 (0.028 mg/L) were all above the WHO, GDWQ value of 0.07 mg/L [21]. Nickel levels in water higher than 0.07 mg/L may cause allergic skin reaction, chronic bronchitis, reduced lung function, and cancer of the lung and nasal sinus [21-22].

Based on the mean concentrations of Mn and Ni in water and whole (raw) sediments of all sample sites for dry and wet seasons, the baseline levels of heavy metals were calculated. The baseline levels of heavy metals in water samples (mg/L) were: Mn (0.129) and Ni (0.209). This revealed that baseline levels of Ni in water samples were higher than the WHO GDWQ of 0.07 mg/kg [21], but that of Mn were lower than the WHO GDWQ of 0.400 mg/L [21]. The baseline levels of Mn and Ni in sediment samples (mg/kg) were: Mn (75.085) and Ni (26.143). Nickel baseline level was higher than Interim Sediment Quality Guidelines – Low (ISQG-L) (trigger value) of 21 mg/kg but lower than Interim Sediment Quality Guidelines – High (ISQG-H) of 52 mg/kg [23]. This was an indication that Ni baseline levels would rarely cause biological effects. The ISQG-L and ISQG-H for Mn were not specified [23].

Total Heavy Metal Levels in the Five Sediment Particle Sizes of Dry and Wet Seasons
The mean total heavy metal levels from the five sediment particle sizes of the five sites for dry and wet seasons (mg/kg) are as presented in Table 1.The mean total heavy metal levels from the five sediment particle sizes had the following decrease order for both dry and wet seasons: clay > silt > fine sand > medium sand >coarse sand. The higher concentration of heavy metals on fine sediment particle sizes than the bigger particle sizes was probably due to the fact that finer sediment particles have larger surface areas than the bigger particle sizes with smaller surface areas. This was in line with a work done by Xuming *et al.* [7].

Heavy Metal Concentration in Different Sediment Particle Sizes of the Sum of Extraction Steps

The mean of sum of extraction steps (exchangeable fraction, bound to carbonates, Fe-Mn oxides bound, organic matter fraction and residual fraction) of two-way ANOVA and its post-hoc Tukey's test ($P< 0.05$) for both dry and wet seasons of all sample sites are given in Table 2.The mean concentrations of Mn and Ni based on sum of speciation extraction steps were all significantly higher in the wet season than the dry season ($P< 0.05$). There was no significant difference on the mean concentration of Mn and Ni on the five sediment particle sizes based on post-hoc Tukey's test for both dry and wet seasons.

Table 1: Total Mn and Ni Levels in Water (mg/L), Whole Sediments and Different Particle Sizes of Sediments (mg/kg) for Dry and Wet Seasons

Sample Code	Mn	Ni	Sample Code	Mn	Ni	Particle sizes	Mn	Ni
WA_1	0.070 ± 0.11	BDL	WB_1	0.273 ± 0.11	0.500 ± 0.21	Clay A	4.930 ± 0.05	0.773 ± 0.010
WA_2	BDL	BDL	WB_2	0.258 ± 0.10	0.594 ± 0.14	Silt A	2.670 ± 0.05	0.541 ± 0.020
WA_3	BDL	BDL	WB_3	0.098 ± 0.01	0.563 ± 0.10	Fine sand A	1.990 ± 0.05	0.261 ± 0.010
WA_4	BDL	BDL	WB_4	0.288 ± 0.13	0.028 ± 0.012	Medium sand A	1.270 ± 0.02	0.051 ± 0.030
WA_5	BDL	BDL	WB_5	0.303 ± 0.10	0.406 ± 0.13	Coarse sand A	0.791 ± 0.030	BDL
TMA_1	14.100 ± 0.67	2.950 ± 0.13	TMB_1	49.600 ± 6.10	45.700 ± 6.10	Clay B	60.100 ± 3.80	22.000 ± 5.00
TMA_2	10.600 ± 4.10	2.860 ± 0.14	TMB_2	45.600 ± 5.90	55.700 ± 7.10	Silt B	52.200 ± 5.90	19.000 ± 2.50
TMA_3	3.990 ± 0.88	2.800 ± 0.11	TMB_3	286.000 ± 15.00	51.000 ± 6.80	Fine sand B	46.800 ± 1.20	16.900 ± 1.40
TMA_4	9.610 ± 2.40	2.640 ± 0.10	TMB_4	127.000 ± 9.10	37.100 ± 4.10	Medium sand B	44.300 ± 5.90	15.600 ± 1.30
TMA_5	15.880 ± 4.30	2.040 ± 0.12	TMB_5	169.000 ± 9.80	58.600 ± 7.40	Coarse sand B	39.200 ± 6.50	14.100 ± 1.90
*WHO (2017)	0.400	0.070	*WHO (2017)	0.400	0.070			
ISQG-LOW	NS	21.000	ISQG-LOW	NS	21.0000			
ISQG-HIGH	NS	52.000	ISQG-HIGH	NS	52.000			

Key: W = Water Samples, TM = Total Metal Levels of whole sediments, A = Dry season, B = wet season, 1-5 = Sample Sites 1 to 5. BDL = Below Detection Limits. NS = Not Specified, *WHO (GDWQ) = WHO Guidelines for Drinking Water Quality (2017), ISQG = Interim Sediment Quality Guidelines (ANZECC AND ARMCANZ, 2000)

Sum of Extraction Steps, Pseudo-total and Percentage Recovery of Heavy Metal Concentration in Different Sediment Particle Sizes

The sum of extraction steps (mg/kg), pseudo-total (mg/kg) and percentage recovery of heavy metal concentration in different sediment particle sizes (mean of all sites) are as presented in Table 3. The results of the sum of five-step sequential extraction procedure were generally in good agreement with the pseudo total digestion results of all sites, with acceptable recoveries ranging from 96.1 – 99.6, 92.2– 98.3, 92.2 – 98.8, 97.6 – 100.0 and 93.7 – 98.5% for clay, silt, fine sand, medium sand and coarse sand sediment particle sizes,

Table 2: Heavy Metal Concentration in Different Sediment Particle Sizes of the Sum of Extraction Steps

HM	Season	Clay Mean ± SD	Silt Mean ± SD	Fine sand Mean ± SD	Medium sand Mean ± SD	Coarse Mean ± SD	F^1	F^2	F^3	P^1	P^2	P^3
Mn	WS	59.30 ± 6.72	51.60 ± 5.12	46.30 ± 5.12	43.20 ± 13.20	38.60 ± 7.19	89.96	0.79	0.36	**<0.001**	0.531	0.839
	DS	4.83 ± 0.56	2.66 ± 1.70	1.96 ± 1.46	1.25 ± 0.20	0.74 ± 0.92						
Ni	WS	22.00 ± 2.75	18.70 ± 1.40	16.60 ± 2.67	15.40 ± 2.31	13.90 ± 1.89	233.24	1.92	1.29	**<0.001**	0.108	0.274
	DS	0.74 ± 1.22	0.53 ± 1.17	0.25 ± 0.73	0.05 ± 0.02	0.00						

WS = wet season, DS = dry season, HM = heavy metals. F^1 = F-value for season, F^2 = F-value for particle size, F^3 = F-value for interaction between season and particle, P^1, P^2 and P^3 corresponding *P-values* for F1, F2 and F3 respectively. Significant difference is expressed in boldface. The metal concentration results are the sum of extraction steps and mean values of all sites

Table 3: Sum of Extraction Steps (mg/kg), Pseudo-total (mg/kg) and Percentage Recovery of Heavy Metal Concentration in Different Sediment Particle Sizes (Mean of all sites)

HM	Particle sizes/ Seasons	Clay Sum of ES	Clay Pseudo-total	Clay % R	Silt Sum of ES	Silt Pseudo-total	Silt % R	Fine sand Sum of ES	Fine sand Pseudo-total	Fine sand % R	Medium sand Sum of ES	Medium sand Pseudo-total	Medium sand % R	Coarse Sum of ES	Coarse Pseudo-total	Coarse % R
Mn	Dry	4.83	4.93	98.00	2.66	2.67	99.60	1.96	1.99	98.50	1.25	1.27	98.40	0.74	0.71	93.70
	Wet	59.30	60.10	98.70	51.60	52.20	99.00	46.30	46.80	98.80	43.20	44.30	97.60	38.60	39.20	98.50
Ni	Dry	0.74	0.77	96.10	0.53	0.54	98.20	0.25	0.26	96.20	0.05	0.05	100.00	0.00	0.00	0.00
	Wet	22.00	22.00	99.60	18.70	19.00	98.30	16.60	16.90	97.90	15.40	15.60	98.60	13.90	14.10	98.50

Key: HM = Heavy Metals, ES = Extraction Steps, % R = Percentage Recovery.

U. A. Augustine, T.A. Tor-Anyiin, R. Sha'Ato and R. A. Wuana: Total Concentration, Speciation and Risk Assessment of Heavy Metals (Mn and Ni) in Sediments and Water from Hunki Ox-Bow Lake, Nasarawa State, Nigeria

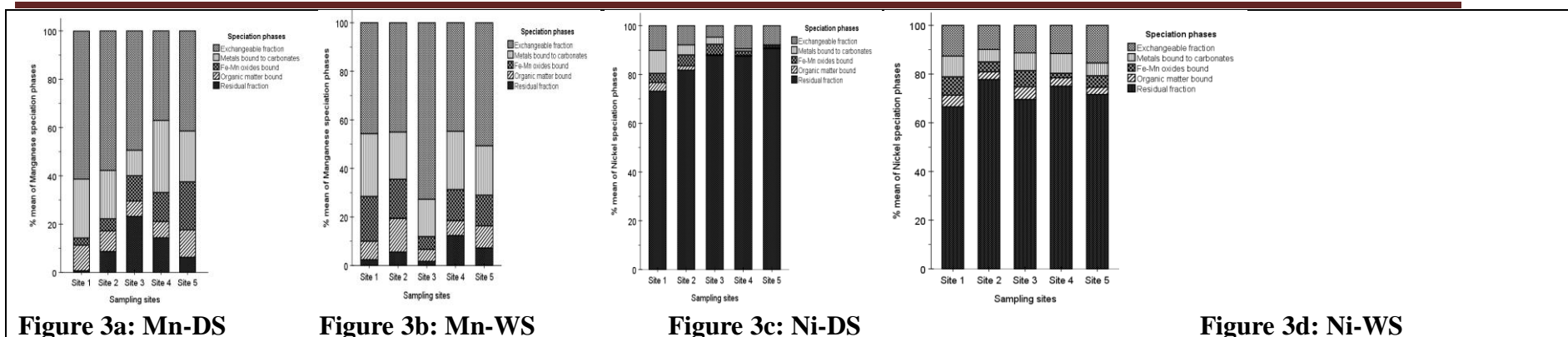**Figure 3a: Mn-DS**   **Figure 3b: Mn-WS**   **Figure 3c: Ni-DS**   **Figure 3d: Ni-WS**

Figure 3: Proportion of Heavy Metals Bound to Different Sediment Speciation Phases of Mn and Ni for Dry and Wet Seasons. Key: DS = Dry season, WS = Wet Season

respectively for the two heavy metals of both seasons, with the exception of Ni from coarse sediment particle size of dry season which had 0.00 mg/kg forsum of extraction steps and pseudo-total. Thus, Ni had 0.0% recovery from coarse sediment particle size in dry season. This, therefore, generally indicated that the five-step Sequential Extraction Procedure (SEP) proposed by Tessier *et al*. [5] used in this research was found reliable and can be reproduced.

Speciation

The percentage proportion of Mn and Ni bound to different speciation phases of the sediments are given in Figure 3. Manganese dominated mostly the exchangeable fraction, followed by the carbonates fraction in both dry and wet seasons as shown in Figures 3a – 3b. This showed that the manganese content from the sediments can easily be mobilized to the water column. Manganese had the following ranges for each of the sequential extraction steps: exchangeable fraction (37.10 – 61.29%), carbonates fraction (10.50 – 29.83%), Fe - Mn oxides fraction (3.07 –12.05%), organic matter fraction (6.64 – 11.35%), residual fraction (0.69 – 23.20%) for dry season, and exchangeable fraction(44.73 – 72.73%), carbonates fraction (15.38 – 25.87%), Fe - Mn oxides fraction (5.24 – 18.46%), organic matter fraction (6.09 – 13.81%), residual fraction (1.72 – 12.32%) for wet season. Manganese had more percentage fraction from the first four steps of sequential extraction (non-residual) which accounted for 85.61 - 99.31% in dry season and 87.68 – 98.28% in wet season out of the percentage total of Mn more than the residual fraction.

This indicated that Mn fractions from sediments was more of anthropogenic than the natural sources. This was in agreement with work done by Tamas and Farsang [9] on Tisza Ox-bow Lake. The partitioning of various fractions of Ni in dry season was in line with that of wet season for all sample sitesas shown in Figures 3c – 3d. Nickel dominated the residual fraction more than other fractions with the following range: 73.14 – 87.79% of the total percentage for dry season

and 66.56 - 77.74 % of Ni total percentage for wet season. The other percentage fractions of Ni from the sediments include: exchangeable fraction (4.70 – 10.15%), carbonates fraction (0.45 – 9.40%), Fe - Mn oxides fraction (0.67 – 3.78%), organic matter fraction (0.28 – 3.53%) for dry

season, and exchangeable fraction (15.48 – 9.89%), carbonates fraction (5.12 – 8.54%), Fe - Mn oxides fraction (1.85 – 7.54%), organic matter fraction (2.95 – 5.18%) for wet season. Despite the residual fraction being the dominant for Ni, the sum of extraction steps one and two, usually easily mobilized to the water column accounted for a bit more than 20% in sample sites one (21.15%) and five (20.72%) of wet season. More dominance of Ni on residual fraction from sediments indicated that the source was more of geochemical or natural (lithogenic) background rather than the anthropogenic sources. This was similar to work done by Gupta *et al.* [24] on a Lake where Ni dominated more of the residual fraction than other fractions.

Figure 4a: Mn-DS and WS varaiation
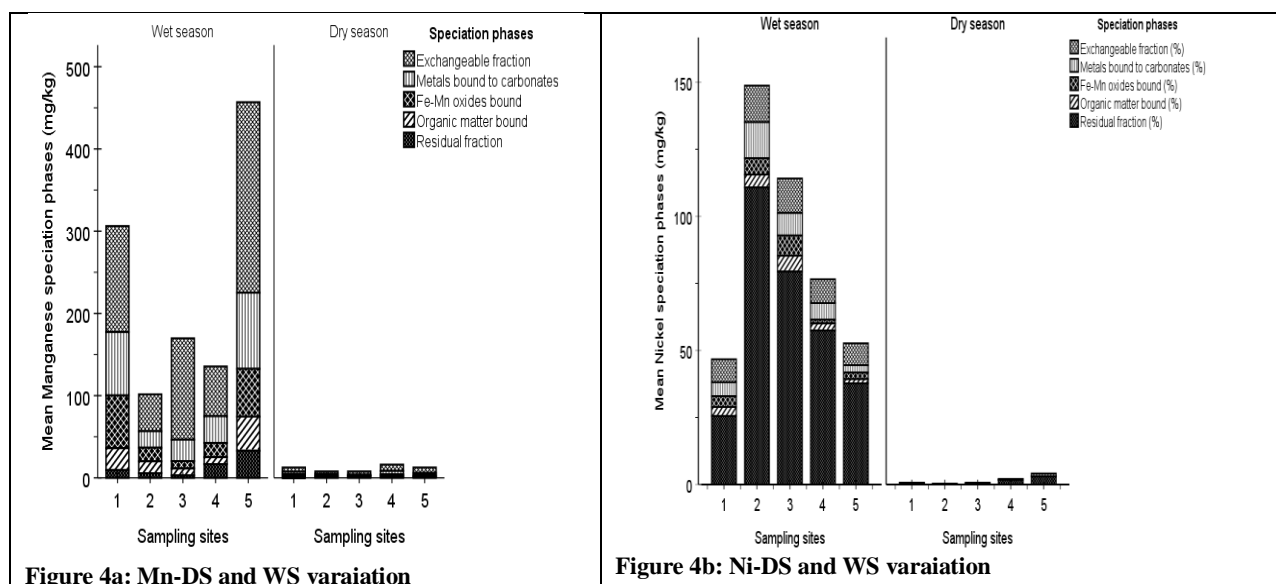
Figure 4b: Ni-DS and WS varaiation

Figure 4: Seasonal Variation of Mn and Ni Concentration Based on Speciation Phases and Sites of the Sediment Samples

The statistical mean of seasonal variation of heavy metals concentration based on sediment phases and sites of the sediment samples (mg/kg) are given in Figure 4. Generally, sediments of the wet season had significantly higher concentration of heavy metals than the dry season ($P< 0.05$). This was similar to a research work done by Ntakirutimana *et al.* [25]. There were significant variations in sites and seasons but not of speciation phases ($P< 0.05$). Manganese had the highest concentration at sample site four (7.55 ± 2.79 mg/kg) ($P< 0.05$) followed by sample site five (6.68 ± 0.42 mg/kg) ($P< 0.05$) of exchangeable fraction with the least concentration at sample site one (0.35 ± 0.17 mg/kg) ($P< 0.05$) of residual fraction in dry season (Figure 4a). Manganese had the highest concentration at sample site five (231.64 ± 34.63 mg/kg) ($P<0.05$) followed by sample site one(128.89 ± 39.99 mg/kg) ($P<0.05$) of exchangeable fraction with the

least concentration at sample site three (2.95 ± 0.39 mg/kg) ($P< 0.05$) of residual fraction in wet season (Figure 4a). Nickel had the highest concentration at sample site five (3.02 ± 0.33 mg/kg) ($P< 0.05$) followed by sample site four (1.75 ± 0.05 mg/kg) ($P< 0.05$) of residual fraction with the least concentration at sample site three (BDL) ($P< 0.05$) of organic matter fraction in dry season (Figure 4b). Nickel had the highest concentration at sample site two (110.75 ± 11.34 mg/kg) ($P< 0.05$) followed by sample site three (79.38 ± 7.96 mg/kg) ($P< 0.05$) of residual fraction with the least concentration at sample site five (1.55 ± 0.06 mg/kg) ($P< 0.05$) of organic matter fraction in wet season (Figure 4b).

RISK ASSESSMENTS BY BIOAVAILABILITY INDEX (BI), MOBILITY FACTOR (MF) AND GEO-ACCUMULATION INDEX (I-GEO)

The risk assessments by Bioavailability Index of Mn ranged from 2.79 to 13.37 (mean of all sites = 5.26) and that of Ni was 0.21 to 3.12 (mean of all sites = 2.37) for both seasons. Mobility Factor (MF) of Mn ranged from 49.0 to 77.71 (mean of all sites = 63.94), and that of Ni was 0.2 to 99.40 (mean of all sites = 41.21) for both seasons, and Geo-accumulation Index of Mn and Ni were less than zero for both seasons. The average BI values of Mn for both seasons were greater than that of Ni. The average BI for wet season was relatively higher than that of dry season. The high BI values of Mn of all sites and some sites of Ni of this study greater than 1 suggested that they may pose potential risk to the aquatic ecosystem and could easily enter the food chain and pose serious threat to man due to its higher toxicity and availability [18].

The mean MF values of Mn were greater than that of Ni irrespective of season. This indicated that Mn will be more mobilizable and bioavailable compared to Ni to the aquatic ecosystem irrespective of seasons [19].

The I-geo values of Mn and Ni for both seasons of this study were less than zero indicating practically unpolluted or very low level of the heavy metals enrichment in sediments [20].

CONCLUSIONS

The aim of this work was to assess the total concentration and speciation of Mn and Ni in water and sediments from Hunki Ox-bow Lake. Particle sizes of the sediments were also characterized. Sediments and water sampling was carried out in dry and wet seasons from five (5) sample sites. Concentrations of heavy metals in water, whole (raw) sediments, different sediments particle sizes and sequential fractions of sediments were determined by Atomic Absorption Spectrophotometer (AAS). Geochemical risk assessment indices of the sediments (bioavailability index, mobility factor and geo-accumulation index (I-geo)) were also calculated.

The results of this study showed that sediment samples of all sites had higher contents of the finer sizes than the larger ones. This evidenced the higher concentration of Mn and Ni in finer sediment particles with larger surface area than the larger ones with smaller surface area. The mean concentration of Ni from water samples for all sample sites of both dry and wet seasons was greater than that of Mn, but Ni was less than Mn in whole (raw) sediment samples. The baseline levels of Mn and Ni in water samples were as follows, irrespective of seasons: Mn (0.129) and Ni (0.209). This revealed that baseline level of Ni in water was higher than the WHO Guidelines for Drinking Water Quality, GDWQ [21]. Baseline level of Ni in sediments was higher than Interim Sediment Quality Guidelines – Low (ISQG-L) of 21 mg/kg but lower than ISQG-H of 52 mg/kg [23]. The mean concentrations Mn and Ni based on sum of speciation extraction steps were all significantly higher in the wet season than the dry season ($P< 0.05$). The results of the sum of five-step sequential extraction procedure were generally in good agreement with the pseudo total digestion results of all sites, with acceptable recoveries with the exception of Ni of dry season coarse sediment particle size which had 0.00 mg/kg for sum of extraction steps and pseudo-total, an indication that the five-step Sequential Extraction Procedure (SEP) proposed by Tessier *et al.* (1979) used in this study was found reliable and can be reproduced. Manganese dominated mostly the exchangeable fraction indicating anthropogenic source, while Ni dominated the residual fraction of the sediments more than other sequential extraction fractions indicating natural source, irrespective of seasons. The mean of Bioavailability index (BI) for wet season was relatively higher than that of dry season. The high BI values of most sites in this study suggested that Mn and Ni may pose potential risk to the aquatic ecosystem and could easily enter the food chain and pose serious threat to man due to its higher toxicity and availability. The mean values of mobility factor revealed that Mn had higher values than that of

Ni. This indicated that Mn will be more mobilizable and bioavailable compared to Ni to the aquatic ecosystem. The I-geo values of Mn and Ni, of both seasons were lower than zero, indicating practically unpolluted. The results obtained from this study will serve as baseline levels to other researchers as there was never a research of this kind in Hunki Ox-bow Lake to the best of our knowledge. This research will also help to create awareness about Mn and Ni exposure or source to the aquatic ecosystem. This study was limited to assessment of total concentration of Mn and Ni in water and whole (raw) sediments, different particle sizes of the sediments, and speciation of Mn and Ni from different sediment particle sizes using AAS. More so, particle sizes of the sediments were analyzed, and geochemical risk assessment indices of the sediments (bioavailability index, mobility factor and geo-accumulation index (I-geo)) were evaluated.

There should be regular monitoring and assessment of total concentration and speciation of heavy metals in water and sediments from Hunki Ox-bow Lake as run-offs of agrochemicals from farm lands continues year after year. There is a need for government and regulatory bodies such as National Environmental Standards and Regulations Enforcement Agency (NESREA) to regularly monitor the quality of agrochemicals such as fertilizer, herbicides and insecticides in order to checkmate their level of contamination with heavy metals and other toxic chemicals. This will minimally reduce the contamination of the Lake through run-offs of agrochemicals from farm lands within and around it.

REFERENCES

[1] Slobodian, M.R., Petahtegoose, J.D., Wallis, A.L., Levesque, D.C. & Merritt, T.J.S. (2021). The Effects of Essential and Non-Essential Metal Toxicity in the Drosophila melanogaster Insect Model: A Review. *Toxics*, 9, 255 - 269. https://doi.org/10.3390/toxics9100269.

[2] Ebany, J., Martinez-Finleya, S. C., Stephanie F. & Michael, A. (2012). Admit One: How Essential and Nonessential Metals Gain Entrance into the Cell. *Metallomics*, 4(7), 593–605. doi:10.1039/c2mt00185c.

[3] Aziza, A. A., Saad, A. E.& Hany, K. (2014). Essential, Non-essential Metals and Human Health. *Blue Biotechnology Journal,* 3(4), 447- 495.

[4] Idris, A.M., Eltayeb, M.A.H., Potgieter-Vermaak, S.S., Grieken, R. & Potgieter, J.H. (2007). Assessment of heavy metal pollution in Sudanese harbours along the Red Sea coast. *Microchemical Journal,* 87, 104-112.

[5] Tessier, A., Campbel, P.G.C. & Bisson, M. (1979). Sequential extraction procedure for the speciation of Particulate trace metals. *Analytical Chemistry*. 51, 844-851.

[6] Namiesnik, J. & Gorecki, T. (2001). Preparation of environmental samples for the determination of trace constituents. *Polish Journal of Environmental Studies,* 10(2), 77-84.

[7] Xuming, K., Jinming, S., Huamao, Y., Liqin, D., Xuegang, L., Ning, L., Xianmeng, L. & Baoxiao, Q. (2017). Speciation of heavy metals in different grain sizes of Jiaozhou Baysediments: Bioavailability, ecological risk assessment and source analysis ona centennial timescale. *Ecotoxicology and Environmental Safety*, 143, 296-306.

[8] Joachim, E. A. & Surendra, P. (2020). Determination and comparison of selected heavy metal concentrations in seawater and sediment samples in the coastal area of Suva, Fiji. *Marine Pollution Bulletin,* 157 (2020) 111157, 1-8.

[9] Tamas, M. & Farsang, A. (2016). Determination of heavy metal fractions in the sediments of ox-bow lakes to detect the human impact on the fluvial system (Tisza River, SE Hungary). *Hydrology and earth system science discussions,*17, 201 -207.

[10] Nigeria Galleria (2005). Nigeria information and guide – Hunki Ox-bow Lake. Galleria media limited. www.NigeriaGalleria.com. Retrieved, 27/8/17.

[11] Guevara-Riba, A., Sahuquillo, A., Rubio, R. & Rauret, G. (2004). Assessment of metal mobility in dredged harbour sediments from Barcelona, Spain. *Science of Total Environment*, 321, 241-255.

[12] Lin, J.G., Chen, S.Y. & Su, C.R. (2003). Assessment of sediment toxicity by metal speciation in different particle-size fractions of river sediment. *Water Science and Technology*, 47 (7–8), 233–241.

[13] Tao, Y., Yan Z. & Yuan, Z. (2012). Distribution and bioavailability of heavy metals in different particle-size fractions of sediments in Taihu Lake, China. *Chemical Speciation and Bioavailability*, 24(4), 205-215.

[14] APHA. (1999). Standard Method for Examination of Water and Wastewater, 18th edn. American Public Health Association, Washington D. C. 1268pp.

[15] Adiyiah, J. & Kelderman, P. (2014). Assessment of the Levels of Heavy Metals in Vertical Sediment Cores of Lake Markermeer in the Netherlands. *International Journal of Engineering Research and Technology*, 3 (1), 584 -590.

[16] Fabunmi, I., Olumodeji, O., Uyimadu, J. P. & Adeleye, A. (2014). Evaluation of the Effectiveness of Different Acid Digestion on Sediments. *International Organization of Scientific Research Journal of Applied Chemistry (IOSR-JAC)*,7(12), 39-47.

[17] Nemati, K., Abu Bakar, N.K., Abas, M.R. & Sobhanzadeh, E. (2011). Speciation of heavy metals by modified BCR sequential extraction procedure in different depths of sediments from Sungai Buloh, Selango. *Malaysian Journal of Hazardous Material*, 192, 402–410.

[18] Yoo, J.C., Lee, C.D. & Yang, J.S. (2013). Fraction characteristics of heavy metals from marine sediments. *Chemical Engineering Journal*, 228, 688–699.

[19] Salbu, B., Kreling, I.& Oughlon, D.H. (1998). Characterization of Radioactive particles in the environment. *Analyst,* 123, 843- 849.

[20] Muller, G. (1969). Index of Geo-accumulation in sediments of the Rhine River. *Geological Journal*, 2(3), 108–118.

[21] WHO (2017). Guidelines for drinking-water quality: fourth edition incorporating the first addendum, Geneva: World Health Organization (WHO); 2017. License: CC BY-NC-SA 3.0 IGO. http://apps.who.int/iris. 631pp.

[22] Sunderman, F.W. Jr., Dingle, B., Hopfer, S.M. & Swift, T. (2007). Acute nickel toxicity in electroplating workers who accidently ingested a solution of nickel sulfate and nickel chloride. *American Journal of Industrial Medicine*,14, 257-66.

[23] ANZECC & ARMCANZ. (2000). Australian and New Zealand guidelines for fresh and marine water quality, October, 2000. National Water Quality Management Strategy, paper No. 4., Australian and New Zealand Environmental and Conservation Council, and Agriculture and Resource Management Council of Australia and New Zealand (ANZECC AND ARMCANZ), Canberra, Australia. 678pp.

[24] Gupta, B., Kumar,R. & Rani, M. (2013). Speciation of heavy metals in water and sediments Of an urban lake system. *Journal of Environmental Science and Health, Part A: Toxic/Hazardous Substances and Environmental Engineering*, 48(10), 1231-1242.

[25] Ntakirutimana, T., Du, G., Guo, J., Gao1, X. & Huang, L. ((2013). Pollution and Potential Ecological Risk Assessment of Heavy Metals in a Lake. *Polish Journal of Environmental Studies*, 22(4), 1129-1134.