PB, ZN, CU, NI AND CO CONTENTS OF WATER AND SEDIMENTS, IN RELATION TO PHYTOREMEDIATION AND TRANSLOCATION BY WATER HYACINTH (EICHHORNIA CRASSIPES MART. SOLMS.) AT SOME CREEKS OF THE GREAT KWA RIVER, SOUTHEASTERN NIGERIA

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ABSTRACT: *A passive phytoremediation study to investigate the environmental purification efficacy of water hyacinth (Eichhornia crassipes) was carried out at Mbat-Abiati and Oberekkai Creeks of the Great Kwa River in Southeastern Nigeria. The study assessed the levels of Pb, Zn, Cu, Ni and Co in the water column and underlying sediments (abiotic monitors) in comparison with their levels in E. crassipes (biomonitor). Generally, observed values of heavy metals in sediment and water hyacinth of the two Creeks did not vary significantly (p>0.05), and the sequence that was frequently encountered in the accumulation of the heavy metals was: SEDIMENT>PLANT ROOTS>PLANT LEAVES>WATER. Relative Accumulation Indices (RAI) revealed that the concentration of the heavy metals in the sediments are much higher than values recorded for the waters. This appear normal since sediments are reservoirs for all contaminants and dead organic matter descending from the ecosystem above. The pattern of heavy metal concentrations in the organs of E. crassipes are closely associated with that of its geological substrate (water and sediments). Although zinc displayed the highest accumulation in both root and leaves tissues, and appeared more mobile from roots to leaves than other heavy metal, the bioconcentration factor (BCF) revealed Co as the metal with the highest phytoaccumulation capability in the area, followed by Ni, Cu, Pb and Zn, in that order. Indication from the study is that water hyacinth (Eichhornia crassipes) can effectively absorb and translocate Pb, Zn, Cu, Ni and Co, even when the concentrations of the metals in the abiotic components of the environment is low.*

KEYWORDS: Water Hyacinth, Phytoremediation, Bioaccumulation, Translocation, Nigeria

INTRODUCTION

In southern Nigeria, the Great Kwa River flow through Obufa Esuk, Esuk Atu, University of Calabar Teaching Hospital (UCTH), University of Calabar, Satellite Town, Esuk Ekpo Eyo, Akpabuyo, Calabar Free Trade Zone and other semi-urban areas, before finally entering the Calabar Estuary (Fig. 1). Wastewaters draining off these residential, farming, industrial, commercial, recreational and dumpsite areas is prone to produce watercourses pollution and violations of various water quality standards, with attendant implications on the ecological integrity and human health. The watershed of the Great Kwa River, which has for a long time been covered by tropical rainforest, has in recent times become a beehive of agricultural, road construction, forestry, industrial, mining and quarrying activities (Efiong, 2011).

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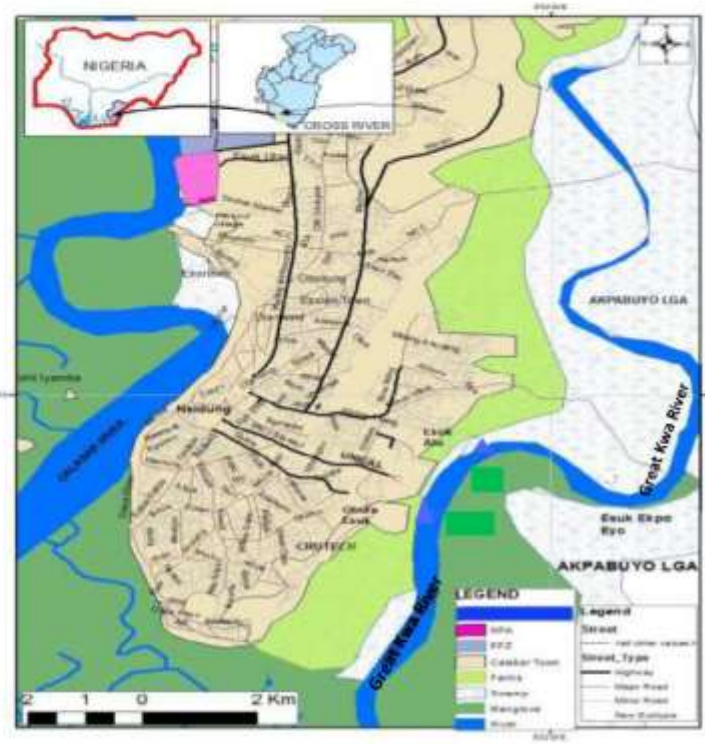

Figure 1. Map showing the Great Kwa River with flow path draining the east side of the city of Calabar in southern Nigeria (modified after Okorafor *et al.*, 2015)

The establishment of mostly the quarrying/mining activities within the catchment area, together with the intense agricultural practice in the area is bound to contribute negatively to the quality of the aquatic ecosystem (Ephraim and Ajayi, 2014; 2015). Other areas of environmental concern in the basin includes the numerous human activities, notably: dredging, logging, fishing, boating, watercraft maintenance, saw-milling, transportation, laundering, bathing and swimming, etc, (Elueze et al., 2001; Ephraim, 2003). To exacerbate the already deplorable situation is the issue of invasion of water hyacinth, Eicchornia crassipes, into the River basin. This weed, which is a fast growing, free-floating aquatic macrophyte with appetite for nutrients and explosive growth rate, constitute an ecological risk as a result of their spectacular growth, ecological impacts (water quality degradation; drastic changes in the plant and animal community; severe effects on light and oxygen diffusion; clogging of irrigation, hydropower and water supply ways and draining of lake), socio-economic implication (hindrance of navigation and water transport; blockage of canals and rivers; hampering fishing, etc), and health effects (fibrous root system provides nesting habitat for a variety of disease vectors, such as lymphatic filariasis, malaria and schistosomiasis) (Bos, 1996; Gopal,1987; Nyanayo et al., 2007). Thus, the aquatic ecosystem of the Great Kwa River is threatened by multiple anthropogenic, geogenic and natural pollution sources, types and nuisance.

Fortunately, despite its numerous shortcomings and nuisance, research, pilot-scale and operational studies conducted in recent years have shown that the aquatic macrophyte, water hyacinths, Eichhornia crassipes, offer a promising, low cost method for removing contaminants from wastewater and polluted natural waters (Nyanayo et al, 2007). The plant has been proven to be very efficient at removing a vast range of pollutants like suspended materials, organic matter, heavy metals and pathogens from water and sediments in aquatic environments, and

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has been applied in the cleaning up of municipal and agriculture wastewater (Lu et al., 2004). The water hyacinth plant accomplishes the act of aquatic ecosystem purification by reducing the levels of organic and inorganic pollutant (Brix 1993, Delgado et al. 1995) and reducing the level of heavy metals (Falbo and Weaks 1990) in the aquatic environment. The plant's capability to assimilate large quantities of trace elements and metals, some of which are essential for plant growth, is of immense value, considering the high toxicity and non-biodegradable nature of heavy metals pollution. According to Ratan and Verma (2014), the mechanism by which the plants absorb metals from the environment is simple and interesting; the heavy metal ions all have positive charges and the roots of plants are negatively charged, this difference in charges causes an attraction between the ions and the roots, and thus the ions are absorbed into the plant.

In the present study, the extent of heavy metal pollution in the water column, sediments and, environmental purification efficacy of water hyacinth *(Eichhornia crassipes)* plants in Mbat-Abbiati and Oberekkai Creeks of the Great Kwa River in southeastern Nigeria is investigated. The specific objectives include: (a) to determine the abundance and distribution of Pb, Zn, Cu, Ni and Co in the water column, sediments and different parts of the invasive water hyacinth *(Eichhornia crassipes)* plant, (b) to evaluate the efficiency of the water hyacinth plant in accumulating the studied heavy metal in the two Creeks, (c) to determine the bioconcentration factors (BCF) of these metals in the plant roots and leaves, and (d) to examine the capability of water hyacinth plant in translocating these metals (TF) from underground to aerial tissues.

METHODOLOGY

Description of Study Region

The study was conducted in Mbat-Abiati Creek in Abiati village and Oberekkai Creek in Oberekkai village, with the delimitation: Latitude 5°05'N – 5°06'N and longitude 8°27'E – 8°29'E. These Creeks are situated within present-day Akamkpa Local Government Area of Cross River State, southeastern Nigeria (Fig. 2), and form parts of the Great Kwa River, which takes its rise from the Oban Hills in eastern Nigeria, flows southwards and discharges into the Cross River Estuary around latitude $4^{o}45'$N and longitudes $8^{o}20'$E.

The lower reaches of the Great Kwa River drains the eastern coast of Calabar Municipality, and is characterized by semi-diurnal tides and extensive mud flats. The study Creeks are characterized by luxuriant proliferation of the aquatic macrophyte – Water Hyacinth (E. crassipes). As riverine areas, the study locations are linked to each other and other surrounding communities by water bodies. Hence, boats and canoes are the main mode of transportation in the whole area. Nevertheless villages and farm settlements close to the study area are interconnected by bush paths, thereby making such areas accessible on foot. Sixty to seventy percent of the free water surface of both Creeks are covered by water hyacinth plants.

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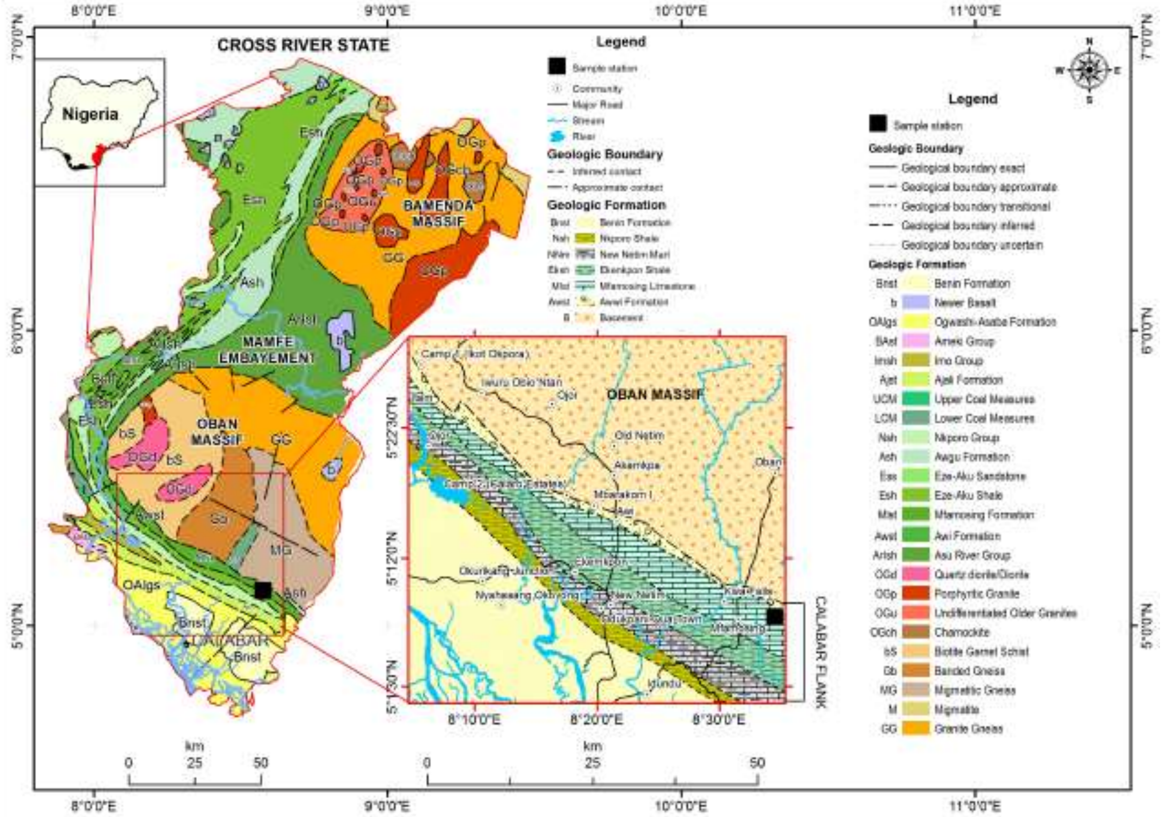

Figure 2. Geological map of Cross River State in southeastern Nigeria, showing the geology of the study area

Like most parts of southeastern Nigeria, the study region is characterized by tropical climate having distinct alternating dry and wet seasons. According to Ephraim and Ajayi (2014; 2015), the area is associated with warm temperatures that ranges between 26 °C to 32 °C and a bi-modal rainfall pattern averaging approximately 2,300 mm annually, while the annual mean daily relative humidity and evaporation is in the range 76 – 86% and 3.85 mm/day respectively. Moist, evergreen forest-type vegetation exists in unaltered areas, while herbs, shrubs and few trees are cultivated in the altered portions of the area. Thick, riparian forest fringes most streams of the area.

The topography of the area is typified by plains under 200m above sea level which dominates the land surface of the area. The study area is also an integral part of the Calabar Flank, which is unique in many respects. In terms of sediments, the Calabar Flank is underlain by Cretaceous Sedimentary rock deposits, comprising sandstones, limestones, marlstones and shales. The Mfamosing Limestone Formation, which is the thickest carbonate body in Nigeria (Reijers & Petters 1987), is the main carbonate – bearing deposit occurring within the area.

Sampling Strategy and Sample Preparations

Six sampling locations within each of the two Creeks were strategically selected to account for the entire Creek area; totaling twelve sampling points for both Creeks. All the sampling points were selected within the main body of the Creeks, to provide adequate coverage of the entire Creek surface. These sampling locations were appropriately located using the Global positioning System (GPS), and identifiable landmarks in adjoining land areas were also documented. Sampling for water hyacinths (plant), sediments and water were accomplished at each of the twelve (12) sampling locations. At each location, water, sediments and plant samples were collected, packaged and labelled accordingly.

Grab samples of water were collected at 15 cm depth below the water surface, and stored in two ½-litre capacity plastic bottles with screw caps. The bottles previously thoroughly washed and rinsed with distilled water before use, following the procedure in Laxen and Harrison (1981). The water samples for heavy metal determination were acidified with 5 mL nitric acid to prevent degradation of the metals by microorganisms, prior to its transportation to the laboratory for analysis. In the laboratory, these water samples were filtered with Whatman No.41 (0.45 µm pore size) filter paper, and both the filtrate and untreated water samples (500 mL each) were preserved with 2 mL concentrated nitric acid to prevent precipitation of metals.

Similarly, grab samples of surface sediment were strategically collected, drained of water in situ and placed into 10% nitric acid pretreated well-labeled, polythene bags. The samples were collected with the help of steel pipe (2 inch diameter) pressed with pressure through the water column to obtain a sediment layer of about one foot (Fishar and Ali, 2005). The choice of surface sediments was due to the fact that this layer controls the exchange of metals between sediments and water (Barakat et al. 2012; El Nemr et al. 2006). Also, Solomons & Forstner (1984) reported that heavy metals tend to be concentrated in the finer grain sizes of sediment. The packaged sediment samples were transported to the Soil Science Laboratory of University of Calabar, Nigeria, for further treatment. In the Laboratory, the sediments were air-dried for three weeks under room temperature of about 30^0C. The drying process was necessary to eliminate organic matter and moisture contents, amongst other undesirable components. After drying, individual samples were disaggregated, and sieved through a 2-mm plastic sieve to remove large debris, gravel-size materials, plant roots, animal shells and other waste materials. Finer fractions, not only concentrate iron oxide/hydroxide, organic matter, aluminum, clay minerals, but also have the largest capacity to bind particle reactive trace metal contaminants relative to coarser particles (>2 mm size). Considerable precautions were taken to avoid contamination during drying, grinding, sieving and storage.

Samples of the water hyacinth plants were picked directly from each of the earmarked locations on the water surface of both Creeks. Adequate attention was paid to the plants' roots to prevent damage. The plants were placed in small, sterile polyethylene bags and labeled accordingly. The plant samples were then transferred to the laboratory to undergo thorough washing in fresh running water to eliminate all adhered soil particles, dust, dirt, possible parasites or their eggs, and then washed again with deionized water. This was followed by careful separation into leaves and roots for each sample location. The roots and leaves were of immense interest because it is in these parts that herbaceous plants retain higher concentration of heavy metal than in stems and fruits (Yargholi and Azimi, 2008). Thereafter, the separated plant samples were dried for 12 hours at 120^oC in a forced air oven according to Brower et al. (1997), to stop enzymatic reactions, removing moisture and to obtain a constant weight. In warm condition, the samples were ground to fine powder using a silica pestle and mortar, passed through 1 mm sieve, and packaged separately into leaves and roots for each sample locations.

Digestion and Analysis

Plant samples were digested using the HNO_3-HCl (Nitric acid-Hydrochloric acid) digestion. The prepared samples were cold-leached with nitric acid, and then digested in a hot water bath. After cooling, a modified Aqua Regia solution of equal parts, comprising of concentrated HCl, HNO_3 and DI H_2O were added to each sample to leach in a heating block of hot water bath.

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The samples were made up to volume with dilute HCl, and then filtered. Sample splits of 1-5g were then analyzed for heavy metals using the ICP-MS (Inductively coupled plasma-Mass Spectrometry) technique.

Sediment samples were digested using the HF-HNO_3-$HClO_4$ acid digestion. Samples were digested to complete dryness with an acid solution of (2:2:1:1) H_2O-HF-$HClO_4$-HNO_3. 50% HCl was added to the residue and heated using a mixing hot block. After cooling, the solutions were transferred to test-tubes and brought to volume using dilute HCl. Sample splits of 0.25g were analyzed for Heavy metals using the ICP-ES (Inductively Coupled Plasma-Emission Spectrometry) technique.

Prior to the heavy metal analysis, the acidified filtrate water samples were concentrated to ten folds on water bath and subjected to nitric acid digestion using microwave-assisted technique, setting pressure at 30 bar and power 700 watts, as per the methods for the examination of water and wastewater.

All analysis for heavy metals were done using the ICP-ES (Inductively Coupled Plasma-Emission Spectrometry) and ICP-MS (Inductively Coupled Plasma-Mass Spectrometry) facilities at the Geochemistry Laboratory of Acme Analytical Laboratories, Vancouver BC, Canada. Operational conditions were adjusted to yield optimal determination. The accuracy of the analytical procedure used was reputedly cheeked by analyzing duplicate samples and repeatedly analyzing relevant reference samples, and comparing the obtained values with the expected values. The quality control samples represented 10% of the total analytical load. The duplicates samples were treated identically. The percentage recovery from 93 to 105%, while precision was within 5%. Details on the sampling, treatments and analysis of the samples are in Ajayi (2014).

RESULTS AND DISCUSSION

Heavy metal content of water, sediment and water hyacinth

The concentration of heavy metal in the water, sediments, plant roots and leaves samples from Mbat-Abiati and Oberekkai Creeks are discussed below under appropriate subheadings:

Heavy metal levels in the waters

The concentration (in mg/l) of heavy metals in water samples from Mbat-Abiati and Oberekkai Creeks of southeastern Nigeria is given in Table 1, and the mean concentration illustrated in Fig. 3.

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Table 1. Concentration (in mg/l) of heavy metals in water samples from Mbat-Abiati and Oberekkai Creeks, southeastern Nigeria.

	MBAT-ABIATI CREEK								*OBEREKKAI CREEK*								*T-TEST DATA*	
	A1	**A2**	**A3**	**A4**	**A5**	**A6**	**Mean**	**SD**	**O1**	**O2**	**O3**	**O4**	**O5**	**O6**	**Mean**	**SD**	**t-score**	**p-level**
Pb	0.0003	0.0003	0.0003	0.0004	0.0003	0.001	0.0004	0.0003	0.001	0.001	0.001	0.001	0.001	0.0003	0.0009	0.0003	2.75	0.02*
Zn	0.03	0.02	0.03	0.02	0.012	0.012	0.0207	0.0081	0.05	0.02	0.02	0.02	0.01	0.01	0.0217	0.0147	0.15	0.89
Cu	0.001	0.001	0.002	0.001	0.002	0.002	0.0015	0.0005	0.004	0.003	0.003	0.002	0.002	0.002	0.0027	0.0008	2.91	0.02*
Ni	0.0002	0.0003	0.0003	0.0003	0.001	0.001	0.0005	0.0004	0.002	0.001	0.001	0.001	0.001	0.001	0.0012	0.0004	2.87	0.02*
Co	0.0002	0.0002	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001	0.001	0.001	0.001	0.001	0.001	0.001	0.0010	0.0000	41.11	0.00*

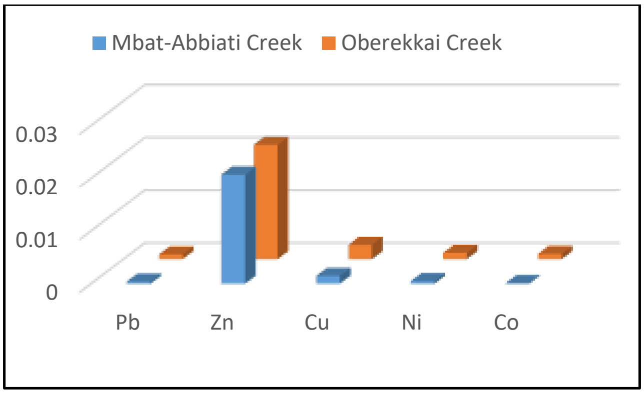

Figure 3. Mean concentration of heavy metals in water samples from Mbat-Abbiati and Oberrekai Creeks of the Great Kwa River, Southeastern Nigeria

As shown (Tables 1; Fig. 3), zinc (Zn) displayed the highest level of heavy metals in the waters of both Creeks, followed by copper, nickel and others in the order: Zn>Cu>Ni>Pb>Co for waters from Mbat-Abiati Creek and Zn>Cu>Ni>Co>Pb for that of Oberekkai Creek (Table 1; Fig. 3). The Zn concentration was in the range: 0.012 – 0.03 mg/l with mean and standard deviation values of 0.0207±0.0081 mg/l for waters from Mbat-Abbiati Creek, and 0.01 - 0.05 mg/l with mean and standard deviation values of 0.0217±0.00147 mg/l for waters from Oberrekai Creek.

Copper levels in the waters vary within 0.0010 and 0.0020 mg/l with mean and standard deviation values of 0.0015±0.0005 mg/l in the waters from Mbat-Abbiati Creek, while the waters from Oberrekai Creek showed 0.002 – 0.004 mg/l variation with mean and standard deviation values being 0.0027±0.0008 mg/l. The highest level (0.001 mg/l) of Pb in the waters from Mbat-Abbiati Creek was observed at station A6, while the lowest concentration of 0.0003 mg/l was measured at stations A1 to A3 and A5. On the other hand, in the waters from Oberrekai Creek, the highest value of 0.001 mg/l was recorded for Pb at stations O1 to O5, while station O6 displayed the lowest level of 0.0003 mg/l. The mean concentration of Pb in the waters from Mbat-Abbiati Creek was 0.0004 mg/l, while that from Oberrekai Creek displayed 0.0009 mg/l (Table 2). Other heavy metals measured in the waters include Ni and Co. The mean and standard deviation values of Ni was 0.0005±0.0004 mg/l for samples from

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Mbat-Abbiati Creek, and 0.0012±0.0004 mg/l for samples from Oberekkai Creeks), while that for Co displayed 0.0001±0.0001 mg/l for samples from Mbat-Abbiati Creek, and 0.001 mg/l for samples from Oberekkai Creeks (Table 1).

Heavy metal levels in the Sediments

The concentration (in mg/kg Dry Weight) of heavy metals in sediments from Mbat-Abiati and Oberekkai Creeks of southeastern Nigeria is given in Table 2, and the mean abundance illustrated in Fig. 4.

As shown in Table 2, metals concentrations in the sediment varied widely and exhibit fluctuations between the different Creeks sampled but no noteworthy differences were observed among the two Creeks studied.

Table 2. Concentration (mg/kg Dry Weight) of heavy metals in sediments from Mbat-Abiati and Oberekkai Creeks, southeastern Nigeria.

	MBAT-ABIATI CREEK								OBEREKKAI CREEK								T-TEST DATA	
	A1	**A2**	**A3**	**A4**	**A5**	**A6**	**Mean**	**SD**	**O1**	**O2**	**O3**	**O4**	**O5**	**O6**	**Mean**	**SD**	**t-score**	**p-level**
Pb	25.22	20.61	18.28	16.58	17.58	16.66	19.16	3.32	26.56	15.55	19.92	37.65	26.24	21.69	24.60	7.60	1.61	0.14
Zn	81.80	86.80	83.90	87.90	82.80	81.10	84.05	2.75	107.80	59.40	82.70	130.60	105.30	73.50	93.22	26.07	0.86	0.41
Cu	22.88	21.88	25.25	27.05	25.94	25.21	24.70	1.94	26.91	16.33	22.55	24.61	26.60	22.21	23.20	3.90	0.84	0.42
Ni	26.60	25.00	25.30	28.50	25.90	24.50	25.97	1.44	30.40	21.20	23.80	51.90	29.90	23.90	30.18	11.25	0.91	0.38
Co	17.10	18.10	20.50	27.00	18.20	21.80	20.45	3.65	27.80	12.20	14.50	14.60	36.10	11.00	19.37	10.19	0.25	0.81

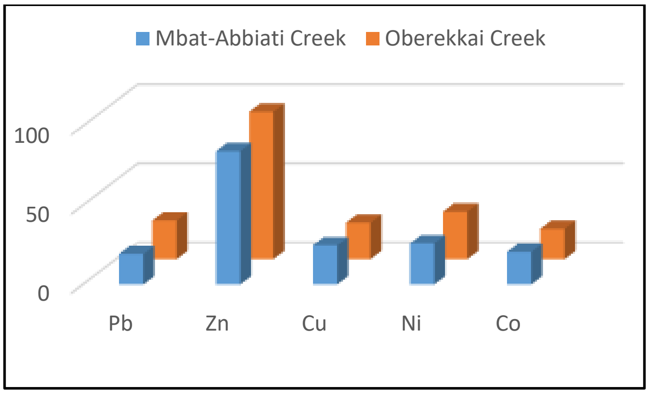

Figure 4. Mean abundance of heavy metals in sediments from Mbat-Abbiati and Oberrekai Creeks of the Great Kwa River, Southeastern Nigeria.

The order of abundance of these metals in the investigated sediments follows the sequence: Zn>Ni>Cu>Co>Pb for sediments from Mbat-Abiati Creek and Zn>Ni>Pb>Cu>Co for that of Oberekkai Creek (Table 2; Fig. 4). Thus, the highest accumulation of heavy metals in sediments for both Creeks was recorded for zinc, followed by nickel. cobalt is the most variable in the sediments of Mbat-Abiati Creek, followed by Pb, Zn, Cu and Ni in that order; while Zn is the

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most variable in Oberekkai Creek sediments, followed by Ni, Co, Pb and Cu in that order (Table 2).

The mean and standard deviation of heavy metals in the sediments varied across sampling stations (Table 2). The concentration of Pb ranged from 16.58 –25.22 mg/kg with mean value of 19.16±3.32 mg/kg for sediments of Mbat-Abiati Creek, while those of Oberekkai Creek ranged from 15.55 – 37.65 mg/kg with mean value of 24.60±7.60 mg/kg. As in the water samples, the highest level of heavy metals from both Creeks was recorded for Zinc. The concentration of Zn ranged from 81.10 –87.90 mg/kg with mean value of 84.05 ± 2.75 mg/kg for sediments of Mbat-Abiati Creek, while those of Oberekkai Creek ranged from 59.40 – 130.60 mg/kg with mean value of 93.22 ±26.07 mg/kg. The highest content of 130.60 mg/kg was measured at station O4 of the Oberekkai Creek (Table 2). Copper content in the sediments display low variability as it ranged from 21.88–27.05 mg/kg with mean value of 24.70 ± 1.94 mg/kg for sediments of Mbat-Abiati Creek, while those of Oberekkai Creek ranged from 16.33– 26.91 mg/kg with mean value of 23.20 ±3.90 mg/kg (Table 2). The highest Cu concentration (27.05 mg/kg) was measured in station A4 in Mbat-Abiati Creek and the least (16.33 mg/kg) in station O2 in Oberekkai Creek. Similarly, Ni vary between 24.50 and 28.50 mg/kg with mean value of 25.97± 1.44 mg/kg for sediments of Mbat-Abiati Creek, while those of Oberekkai Creek vary between 21.20 and 30.40 mg/kg (excluding station O4 which had excessive content of 51.90 mg/kg) with mean value of 30.18 ±11.25 mg/kg (Table 2). Finally, the concentration of Co ranged from 17.10–27.00 mg/kg with mean value of 20.45 ±3.65 mg/kg for sediments of Mbat-Abiati Creek, while those of Oberekkai Creek ranged from 11.00– 36.10 mg/kg with mean value of 19.37 ±10.19 mg/kg.

Heavy metal levels in the water hyacinth plant

The concentration (in mg/kg) of heavy metals in the various organs of water hyacinth from Mbat-Abiati and Oberekkai Creeks of southeastern Nigeria is given in Table 3, and the mean abundance illustrated in Fig. 5.

Table 3. Concentration (in mg/kg Dry Weight) of heavy metals in water hyacinth plant from Mbat-Abiati and Oberekkai Creeks, southeastern Nigeria.

		MBAT-ABIATI CREEK								OBEREKKAI CREEK								T-TEST DATA	
		A1	A2	A3	A4	A5	A6	Mean	SD	O1	O2	O3	O4	O5	O6	Mean	SD	t-score	p-level
ROOTS	Pb	0.95	1.79	1.84	1.04	0.73	0.74	1.18	0.51	2.46	2.30	0.78	2.25	3.29	2.71	2.30	0.84	2.80	0.02*
	Zn	81.70	43.80	44.00	30.40	21.90	28.90	41.78	21.42	80.40	51.80	26.00	30.10	37.40	29.50	42.53	20.71	0.06	0.95
	Cu	8.27	6.27	6.50	6.13	4.29	4.61	6.01	1.44	9.89	6.89	4.28	5.63	8.97	5.79	6.91	2.14	0.85	0.41
	Ni	7.00	3.80	4.20	5.60	2.90	3.60	4.52	1.51	3.50	3.80	4.50	3.70	4.60	3.20	3.88	0.56	0.96	0.36
	Co	20.59	13.70	12.58	13.17	6.44	6.05	12.09	5.38	19.05	13.56	11.94	11.40	14.77	11.17	13.65	2.99	0.62	0.55
LEAVES	Pb	0.29	0.26	0.27	0.37	0.33	0.56	0.35	0.11	0.54	4.11	0.32	0.55	0.37	0.31	1.03	1.51	1.11	0.29
	Zn	70.20	63.70	74.50	77.50	48.10	51.30	64.22	12.21	65.70	70.50	52.20	48.70	61.40	47.00	57.58	9.67	1.04	0.32
	Cu	1.77	1.14	1.45	1.74	1.35	1.77	1.54	0.26	2.13	2.25	1.78	1.56	1.21	1.08	1.67	0.48	0.59	0.57
	Ni	1.00	0.70	0.90	0.80	0.50	1.30	0.87	0.27	0.80	0.80	0.80	0.40	0.70	0.50	0.67	0.18	1.51	0.16
	Co	1.03	1.37	0.61	0.53	0.72	0.53	0.80	0.34	0.87	0.86	0.99	0.44	1.00	0.75	0.82	0.21	0.12	0.90

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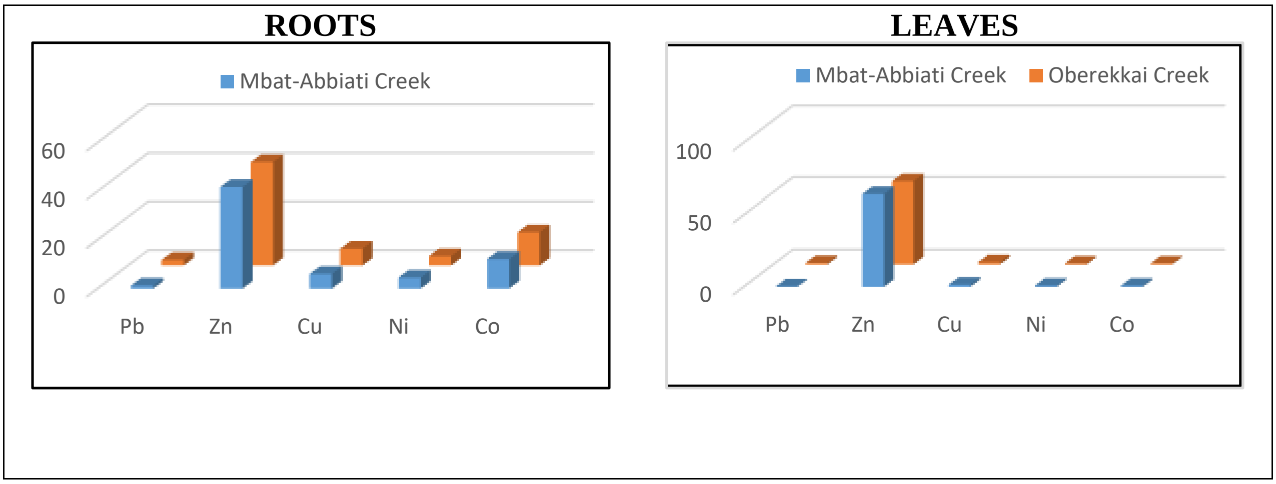

Figure 5. Mean abundance of heavy metals in roots and leaves of water hyacinth from Mbat-Abbiati and Oberrekai Creeks of the Great Kwa River, Southeastern Nigeria.

As shown in the presented data (Table 3; Fig. 5), and following observed trend in the water and sediment earlier reported, the highest accumulation of heavy metal in both the roots and leaves of the plants was recorded for Zn, the Creek considered notwithstanding. The nearest in abundance to Zn in the plant root was cobalt, while copper constituted the nearest in abundance to zinc in the plant leaves. At all the studied locations, water hyacinth accumulated higher concentrations of Pb, Cu, Ni and Co in the roots (Table 3; Fig. 5).

In the plant root, Zn ranged from 21.90 to 81.70 mg/kg with mean and standard deviation values as 41.78±21.42 mg/kg for samples from Mbat-Abbiati Creek, and from 26.00 to 80.40 mg/kg with mean and standard deviation value of 42.53±20.71 mg/kg for samples from Oberekkai Creeks (Table 3). Similarly, in the leaves, Zn ranged from 48.10 to 77.50 mg/kg with mean and standard deviation values as 64.22±12.21 mg/kg for samples from Mbat-Abbiati Creek, and from 47.00 to 70.50 mg/kg with mean and standard deviation values of 57.58±9.67 mg/kg for samples from Oberekkai Creeks (Table 3).

The nearest in content to zinc in the plant root was cobalt, which displayed mean and standard deviation values of 12.09±5.38 mg/kg for samples from Mbat-Abbiati Creek, and 13.65±2.99 mg/kg for those of Oberekkai Creeks. On the other hand, cobalt was the third in order of abundance of the measured heavy metals in the leaves. It displayed mean and standard deviation values of 0.80±0.34 mg/kg for the leave samples from Mbat-Abbiati Creek, and 0.82 ± 0.21 mg/kg for leave samples from Oberekkai Creeks.

The next in abundance to zinc in the plant leaves was Cu, which ranged between 1.14 and 1.77 mg/kg with mean and standard deviation values of 1.54±0.26 mg/kg in leave samples from Mbat-Abbiati Creek, and within 1.08 and 2.25 mg/kg with mean and standard deviation values of 1.67±0.18 mg/kg for leave samples from Oberekkai Creeks (Table 3). In the plant root, Cu displayed mean and standard deviation values of 6.01±1.44 mg/kg for samples from Mbat-Abbiati Creek, and 6.91±2.14 mg/kg for samples from Oberekkai Creeks),

Nickel concentrations in the root samples displayed mean and standard deviation values of 4.52±1.51 mg/kg for samples from Mbat-Abbiati Creek, and 3.88±0.56 mg/kg for samples from Oberekkai Creeks. Similarly, Ni levels and variation in the leave samples was 0.87±0.27

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mg/kg for samples from Mbat-Abbiati Creek, and 0.67±0.18 mg/kg for samples from Oberekkai Creeks.

Lead concentration was about the lowest and among the least variable heavy metals in both plant organs studied. In the root tissue, it showed 1.18±0.51 mg/kg for samples from Mbat-Abbiati Creek, and 2.30±0.84 mg/kg for samples from Oberekkai Creeks. Lead contents in the leaves ranged within 0.26 – 0.56 mg/kg with mean value of 0.35±0.11 mg/kg for leave tissues from Mbat-Abiati Creek, while those of Oberekkai Creek ranged within 0.31– 0.55 mg/kg with mean value of 0.42±1.51 (excluding station O2 which had excessive content of 4.11 mg/kg).

Bioconcentration of Heavy Metals (Pb, Zn, Cu, Ni and Co) By Water Hyacinth

Bioconcentration can be appraised with the aid of Bioaccumulation Factors (BCF). Bioaccumulation Factors (BCF) provides an index of the ability of the plant to accumulate the metal with respect to the metal concentration in the substrate. It is calculated as the metal concentration in plant tissue divided by the metal concentration in water, and is a dimensionless parameter (Wang and Lewis, 1997; Zayed, et al., 1998). A larger ratio implies better phytoaccumulation capability. Wang and Lewis, (1997) observed that when the metal concentration in water increases, the amount of metal accumulation in plant increases, whereas the BCF values decrease.

Bioaccumulation factors of Pb, Zn, Cu, Ni and Co in Eichhornia plants from Mbat Abiati and Oberakkai Creeks of the Great Kwa River, Southeastern Nigeria, were computed with the formula:

$$\text{BCF} = \frac{\text{Metal concentration in plant tissue}}{\text{Metal concentration in water}}$$

The results of the Bioaccumulation computation are presented in Table 4, and illustrated in Figure 6.

Table 4. Bioaccumulation factors (BCF) of Pb, Zn, Cu, Ni and Co in Eichhornia crassipes from Mbat Abiati and Oberakkai Creeks of the Great Kwa River, Southeastern Nigeria.

	ROOT		**LEAVES**	
	MBAT-ABIATI CREEK	*OBEREKKAI CREEK*	*MBAT-ABIATI CREEK*	*OBEREKKAI CREEK*
Pb	3507 ± 2130	3352 ± 2899	886 ± 179	1154 ± 1470
Zn	2022 ± 504	2282 ± 968	3361 ± 820	3454 ± 1738
Cu	4728 ± 2515	2732 ± 1007	1156 ± 492	633 ± 106
Ni	14472 ± 11786	3592 ± 1043	2467 ± 1548	600 ± 190
Co	92308 ± 32075	13648 ± 2985	5983 ± 880	818 ± 207

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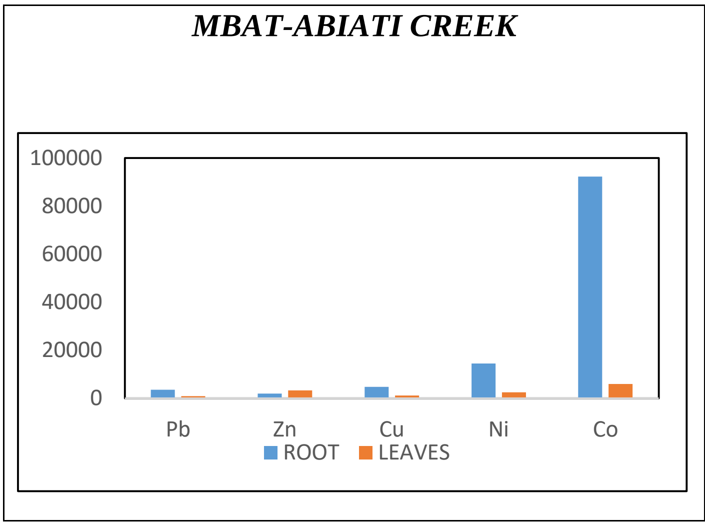

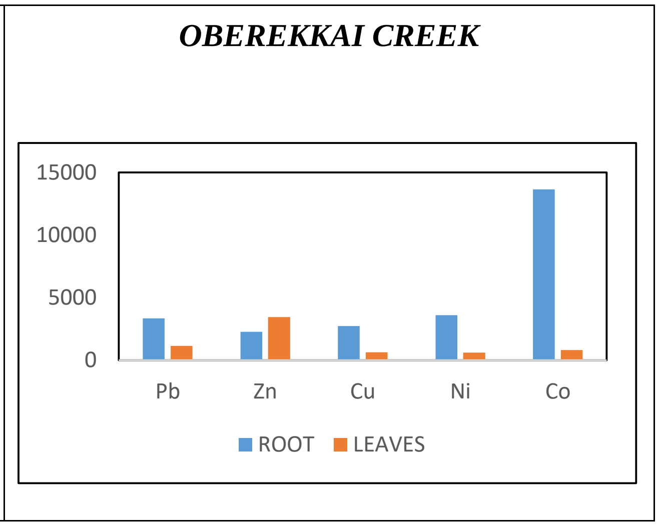

Figure 6. Bioaccumulation factors (BCF) of Pb, Zn, Cu, Ni and Co in Eichhornia crassipes from Mbat Abiati and Oberakkai Creeks of the Great Kwa River, Southeastern Nigeria.

A cursory appraisal of the presented data (Table 4; Fig 6) confirm that the uptake of all metals is stronger in the roots than in the leaves of the plant. For instance, the respective mean ± standard deviation bioaccumulation factor of Pb, Zn, Cu, Ni and Co in the root of water hyacinth from Mbat-Abiati Creek was 3507 ± 2130, 2022 ± 504, 4728 ± 2515, 14472 ± 11786, and 92308 ± 32075; whereas those of the leaves from the same Creek is 886 ± 179, 3361 ± 820, 1156 ± 492, 2467 ± 1548, and 5983 ± 880. Similarly, the respective mean ± standard deviation bioaccumulation factor of Pb, Zn, Cu, Ni and Co in the root of water hyacinth from Oberekkai Creek is 3352 ± 2899, 2282 ± 968, 2732 ± 1007, 3592 ± 1043, and 13648 ± 2985; while the leaves from the same Creek displayed 1154 ± 1470, 3454 ± 1738, 633 ± 106, 600 ± 190 and 818 ± 207. Judging from the relative magnitude of the BCF for the various heavy metals (Table 4; Fig 6), it can be deduced that Co has the highest accumulation potential in the area, followed by Ni, Cu, Pb and Zn in that order.

Translocation Factor

Translocation factors (Tf) is the ability of plant to accumulate, tolerate and translocate metals from underground tissues to aerial tissues. Hammad (2011) observed that translocation is primarily controlled by two processes: root pressure and leaf transpiration (Lasat, 2000); some metals are accumulated in roots, probably due to some physiological barriers against metal transport to the aerial parts, while others are easily transported in plants (Lu, et al., 2004).

In the present study, transpiration indicate the extent of metal transfer from root to leaves, and is defined by ratio of heavy metal concentration in the leaf to concentration in the root of the plant, as follows:

$$\mathrm{Tf} = \frac{\text{Metal concentration in the leaves}}{\text{Metal concentration in the roots}}$$

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(Baker and Brooks, 1989; Fayiga and Ma, 2006; Luo et al., 2005; MacFarlane and Burchett, 2002; Megaji et al, 2018; Nouri, 2009; Wang et al, 2010; Zheng et al., 2002).

TF>1 is an indication that translocation of metals was effectively made to the leaves from the root (Baker and Brooks, 1989; Rezvani and Zaefarian, 2011; Zhang et al., 2002; Fayiga and Ma, 2006).

The efficiency of translocation (in %), which depicts the ability of the plant to translocate metal species from roots to leaves at different concentrations (Das et al., 2014), is calculated as follows:

$$\text{Efficiency (\%)} = \text{metal in leaf (mg kg–1)/metal in roots (mg kg–1)} \times 100.$$

The results of the Translocation Factors computation are presented in Table 5, and that of Efficiency of Translocation illustrated in Figure 7.

As shown in Table 5, apart from Zn that had TF>1, all other metal had TF values<1, indicating poor transmission from root to leaves. The efficiency of translocation of the heavy metals follow the sequence: Zn > Pb > Cu > Ni > Co for Mbat-Abiati Creek, and Zn > Cu > Pb > Ni > Co for Oberekkai Creek (Fig. 7). Thus Zn has the highest translocation capabilities, while Co has the least.

Table 5. Translocation Factor (leaves / root ratio) of Pb, Zn, Cu, Ni & Co in Eichhornia crassipes from Mbat Abiati and Oberakkai Creeks of the Great Kwa River, in Southeastern Nigeria.

	MBAT-ABIATI CREEK	OBEREKKAI CREEK
Pb	0.36 ± 0.23	0.48 ± 0.65
Zn	1.75 ± 0.59	1.51 ± 0.40
Cu	0.27 ± 0.08	0.26 ± 0.10
Ni	0.20 ± 0.08	0.17 ± 0.04
Co	0.07 ± 0.03	0.06 ± 0.02

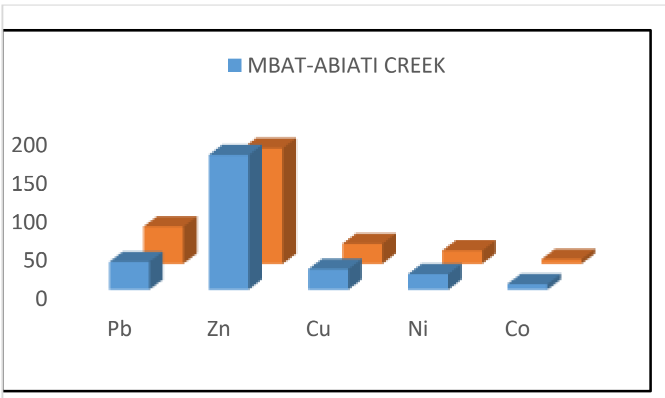

Figure 7. Efficiency of translocation (in %) of Pb, Zn, Cu, Ni and Co in Eichhornia crassipes from Mbat Abiati and Oberakkai Creeks of the Great Kwa River, in Southeastern Nigeria.

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DISCUSSIONS AND CONCLUSIONS

A cursory appraisal of the T-test data provided in Table 1 showed that the measured concentration of most of the heavy metals (Pb, Cu, Ni, Co) in the water samples from the two Creeks studied vary significantly ($p < 0.05$); the only exception being Zn. On the other hand, no noteworthy differences were observed in the contents of the various heavy metal in the sediments of the two Creeks (Table 2). Similarly, Pb accumulation in the roots of the water hyacinth plants displayed significant differences ($p<0.05$) in the two Creeks (Table 3). Apart from these, there was no other significant differences ($p>0.05$) in the levels of the various heavy metals measured in the organs of the water hyacinth plant of the two Creeks studied (Table 3).

The analytical results of the waters of the two Creeks shows that the concentrations of most of the heavy metal are low and, hence accommodated within the respective permissible limits of the Standard Organization of Nigeria (SON, 2007), and World Health Organization (WHO, 2008). The concentration of these heavy metals in the waters could be attributed to anthropogenic sources from wastewaters draining residential, farming, mining, industrial, commercial, recreational and dumpsite areas located within the locality. Similarly, results for the sediments showed that although the heavy metals levels were the highest compared to those of other media sampled, the concentrations were generally within the limits normally quoted as EPA Ecological Screening Values (EPA, 1995), Canadian Interim Sediment Quality Guidelines, comprising Threshold Effect Concentration (TEC) and Probable effect concentration (PEC) (Environment Canada 1995, 2002), as well as Target and Intervention values of the Dutch Soil Quality Standards (MHSPE, 1994) (Table 2), and the World average shale composition of Turekian & Wedepohl (1964).

Relative Accumulation Indices (RAI), which is calculated as the ratio concentration in sediment to concentration in water, provides a means of assessing the relative levels of accumulation of heavy metals in the abiotic monitors. The larger the RAI ratio the higher the relative accumulation.

Relative Accumulation Indices (RAI) of Pb, Zn, Cu, Ni and Co in Sediment from Mbat Abiati and Oberakkai Creeks of the Great Kwa River were computed with the formula:

RAI = concentration in sediment / concentration in water

Judging from the values obtained, it is concluded that the levels of Pb, Zn, Cu, Ni and Co in the sediments are at least; 15,550; 2,156; 5,443; 15,200 and 11,000 times higher than their respective levels in the waters. It is not uncommon to observed heavy metals accumulating more in sediments than in the overlying water column (see for example: Aderinola, et al., 2009; Davies et al., 2006; Hamed, 1998; Lokeshwari and Chandrappa, 2006; Ndimele and Jimoh, 2011; Nguyena et al. 2005; Patel et al., 1985; Saeed and Shaker, 2008). This may be due to the fact that sediments are reservoirs for all contaminants and dead organic matters descending from the ecosystem above. River sediments do not only constitute an integral and dynamic part of stream basins, but often originate from the weathering of minerals and soils upstream. Natural concentrations of heavy metals as a result of the weathering processes of mineral deposits can be quite high in stream sediments close to the deposit, but decrease with increasing distance downstream, due to dissipating energy and dilution of sediments from other un-polluting sources (Plumlee, 1999). Zabetoglou et al (2002) and Defew et al (2004) agree that the bioavailability of even a minute fraction of the total sediments' heavy metal often assume considerable importance.

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In the present study, the sequence of the sampled media favoured in the accumulation of most of the heavy metals follow the trend: SEDIMENT>PLANT ROOTS>PLANT LEAVES>WATER, the only exception being Zn which registered the trend: SEDIMENT>PLANT LEAVES>PLANT ROOTS>WATER. The concentration of the heavy metals was highest in the sediment, while the levels in the sampled waters displayed the lowest values. Among the water hyacinth tissues considered, the root had the highest accumulation of heavy metals, notably, Pb, Cu, Ni and Co. Stratford et al. (1984) document the trend: ROOTS>STEMS>LEAVES for metal accumulations in water hyacinth plants. However, in the present study, only roots and leaves of the macrophyte were employed, stems were not considered. Hence, the biomonitors in our work favoured the trend: ROOTS>LEAVES, which is a slight modification of that of Stratford et al. (1984). Accordingly, at most of the studied locations, higher concentrations of Pb, Zn, Cu, Ni and Co were accumulated in the roots tissue of the water hyacinth, rather than in the aerial parts (Table 3 & Figures 5). Similarly, the Bioaccumulation factors of the roots was higher than those of the leaves for most of the metals (Table 4), which supports the assertion that the roots accumulated more heavy metals than the leaves. This is consistent with observation elsewhere (e.g., Abd- Elhamid, 1996; Lyngby and Brix, 1982; Robb and Pierpoint, 1983; Soltan and Rashed, 2003; Veranda et al., 2008; Yahya, 1990; Zhu, et al., 1999). Denny (1980, 1987), Kevin et al, (2000), Matagi et al. (1998), Mehra et al, (2000) and Zhu, et al. (1999) agree that the main route of heavy metal uptake in wetland plants is through the roots in the case of emergent and surface-floating plants like water hyacinth. Other workers, including Abd- Elhamid, (1996), Jana (1988), Lyngby and Brix (1982), Robb and Pierpoint (1983), Veranda et al. (2008) and Yahya (1990) added that a greater proportion of absorbed metals in mecrophyte plants are frequently preferentially retained by the root system rather than being translocated to other plant organs. The root is considered crucial for the absorption of elements in free-floating plants (Sharma and Gaur, 1995) rather than the shoots because roots are very sensitive in producing glutathione (GSH), cysteine, and PCs – a binding site for metals (Rauser, 2003). Relatively lower accumulation of metal in leaves can be associated with protection of photosynthesis from toxic levels of heavy metals (Landberg and Greger, 1996). Lu et al., (2004) advanced the views that stems and leaves have low heavy metals accumulation rate, compared to roots. This is due to some physical barriers in roots against metal transport to the aerial part (stems and leaves). High concentration of metals in the roots of the plant is an indication that this plant could be useful in the removal of heavy metals through rhizofiltration process which accumulate contaminants in the roots (USEPA. 2000; David and David 2001). This is because Eichhornia crassipes, has well established roots than terrestrial plants. This root system facilitates effective phytoremediation in the aquatic ecosystems for heavy metals and wastewater remediation. The rapid growth and significant biomass processing potentials supports higher pollution uptake and better purification method due to direct contact with the water column. (Irfan and Alatawi, 2017). Other plants that have similar phytoprocess (removed pollutants through rhizofiltration) capabilities are water mimosa, duckweed, water spinach, and calamus (Veschasit et al., 2012; Wang, et al., 2012 and USEPA. 2000]. However, consideration of the amount of pollutant accumulated by plant roots is an important factor for phytoremediation of wastewater (Wang, et al., 2012).

The mean heavy metals accumulations in the study area were detected in the order: Zn>Cu>Ni>Pb>Co for waters from Mbat-Abiati Creek and Zn>Cu>Ni>Co>Pb for Oberekkai Creek (Table 1; Fig. 3); Zn>Ni>Cu>Co>Pb for sediments from Mbat-Abiati Creek and Zn>Ni>Pb>Cu>Co for that of Oberekkai Creek (Table 2; Fig. 4); Zn>Co>Cu>Ni>Pb for the roots of the water hyacinth plants in both Creeks, and; Zn>Cu>Ni>Co>Pb for leaves of the

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water hyacinth plants from Mbat-Abiati Creek and, Zn>Cu>Pb>Co>Ni for those of Oberekkai Creek (Table 3; Fig. 5). Indication is that the pattern of heavy metal concentrations in the various organs of E. crassipes. (biomonitor) are closely associated with the order of abundance in the geological substrate (water and sediments). A similar remarkable relationship between heavy metals concentrations in aquatic plant/organisms and sediments was documented in Ibrahim et al. (2000) and Ibrahim and El-Naggar (2006).

The consistency displayed by Zn as the metal with the highest accumulation, and variability in all the media studied need special considerations. Zinc has been revealed in the study as the metal that display the highest accumulation in both the root and leaves tissues, while Pb constituted the least. Indication is that the affinity of water hyacinth in accumulating Zn is higher than that for other heavy metals, and least for Pb. Interestingly, at most of the studied locations, Zn recorded relatively higher levels of accumulation in the leave tissues, compared to its levels in the root system followed by Cu then by Ni. This demonstrated that Zn is more mobile from roots to leaves than Pb, Cu, Ni and Co. Similar observations have been documented in Barry and Clark, (1978) and Baldantoni et al. (2008).

The present study revealed metal accumulation in the root of the water hyacinth plant in the range: 0.73 – 3.29 mg/kg dry wt. for Pb, 21 – 81.7 mg/kg dry wt. for Zn, 4.28 – 9.89 mg/kg dry wt for Cu, 2.9 – 7.0 mg/kg dry wt. for Ni, and 6.05 – 20.59 mg/kg dry wt. for Co. Similarly the recorded range in the leaves were: 0.26 – 4.11 for Pb, 47.0 – 77.5 for Zn, 1.08 – 2.25 for Cu, 0.4 – 1.3 for Ni, and 0.44 – 1.37 for Co. This appear quite high, considering the permissive range of 5-75 mg/kg dry wt. for Zn, 5-20 mg/kg dry wt. for Cu, and 0.02-5 mg/kg dry wt. for Ni (Bowen, 1979; Chapman and Pratt, 1961) documented for plant tissues. According to Rugigana (2007), high metal concentration is toxic to the growth of water hyacinth plant.

The present study recorded very high values of bioaccumulation factors despite the low concentration of the respective metals in the sampled waters (Table 1). This agree with observation of several workers that when metal concentration in water increases, the amount of metal accumulation in plant increases, whereas the BCF values decrease (Carvalho and Martin, 2001; Lu, et al., 2004; Soltan and Rashed, 2003; Wang and Lewis, 1997; Weiliao and Chang, 2004). Lu, et al. (2004) submitted that metal accumulations by macrophytes can be affected by metal concentrations in water and sediments (Lin and Zhang, 1990). Weiliao and Chang (2004) reported highest BCF of roots associated with low concentration of Cu in the external environment. Lu, et al. (2004) reported that BCF values of Zn in water hyacinth roots and shoots decreased when the ambient water concentration of Zn increased. According to Soltan and Rashed (2003), water hyacinth effectively removes appreciable quantity of heavy metals (Cd, Co, Cr, Cu, Mn, Ni, Pb and Zn) from freshwaters, especially at low concentrations. Carvalho and Martin (2001) observed large BCF values associated with low concentrations of Cd, Cu, Ni, Pb, and Zn. Rugigana (2007) concluded that bioaccumulation factor increases with low metal concentration and decreases with increasing metal concentration because high metal concentration is toxic to the growth of water hyacinth plant.

The ambient levels of Co in the waters at all the studied locations were lower than those for Zn & Cu (Table 3); but this was accompanied by the highest BCF values in both water hyacinth roots & leaves. Thus, the bioaccumulation study revealed Co as the metal with the highest accumulation potential in the area, followed by Ni, Cu, Pb and Zn in that order.

The translocation factor data revealed Zn as possessing the highest translocation capabilities, and Co as the least. Thus Zn appear to be more mobile from roots to leaves, than other elements

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investigated. Similar observations were made in Baldantoni et al. (2008), Barry and Clark (1978), Brun et al., (2001), Vesk et al. (1999), etc.

Zayed, et al. (1998) submitted that the appropriateness of a plant for phytoremediation potential is often determined by the magnitude of its bioaccumulation (BCF) values, and BCF values greater than 1000 are generally considered evidence of a useful plant for phytoremediation. The present study revealed mean BCF values of above 1000 for each of the metals studied, indicating that the water hyacinth plant is a good hyper accumulator of Co, Ni, Cu, Pb and Zn.

The results of the present study showed that water hyacinth, Eichhornia crassipes, is a good accumulator of Zn, and to a lesser extent, Co and Cu. Other studies have portrayed the plant as a good accumulator of Zn, Cr, Cu, and Cd (Yapoga et al. 2013), Cd and Cr (Muramoto and Oki (1983). Its encroachment into the waters of the Great Kwa River is undoubtedly a blessing in disguise.

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