HEAVY METAL STATUS OF WATER HYACINTH (*Eichornia crassipes*) IN WARRI RIVER, NIGERIA

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Abstract: The status of metals in water hyacinth (*Eichornia crassipes*) of Warri River, Nigeria was investigated in this study. Water hyacinth samples were collected from six sampling points along the Warri River on a monthly basis for a period of one year between April 2014 and March 2015. Samples were digested with aqua regia and analyzed for heavy metals using atomic absorption spectrophotometry. The results of the measured mean concentrations of metals in the water hyacinth were : Cd (3.07-4.55 mg/kg), Pb (8.47 – 9.68 mg/kg), Cr (1.20 – 2.01 mg/kg), Cu (1.62-3.94 mg/kg), Ni (12.7-16.2 mg/kg), Co (0.22-0.83 mg/kg), Mn (4.96 – 7.32 mg/kg), Ba (0.10-0.17 mg/kg), Zn (26.3-37.1 mg/kg) and Fe (428-594 mg/kg). The results also showed significant spatiotemporal and seasonal variations ($p<0.05$) in the metal concentrations in the water hyacinth of the Warri River. The concentrations of metals in the water hyacinth followed the order Fe > Zn > Ni > Pb > Mn > Cd > Cu > Cr > Co > Ba and the concentrations of Cd, Pb, Cr and Fe were higher than FAO/WHO maximum permissible limits.

Keywords: Water hyacinth, Warri River, heavy metal, *Eichornia crassipes*

Introduction

Environmental problems are among daily life troubles in Nigeria as in the world at large. Such problems are caused by erosion, increase in population, rapid industrialization, distortion of shores, chemicals used in industries, oil exploration and exploitation, industrial activities, technological development among others. Heavy metal (HM) pollution has turned out to be one of the most serious environmental problems today. With the rapid development of many industries, wastes containing metals are directly or indirectly being discharged into the environment especially the aquatic environment. The release of HMs into the aquatic ecosystem has been increasing continuously as a result of industrial activities and technological development which are posing a significant threat to the aquatic ecosystem and public health because of their toxicity and persistence nature (Rizo *et al*., 2011; Li *et al*., 2012; Sheng *et al*., 2012). Heavy metals have been the object of many studies and several aims have been pursued such as the impact of HMs pollution on natural ecosystem (Carreras and Pignata, 2002).

Plants have the ability to accumulate heavy metals and this ability could be harnessed to remove HMs from the environment. Approximately four hundred different species of plants have been identified as heavy metal hyperaccumulators and water hyacinth (*Eichhornia crassipes*) is one of them (Prasad and Freitas, 2003; Nnamonu *et al*., 2015). Water hyacinth (WH) is a fast growing perennial aquatic macrophyte. It is a noxious freshwater weed with flourishing roots and is listed as one of the world's worst aquatic plants (Malik, 2007; Gichuki *et al*., 2012). It is well known for its duplication potential and the plant can double its population in only twelve days (Lissy and Madhu, 2010). Water hyacinth is also known for its ability to grow in severely polluted waters and a mat of medium sized plants may contain 2 million plants per hectare that weigh 270 to 400 tons (Malik, 2007). Its high yield and ability to tolerate variations in nutrients, temperature and pH levels have led to many environmental and economic problems, such as blockage of navigation routes, reduction of biodiversity, irrigation, recreation and power generation (Zheng, *et al*., 2009; Bhattacharya and Kumar, 2010). Water hyacinth, among other aquatic macrophytes, has been shown to have a great potential to remove pollutants when being used as a biological filtration system (Brahma and Misra, 2014). It contains many polyfunctional metal-binding sites for both cationic and anionic metal complexes. Water hyacinth could remove several heavy metals and other pollutants (Upadhyay and Tripathi, 2007; Hussain *et al*., 2010; Mahamadi, 2011; Brahma and Misra, 2014).

In recent times, there is increasing interest in major parts of the world in the conversion of WH into a profitable resource such as fodder for animal feed, fertilizer, biogas production, paper production and pollution control (Okoye *et al*., 2000; Akmal *et al*., 2014;Naseema *et al*., 2004; Al Moustapha *et al*., 2009; Matindi, 2016). Water hyacinth contains vital nutrients as well as high degree of fermentable materials which makes it a potentially useful material. However, it is also known to accumulate high levels of heavy metals from polluted waters (Matindi, 2016). Therefore, before using WH for any profitable purpose, it is imperative to analyze the heavy metal content of the water hyacinth. If the metal content is too high in the plant material, it will be challenging to utilize water hyacinth. Thus, the objective of this study is to determine the distribution of heavy metals in WH in the Warri River.

Materials and Methods

Sampling locations

Six locations designated as SW1 to SW6 were strategically selected along the Warri River for this study. The six sampling locations were chosen based on the anthropogenic activities taking place in these locations. The geographical position system coordinates of the sampling locations are shown in Table 1.

Table 1: The geographical position system coordinates of the sampling locations

Sampling Points	Latitude	Longitude
SW1	5.3149 N	5.4243 E
SW2	5.3052 N	5.4410 E
SW3	5.3243 N	5.4231 E
SW4	5.3242 N	5.4748 E
SW5	5.3052 N	5.4359 E
SW6	5.3043 N	5.4443 E

Sample and sample collection

The *Eichhornia crassipes* samples were collected by hand into black polythene zip-bags at each sampling point. The collected samples were labelled appropriately, stored in a block of ice, and taken to the laboratory where they were washed with distilled water, oven dried and pulverized with porcelain mortar and pestle and kept prior to analysis.

Determination of metals in water hyacinth samples

About 0.5 g of the dried and grounded water hyacinth samples was placed in a beaker followed by the addition of 12 mL of aqua regia (3:1 $HCl:HNO_3$), swirled to wet the sample, stoppered with a watch glass then allowed to stand overnight. The next day, the beaker was heated on a hotplate at 50^oC for 30 min. At the end of the digestion, which was signalled by the appearance of a clear solution, the beaker was removed and allowed to cool. The beaker wall and watch glass were washed down with 0.25 M HNO_3. Thereafter, the sample was filtered into a 25 mL standard volumetric flask and then made to mark with 0.25 M HNO_3 (Radojevic and Bashkin, 1999). The sample solutions were subsequently analysed for heavy metals (Ba, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb and Zn) using atomic absorption spectrophotometry (Perkin Elmer Analyst 200).

Quality control and assurance

All the reagents utilized were of analytical grade (Merck). All glasswares used were first washed with detergent and then left to soak for approximately 24 h in 2% nitric acid. Spike recovery studies was carried out on already analysed samples with known concentration of the individual metals and reanalysed. The percentage recovery was calculated for each sample analysed. The percent recovery ranged from 94.3 to 98.5%. Blanks were analysed for metals along with samples and the results for blanks were subtracted from those obtained for samples before data analysis and interpretations.

Data analysis

The student's t-test statistical tool was used to determine if there is significant seasonal variation in the metal concentrations while Analysis of Variance (ANOVA) was used to determine if there is a significant spatiotemporal variation in the metal concentrations. A p-value <0.05 indicated significant variation while p-value >0.05 indicated no significant variation. The Pearson's correlation analysis was used to determine the relationships among the metals in the water hyacinth. All statistical analysis was done using SPSS version 19.0.

Results and Discussion

Metal concentrations in water hyacinth (Eicchornia crassipes) samples

The concentrations of metals in the water hyacinth samples from the Warri River in this study are shown in Table 2. Analysis of variance showed that there is significant spatiotemporal variation ($p < 0.05$) in the metals concentrations in the water hyacinth samples from the different sampling points. The significant variation in the metal concentrations in the water hyacinth among the sampling points may be attributed to varying degree of absorption of metals by the water hyacinth. Also, significant seasonal variation ($p<0.05$) was also observed in the concentrations of metals in the water hyacinth samples. The seasonal variation of metals in the water hyacinth samples of the Warri River are shown in Fig. 1.

Table 2: Metal concentrations (mg/kg) in water hyacinth *(Eicchornia crassipes)* during the entire study period

	SW1	SW2	SW3	SW4	SW5	SW6
Cd	3.20±1.00	3.07±1.14	3.11±0.85	3.94±1.42	4.55±1.39	3.80±1.64
	(1.45-4.76)	(1.09-4.48)	(2.08-5.08)	(1.75-6.23)	(2.05-7.14)	(1.39-6.74)
Pb	8.47±5.02	8.91±6.06	9.36±4.91	8.75±4.07	9.03±4.19	9.68±6.72
	(0.13-18.8)	(0.37-22.1)	(0.14-17.9)	(0.44-13.3)	(0.59-16.9)	(0.39-24.9)
Cr	1.81±1.33	1.75±1.31	1.83±0.89	2.01±0.97	1.20±0.61	1.78±1.00
	(0.76-5.78)	(0.86-5.56)	(0.72-4.06)	(0.76-4.01)	(0.02-2.04)	(0.66-4.41)
Cu	1.81±0.80	2.83±1.64	2.84±0.94	3.94±2.53	2.01±0.87	1.62±1.29
	(0.96-3.78)	(0.86-6.21)	(0.98-4.57)	(1.43-8.69)	(0.92-3.44)	(0.33-4.73)
Ni	16.18±4.82	13.60±2.48	15.33±5.41	12.71±3.07	14.53±5.12	13.9±3.00
	(7.73-23.7)	(9.03-18.01)	(3.39-23.5)	(7.47-17.6)	(9.26-27.5)	(9.18-17.5)
Co	0.29±0.21	0.31±0.20	0.22±0.15	0.83±1.11	0.51±0.44	0.47±0.46
	(0.11-0.69)	(0.09-0.78)	(0.09-0.64)	(0.12-3.49)	(0.05-1.54)	(0.11-1.61)
Mn	4.96±2.42	5.13±3.81	7.32±4.89	5.96±3.69	5.23±3.01	6.86±5.45
	(1.11-10.2)	(1.37-13.7)	(2.36-18.8)	(2.38-12.4)	(2.05-12.3)	(2.68-19.9)
Ba	0.10±0.21	0.15±0.26	0.10±0.21	0.17±0.37	0.10±0.16	0.15±0.36
	(0.01-0.76)	(0.02-0.86)	(0.02-0.75)	(0.01-1.20)	(0.02-0.54)	(0.01-1.29)
Zn	37.1±12.2	26.31±7.77	35.8±13.1	30.77±8.95	33.9±12.8	29.83±4.51
	(17.5-55.5)	(12.2-41.2)	(17.3-61.0)	(16.5-41.7)	(14.1-58.5)	(19.5-38.5)
Fe	538±347	594±446	428±293	561±298	482±268	581±302
	(79.9-1300)	(98.7-1501)	(119-1268)	(55.2-916)	(56.9-895)	(264-1438)

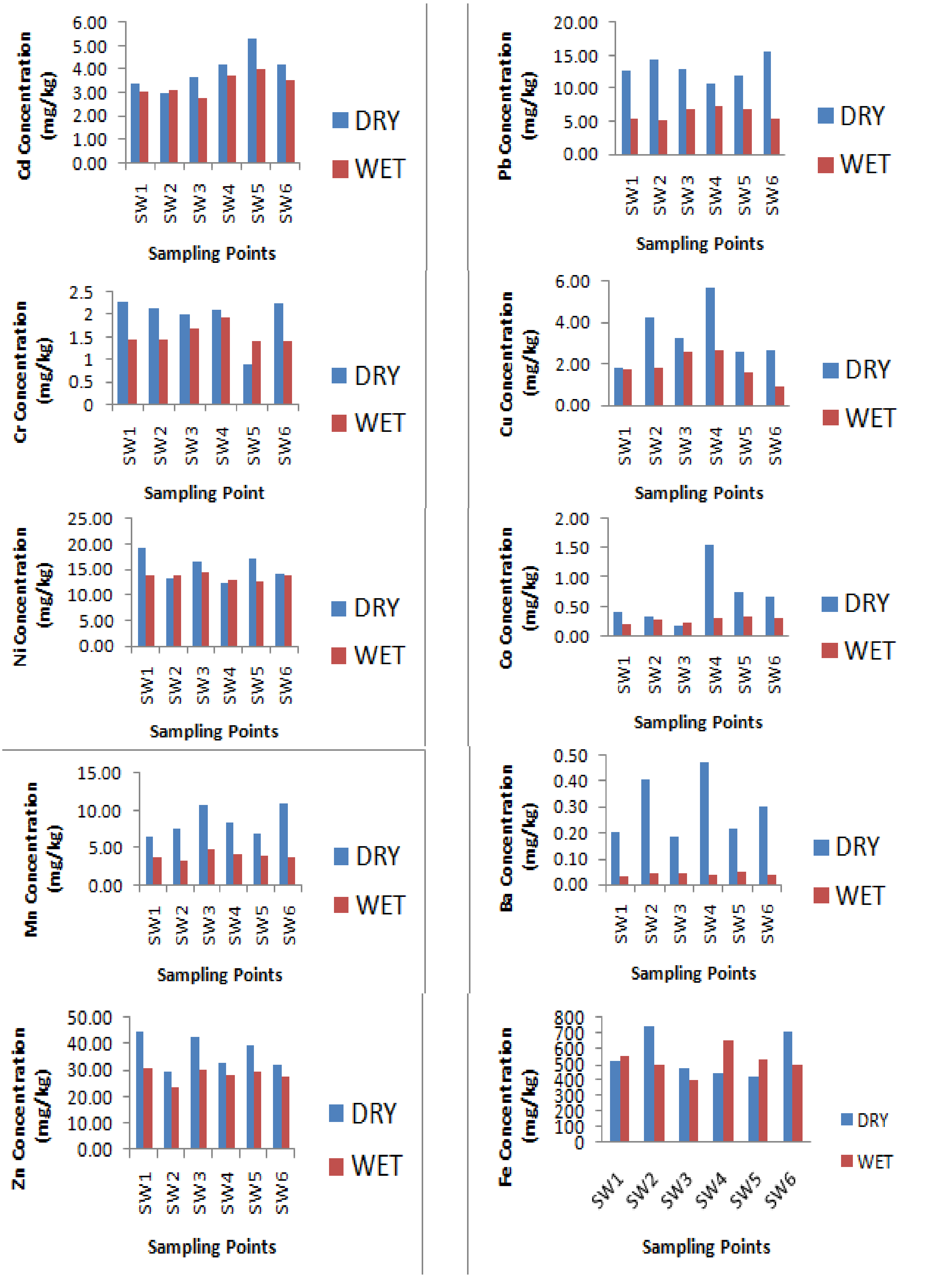

Fig. 1: Seasonal variations of metals in water hyacinth of the Warri River

The mean concentration of Cd for the entire study period in the water hyacinth ranged from 3.07 to 4.55 mg/kg. Sampling points SW5 and SW2 have the highest and lowest concentrations of Cd respectively. The concentrations of Cd in the water hyacinth followed the order SW5 > SW4 > SW6 > SW1 > SW3 > SW2. The concentrations of Cd obtained in water hyacinth in the Warri River were higher than those reported in literatures (Kisamo, 2003; Nnamonu *et al*., 2015; Omafuvwe, 2017). For instance, Nnamonu *et al*. (2015) reported Cd concentrations in the range of 0.65 to 1.28 mg/kg in water hyacinth in River Benue while Omafuwe (2017) reported Cd concentrations in the range of 0.01 to 0.09 mg/kg in Ikpoba and Ologbo Rivers in Edo State Nigeria. The concentrations of Cd obtained in this study were also higher than the maximum permissible limit of 0.1 mg/kg set by Food and Agriculture Organization/World Health Organization (FAO/WHO) (2001).

The mean concentrations of Pb for the entire study period in the water hyacinth range from 8.47 to 9.68 mg/kg. Among the sampling points the concentrations of Pb in the water hyacinth followed the order; SW6 > SW3 > SW5 > SW2 > SW4 > SW1. The concentrations of Pb obtained in the study were similar to those reported by Nnamonu *et al*. (2015) for River Benue and Kisamo (2003) for Lake Victoria Basin in Tanzania. However, they were higher than those reported by Ndimele and Jimoh (2011) for Olige Lagoon, Lagos and Omafuvwe (2017) for Ikpoba and Ologbo Rivers. The higher concentration of Pb obtained in this study in comparison with those obtained for Olige lagoon, Ikpoba and Ologbo Rivers may be as a result of the high anthropogenic activities along the Warri River. The concentrations of Pb obtained in this study were within the normal range of 0.2 to 20 mg/kg found in plants (Kabata-Pendias and Pendias, 1992) but higher than the maximum permissible limit of 2 mg/kg set by Food and Agriculture Organization/ World Health Organization (FAO/WHO) (2001).

The mean concentration of Cr in the water hyacinth in this study for the entire study period ranged from 1.20 to 2.01 mg/kg at sampling point SW4. The concentrations of Cr in the water hyacinth followed the order SW4> SW3> SW1> SW6> SW2 > SW1. The concentration range of Cr in the water hyacinth in this study was higher than the range of 0.01 to 0.59 mg/kg reported for Ikpoba and Ologbo Rivers (Omafuvwe, 2017) but similar to the range reported for River Benue and Lake Victoria Basin, Tanzania (Nnamonu *et al*., 2015; Kisamo, 2003). The concentrations of Cr in water hyacinth in this study were higher than the maximum permissible limit of 0.1 mg/kg set by Food and Agriculture Organization/ World Health Organization (FAO/WHO) (2001).

The mean concentration of Cu in these water hyacinths for the entire study period ranged from 1.62 to 3.94 mg/kg. The highest and lowest Cu concentrations were observed at sampling points SW4 and SW6, respectively. Among the sampling points the concentrations of Cu in the water hyacinth followed the order; SW4 > SW3 > SW2 > SW5 > SW1 > SW6. The concentrations of Cu in the water hyacinth of the Warri River were comparable to those reported by Nnamonu *et al*. (2015) for River Benue.

The mean concentration of Ni ranged from 12.7 to 16.2 mg/kg. The concentration of Ni at sampling points SW1 and SW4 were the highest and lowest respectively. The concentrations of Ni in the water hyacinth followed the order SW1 > SW3> SW5 > SW6 > SW2 > SW4. The concentration of Ni obtained in this study were higher than those reported for Ikpoba and Ologbo Rivers in Edo State, Nigeria (Omafuvwe, 2017) and those reported by Abdel-Sabour *et al*. (1996) for water hyacinth in Egyptian water bodies.

The mean concentration of Co in the water hyacinth of the Warri River ranged from 0.22 mg/kg at sampling point SW3 to 0.83 mg/kg at sampling point SW4. There was significant ($p<0.05$) spatiotemporal and seasonal variation in the concentrations of Co in the water hyacinth samples of Warri River. The concentration of Co was highest in water hyacinth from the midstream, followed by those from downstream while the least concentration was observed for those from upstream. The concentrations of Co in the water hyacinth followed the order; SW4 > SW5 > SW6 > SW2 > SW1 > SW3.

The mean concentration of Mn obtained in the water hyacinth of the Warri River during the entire study period ranged from 4.96 to 7.32 mg/kg. The highest and lowest concentrations of Mn were found at sampling points SW3 and SW1, respectively. The concentrations of Mn in the water hyacinth followed the order SW3 > SW6 > SW4 > SW5 > SW2 > SW1. The concentrations of Mn obtained in this study were higher than those reported for Ologe lagoon in Lagos, Nigeria (Ndimele and Jimoh, 2011) but comparable to those reported for River Benue (Nnamonu *et al*., 2015). The concentrations of Mn were, however, lower than the maximum permissible value of 500 mg/kg set by FAO/WHO (2001).

The mean concentration of Ba obtained in water hyacinth of the Warri River during the entire study period ranged from 0.10 to 0.17 mg/kg. The highest concentration of Ba in this water hyacinth was found at sampling point SW4. Among the sampling points, the average concentrations of Ba in the water hyacinth during the entire study period followed the order; SW4 > SW2= SW6 > SW1 = SW3 = SW5.

The mean concentration of Zn in the water hyacinth samples in this study during the entire study period ranged from 26.3 mg/kg at sampling point SW2 to 37.1 mg/kg at sampling point SW1. The concentrations of Zn in the water hyacinth followed the order SW1 > SW3 > SW5 > SW4 > SW6 > SW2. The concentration of Zn in water hyacinth in this study was higher than the range of 1.73 to 4.63 mg/kg found in the water hyacinth in Ikpoba and Ologbo Rivers (Omafuvwe, 2017). The concentration of Zn in water hyacinth in this study was, however comparable to those reported in River Benue (Nnamonu *et al*., 2015). The concentration of Zn obtained in water hyacinths in this study were within the normal range of 1 to 400 mg/kg found in plants (Kabata-Pendias and Pendias, 1992) and the maximum permissible limit of 99.4 mg/kg set by FAO/WHO (2001).

The mean concentration of Fe in the water hyacinth samples of the Warri River during the entire study period ranged from 428 to 594 mg/kg. The highest and lowest concentrations of Fe in the water hyacinth were found at sampling points SW2 and SW3, respectively. The concentrations of Fe in the water hyacinth followed the order; SW2 > SW6 > SW4 > SW1 > SW5 > SW3. The concentrations of Fe found in water hyacinth on the Warri River in this study were far higher than those reported in literature (Kisamo, 2003; Ndimele and Jimoh, 2011; Nnamonu *et al*., 2015, Omafuvwe, 2017). The concentrations of Fe obtained in water hyacinths in this study were within the normal range of 20 to 1000 mg/kg found in plants (Kabata-Pendias and Pendias, 1992). They were, however, higher than the maximum permissible value of 426 mg/kg set by FAO/WHO (2001). The Fe content of water hyacinth plants in this study may be due to the absorption from water and the atmosphere (Nnamonu *et al*., 2015).

Correlation analysis of metals in water hyacinth

The results of the Pearson's correlation analysis of metals in water hyacinth from the Warri River for the dry and wet seasons are shown in Table 3. During the dry season, Co correlate positively with Cd and Cu, Mn correlate with Pb, Ba correlate with Cu and Co, Zn correlates with Ni while Fe correlates with Pb and Cr. During the wet season, Cr correlate with Pb, Cu correlates with Pb and Cr, Co correlates with Cd while Mn correlates with Pb, Cr and Cu. Also, Zn correlates with Pb and Mn while Fe correlates with Cd.

Table 3: Pearson's correlation coefficients of metals in water hyacinth of Warri River

Parameter	Cd	Pb	Cr	Cu	Ni	Co	Mn	Ba	Zn	Fe
Dry Season										
Cd	1.00	-0.34	-0.80	-0.12	0.09	0.50*	-0.04	-0.17	0.10	-0.57
Pb		1.00	0.35	-0.38	-0.14	-0.56	0.50*	-0.14	-0.35	0.89**
Cr			1.00	0.18	-0.25	-0.09	0.32	0.32	-0.20	0.53*
Cu				1.00	-0.83	0.63*	0.08	0.88**	-0.63	-0.05
Ni					1.00	-0.50	-0.36	-0.88	0.92**	-0.40
Co						1.00	-0.10	0.67*	-0.37	-0.38
Mn							1.00	-0.05	-0.19	0.25
Ba								1.00	-0.83	0.26
Zn									1.00	-0.62
Fe										1.00
Wet Season										
Cd	1.00	0.41	0.00	-0.26	-0.93	0.81**	-0.23	0.04	-0.07	0.64*
Pb		1.00	0.71**	0.63*	-0.52	0.24	0.71**	0.24	0.50*	0.28
Cr			1.00	0.83**	-0.14	-0.01	0.59*	-0.02	0.22	0.37
Cu				1.00	-0.01	-0.26	0.57*	0.17	0.24	0.14
Ni					1.00	-0.66	0.20	-0.01	-0.01	-0.76
Co						1.00	-0.27	0.48	-0.54	0.30
Mn							1.00	0.18	0.67*	-0.32
Ba								1.00	-0.42	-0.50
Zn									1.00	0.00
Fe										1.00

**Pearson correlation is significant at 0.01 level of significance (1 tailed) *Pearson correlation is significant at 0.05 level of significance (1 tailed)

Table 4: PCA factor loadings after Varimax with Kaizer Normalization Rotation for metals in water hyacinth

Metals	Dry Season			Wet Season			
	Components			Components			
	Factor 1	Factor 2	Factor 3	Factor 1	Factor 2	Factor 3	Factor 4
Cr			**.848**		**.946**		
Ba	**.964**						**.969**
Pb		**.915**	.300	.481	**.629**	.574	
Co	**.755**	-.349	-.376	**.793**		-.316	.467
Fe		**.765**	.541	**.695**	.306		-.617
Cd			-.981	**.991**			
Zn	-.815	-.496				**.926**	-.348
Ni	-.921	-.357		-.964			
Cu	**.923**				.945		
Mn		**.661**			.491	**.780**	
% Variance	**41.50**	**32.24**	**12.97**	**34.43**	**33.52**	**18.21**	**10.69**

Principal component analysis of metals in water hyacinth

The results of the PCA of metals in water hyacinth during the dry and wet seasons are shown in Table 4. During the dry season, three components were extracted and accounted for 86.71% of the variability in the data. Factor 1 was dominated by Ba, Co and Cu and accounted for 41.5% of the total variance. These metals are associated with anthropogenic activities. The presence of these metals in factor 1 confirms the results of the correlation analysis. Factor 2 which explains 32.24% of the total variance was dominated by Pb, Fe and Mn while factor 3 was characterized by Cr with negative bipolarity with Cd. Factor 3 accounted for 12.97% of the total variance.

During the wet season, four components were identified and accounted for 96.85% of the variability in the data set. Factor 1 accounted for 34.43% of the total variance and was characterized by Co, Fe and Cd. Factor 1 was also characterized by negative bipolarity with Ni. This agrees with the correlation results as there was a positive correlation between Co and Cd and between Fe and Cd. Factor 2 which accounted for 33.52% of the total variance was dominated by Cr, Pb and Cu. Factor 3 was dominated by Zn and Mn while factor 4 was characterized by Ba. Factors 3 and factor 4 were responsible for 18.21 and 10.69% of the total variance, respectively.

Conclusion

This study has shown the heavy metal status of water hyacinth (*Eichornia crassipes*) of the Warri River, Nigeria. The concentrations of metals in the water hyacinth followed the order Fe > Zn > Ni > Pb > Mn > Cd > Cu > Cr > Co > Ba and the concentrations of Cd, Pb, Cr and Fe were higher than FAO/WHO maximum permissible limits.

Conflict of Interest

Authors declare that there are no conflicts of interest

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