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Assessment of Pb, Cd, Cr and Ni in Water and Water Hyacinth (*Eichhornia crassipes)* Plant from Woji Creek, Rivers State, Nigeria

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ABSTRACT: This study evaluates the levels of Pb, Cd, Cr and Ni and the potential ability of water hyacinth (*Eichhornia crassipes)* plant to bioaccumulate these metals in Woji Creek, Rivers State, Nigeria by collecting water and water hyacinth samples along a 1.3 km stretch of the creek between 2018 and 2019 for analysis. Water samples and plants were collected from five stations across the creek from June to October of both years. The trend of metal concentration in the surface water is Pb > Cr > Ni > Cd in 2018 and Pb > Ni > Cr > Cd in 2019. In 2018, metal concentration in the root are in the order: Cr > Ni > Pb > Cd, while the trend for the shoot is Cr > Pb > Ni > Cd. In 2019, Cd was detected in the roots ranging from 1.009 ± 0.001 to 9.545 ± 0.006, while Pb ranged from 0.298 ± 0.006 mg/kg to 121.006 ± 0.005 mg/kg. There was substantial bioaccumulation of Pb, Ni and Cr in the roots with most plant roots having BCF > 1. In the shoot, BCF was > 1 for Pb and Cr only, while Ni had BCF < 1. The findings from this research also assert that the *E. crassipes* can be used in the application of rhizofiltration as phytoremediation technique in Woji creek.

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Keywords: Metal accumulation, phytoremediation, Translocation, Bioconcentration, Woji creek

Terrestrial heavy metals are usually washed into the aquatic ecosystem through industrial and municipal runoffs and therefore, makes estuaries and coastal ecosystems the major recipient and accumulators of aquatic pollutant (McComb *et al.,* 2014). Human activities such as oil and gas exploration, boat fabrication and maintenance and other industrial activities have also led to the input of these elements into the ecosystem (Freije, 2015; Turner, 2014; Turner and Rees, 2016). Although some of these trace elements are essential for the ecosystem (Zoroddu *et al.,* 2019), at relatively high concentrations, they can harm the biotic components of aquatic ecosystem; as well as damage the aesthetic and cultural properties of the water (Koller and Saleh, 2018). Previous study revealed that the uptake and translocation of metals by plants can be inhibited by the presence of other metals in the environment (De Oliveira *et al.,* 2014). The uptake of synthetic Cr (VI) and Cr (III) by the water hyacinth plant as a proposed means of phytoremediation of industrial mine waste was investigated. The accumulation over time in the root, shoot and leaves of the *Eichhornia crassipes* were compared (Saha *et al.,* 2017). The investigators recognised that the roots of the plant had higher concentration of the studied metal species and that these species are not adequately translocated to the shoots and leaves. Results from another study carried out in a laboratory to assess the sequestration of precious and pollutant metals in biomass of cultured water hyacinth in a single-metal tub trial, using arsenic (As), gold (Au), copper (Cu), iron (Fe), mercury (Hg), manganese (Mn), uranium (U), and zinc (Zn) (Newete et al., 2016), they concluded that water hyacinth can be proposed as a phytoremediation species for the removal of metals. However, some important notes were taken; over 80 % of the total amount of metals removed was accumulated in the roots, of which 30 – 52 %was adsorbed onto the root surface; furthermore, 73 – 98% of the total metal assimilation by water hyacinth took place in the roots. This confirmed the difficulty of translocation of a reasonable amount of metals from the root to other parts of the plant. However previous research on the treatment of heavy metals from water by electro-phytoremediation technique proposed that under electrified condition, maximum amount of Cd and Cu were accumulated in the aerial parts of *Eichhornia crassipes* (Puthenveedu *et al.,* 2017). The present work is designed to investigate the accumulation of lead (Pb), nickel (Ni), cadmium (Cd) and chromium (Cr) in surface water and plant (root and shoot), and assess the phytoremediation potential of *Eichhornia crassipes*.

MATERIALS AND METHODS

Study area: Woji creek of Obio/ Akpor Local Government Area, Rivers State, Nigeria is important to the City of Port Harcourt because it is used as a transportation route for goods and services within and outside the State. This creek is also important to the local and surrounding communities due to the business of gathering seafood in large quantities for

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consumption and sales. This creek is usually affected by petroleum spill through legal and illegal oil bunkering activities; as well as several point source pollutions that impact on the general environmental conditions of the river. Studies have shown that the most impacted area on our study river is Station 3 (Dibofori- Orji *et al.,* 2019); which hosts an abattoir whose effluent empties into the river. Station 3 also has a sight for boat maintenance and manufacturing.

Downstream, in Station 1 there is another boat packing site along the creek where they clean and empty tanks of condemned diesel into the river. In addition to the point sources of pollution, there is urban runoff from precipitation on the watershed which is densely populated and would, therefore, affect the physicochemistry of the river from its municipal wastes (Dibofori- Orji *et al.,* 2019; Ihunwo et al., 2019).

Table 1 Location for the collection of surface water samples along Woji creek

Station Number	Location
St 1	4°49'39.5"N 7°02'35.0"E
St 2	4°49'09.3"N 7°02'44.0"E
St 3	4°48'51.6"N 7°02'47.0"E
St 4	4°48'41.7"N 7°03'01.0"E
St 5	4°48'26.6"N 7°03'31.0"E

Sample collection: With the aid of a canoe, water and plant samples were collected for this study in 2018 and 2019 from June to October. Five plants and water samples were collected from five stations (Table 1) along the river. These five stations covered about 1.3km stretch of the river and samples were collected in both reverse and free flow (that is, from upstream to downstream and downstream to upstream).

Five water samples were collected transversely across each station and mixed to form a composite sample representing each station (Patil, 2002). Sterilized plastic containers were used to collect samples of surface water. Three drops of nitric-acid (HNO_3) was added for the preservation of the water samples (APHA, 1999; ASTM, 2016).

Plant samples collected were put into Ziploc bags. The surface water and plant samples were put into an ice chest and transported immediately to the laboratory for analysis.

Table 2. Analytical methodology employed

Parameter	Methodology
Chromium	ASTM D1687
Cadmium	ASTM D3557
Nickel	ASTM D1886
Arsenic	ASTM D2972
Lead	ASTM D3559

(ASTM, 2010)

Sample preparation and analysis: In the laboratory, plants samples were divided into root and shoot. Before analysis, plant samples were homogenised using a laboratory high-pressure homogenizer. Water and plant samples were analysed for four metals: Pb, Ni, Cr, Cd. A summary of analytical methodology for the five metals analysed is presented in Table 2.

Data analysis: Bioconcentration factor (BCF) is the ability of plants to accumulate elements from the substrate (Wu *et al.,* 2011). BCF will be measured for the root and shoot using equation 1.

$$BCF = \frac{Concentration\ of\ metal\ in\ the\ part\ of\ plant}{Concentration\ of\ metal\ in\ the\ water} \quad (1)$$

Translocation factor (TF) is important in the assessment of the phytoremediation potential of a plant. It compares the concentration of each element in the shoot to those in the root (Wu et al., 2011). TF will be calculated using equation 2

$$TF = \frac{Concentration\ of\ metal\ in\ the\ shoot}{Concentration\ of\ Metal\ in\ the\ root} \quad (2)$$

RESULTS AND DISCUSSION

Heavy metals in surface water and plants: Surface water samples collected in 2018 had a mean concentration of Pb of 0.9898 ± 0.5510 mg/l and mean Cd concentration of 0.1022 ± 0.070 mg/l (Fig. 1). The trend of metal concentration in the surface water is Pb> Cr> Ni> Cd. In 2019, surface water samples collected from the creek had mean concentrations of Pb of 1.3158 ± 0.6200 mg/l, Ni of 0.3545 ± 0.1652 mg/l, Cd of 0.1893 ± 0.0894 and Cr of 0.3047 ± 0.0334 mg/l (Fig. 1). The trend of metal concentration in the surface water is Pb > Cr > Ni > Cd in 2018 and Pb > Ni > Cr > Cd in 2019.

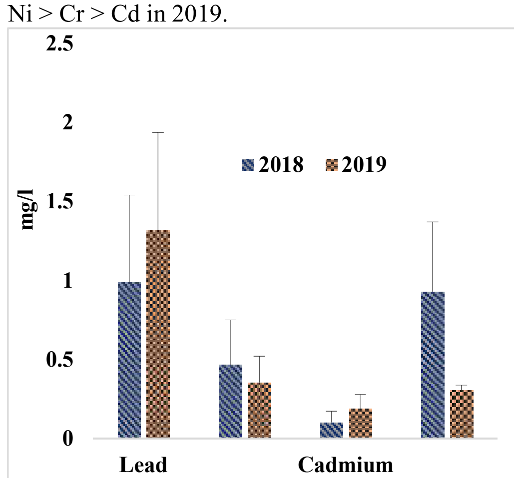

Fig 1: Mean ± standard deviation of metals across the creek

Plant samples were analysed in triplicate, and the concentration of studied metals in the plants were found to differ. In 2018, metal concentration in the root are in the order: Cr > Ni > Pb > Cd, while the trend for the shoot is Cr > Pb > Ni > Cd. Metal concentration in the roots was generally higher than those measured in the shoot. The plants sampled in 2018 had Cr concentrations ranging from 100.88 ± 0.07 mg/kg to 139.17 ± 0.30 mg/kg (Fig. 2). Cd was not detected in the roots of the sampled plants in 2018. Concentration of Chromium in the shoot ranged from 21.01 ± 0.03 mg/kg to 38.00 ± 0.10 mg/kg (Fig. 3).

1.009 ± 0.001 to 9.545 ± 0.006 (Fig. 4), while Pb ranged from 0.298 ± 0.006 mg/kg to 121.006 ± 0.005 mg/kg. Although Chromium was detected in every shoot sample, the other metals were not detected in every plant shoot sample. Unlike samples collected in 2018, the samples collected in 2019 recorded chromium in the shoot with concentrations ranging from 0.003 ± 0.001 mg/kg to 2.24 ± 0.02 mg/kg (Fig. 5). Unlike some metals, Pb has no biological function in organisms, however, with increasing technological development, there have been an exponential increase in Pb emission (Clemens, 2013).

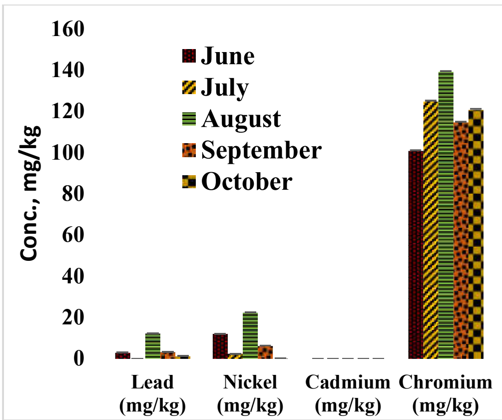

Fig 2: Mean concentration of metals in plant root in 2018

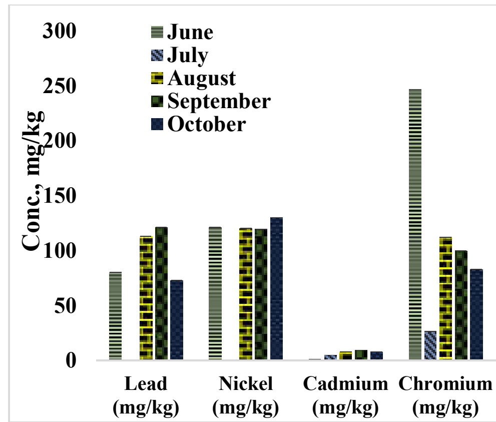

Fig 4: Mean concentration of metals in plant root in 2019

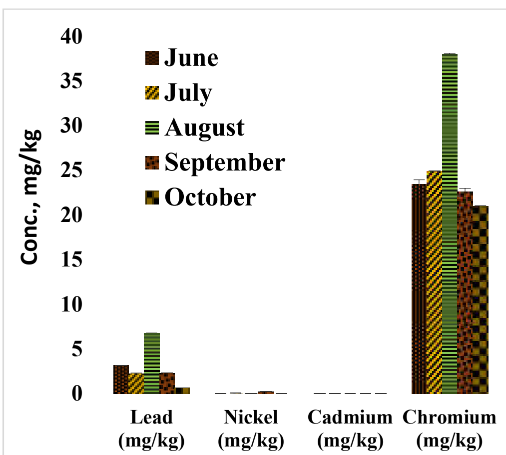

Fig 3: Mean concentration of metals in plant shoot in 2018

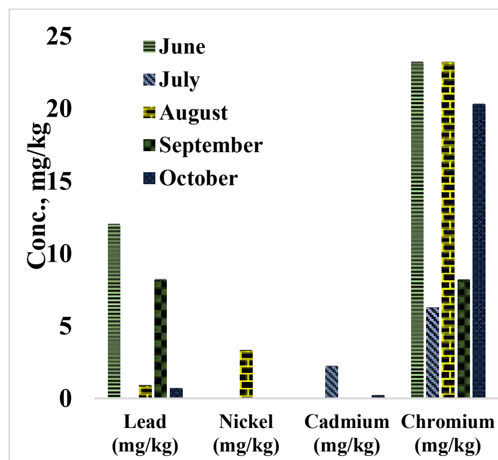

Fig 5: Mean concentration of metals in plant shoot in 2019

Lead ranged from 0.673 ± 0.003 mg/kg to 6.816 ± 0.006 mg/kg. Nickel had the lowest metal concentration in shoot samples (0.007 ± 0.002 mg/kg). Although the metal concentration trends were relatively similar, concentrations of metals in the plants collected in 2019 were higher than those analysed in 2018. In the root chromium metals ranged from 26.33 ± 0.01 mg/kg to 247.02 ± 0.01 mg/kg (Fig. 4). In 2019, Cd was detected in the roots ranging from

Lead has an abundance of 14 mg/l in the earth´s crust (Rankin, 2009), 50% of atmospheric Pb originates from natural sources such as weathering of soil, forest fires and volcanoes (ILA, 2019). Through anthropogenic activities such as an accidental spill of fuel laced with lead, combustion of coal and wood, lead-painted boats, as well as various processes of metalwork and manufacturing, Pb particles can wash into water bodies (Dibofori- Orji *et al.,* 2019;

Needleman and Gee, 2013; Rees *et al.,* 2014; Turner, 2014). In the case of Woji creek, it has been identified that the potential sources of Pb contamination in the surface water could be from abandoned lead-painted boats, metal wors and fuel/ oil spill (Dibofori- Orji *et al.*, 2019). Under the stated environmental conditions in the surface water, Pb forms a hexameric hydrolysis species. In plants, ionic Pb uptake is driven by negative membrane potential of the root cells, it is assumed that Pb^{2+} transport in plants is mediated by the uptake of Ca^{2+} (Pourrut *et al.,* 2011). Research has also shown that most of the Pb in the root of plants is not due to transportation into cell roots but precipitates in the apoplast and adsorption of organic matter containing metals on the plant roots (Clemens, 2013). Most of the Pb in the shoot of plants have been attributed to deposition on the leaves of plants rather than translocation (Clemens, 2013). This, therefore, may account for the lower concentration of Pb in the shoot compared to the root of the plants, and the generally low concentration of Pb in the plant compared to Cr.

Nickel plays an essential role in biological systems, it is essential in the enzymatic activity of glyoxalase-I and urease required for nitrogen metabolism in higher plants (Mustafiz *et al.,* 2014). The deficiency of Ni in plant disrupts the metabolism of ureides, amino acids and organic acids in plants (Bai *et al*., 2006). In the human body, Ni is an essential micronutrient for proper function and it is involved in human hormonal activities and lipid metabolism (Zdrojewicz *et al*., 2016). Ni ion uptake in a plant is regulated by amino acids such as histidine; this is done by the amino acids acting as chelators in the formation of complexes with Ni ions thereby enhancing its uptake by the plant (Dalir and Khoshgoftarmanesh, 2015). The process of metal chelation is a major means through which most metals are taken up by the roots of plant. It is proposed that the uptake process involves the initial absorption of Ni by the root cells in the form of free hydrated cation after which Ni-amino acid complexes are formed inside the root symplast of the apoplast (Dalir and Khoshgoftarmanesh, 2014, 2015). However, when an excess of Ni is absorbed by the plant, it disrupts the plant anatomical, physiological and biochemical processes (Ahmad *et al*., 2011; Ashraf *et al*., 2011; Muhammad *et al*., 2013; Shahzad *et al*., 2018). Ni is the second most absorbed metal in the plant root and third most abundant in the shoot (Fig. 2- 5). This is similar to the result of a study designed to assess the accumulation of Ni in *Eichhornia crassipes* exposed to different concentrations of Ni for 72 hrs (González *et al*., 2015). Cadmium has an abundance of 0.15 ppm in the earth's crust (Rankin, 2009), it is a rare element and does not exist in the pure state, meaning that Cd occurs in association with the sulphide ores of zinc, lead and copper (Van Horn, 2013). Industrial production of Cd is generated as a by-product of the production of zinc from sulphide ore concentration (Namieśnik and Rabajczyk, 2010). Cadmium is a nonessential element, Cd^{2+} is a readily available environmental contaminant (Nawrot *et al.,* 2010). In human beings, long-term exposure to cadmium can lead to skeletal damage, lung disease and cancer (Van Kerkhove *et al.,* 2013). At the cellular level, Cd can lead to cell death (Moulis, 2013). Cd^{2+} has a reactive similarity with Zn^{2+} which is an essential micronutrient; and therefore, leads to the replacement of Zn^{2+} by Cd^{2+} in critical biochemical processes (Andresen & Küpper, 2013; Sigel et al., 2013). For this reason, the transport process of Cd^{2+} in plants is similar to that of Zn^{2+}.

In a study designed to assess the absorption behaviours of Cu (II) and Cd (II) in water by water hyacinth roots in both single- and binary-metal systems, they discovered that Cu (II) and Cd (II) were individually removed by water hyacinth roots at high efficiency, accompanied with the release of protons and cations such as Ca^{2+} and Mg^{2+}. However, in a binary-metal arrangement, the results showed that Cd (II) sorption was significantly inhibited by Cu (II), and the higher sorption affinity of Cu (II) accounted for its competitive sorption advantage (Zheng *et al.,* 2016). In the present study, sorption of Cd (II) is similarly limited when compared to other metals. This could be attributed to the presence of other metals in the surface water inhibiting the uptake of Cd (II). Chromium is not known to play any beneficial role in plant physiology and biochemistry (Reale *et al*., 2016). It is toxic to most plants and is detrimental to their growth, they do not possess specific uptake mechanisms in plants unlike essential metals (Shanker *et al.,* 2005). The uptake of Cr (III) in plants is not affected by metabolic inhibitor and research has shown that the rate of uptake of Cr (VI) in plants is higher than that of Cr (III) (Pradas-del-Real *et al*., 2013). This is because Cr (VI) can easily cross the cell membrane and can be transported with phosphate-sulphate carriers. On the other hand, Cr (III) does not utilise specific membrane carriers and can diffuse into the roots of plants after the formation of appropriate lipophilic ligands (Chandra and Kulshreshtha, 2004). When Cr gets into plant root as Cr (VI) at a low concentration, it is converted to Cr (III) (*Shanker et al*., 2005). Cr (III) has shown more toxicity to plants compared the Cr (VI); it can lead to stunted growth inhibition of the uptake of macronutrients and micronutrients (Gardea-Torresdey *et al.,* 2005). Studies have shown that chromium accumulation in plants tissues are predominantly in the root (Shahid *et al*., 2017; Yadav *et al.,* 2019) which is similar to results in this study. Through the processes of complexation by organic ligands, compartmentation into the vacuole, and scavenging reacting oxygen species (ROS) via antioxidative enzymes, the toxicity of Cr is tolerated by plants, accounting for the high concentration of Cr in the plants compared to other metals. In the present study, Cr exhibited the highest concentration in the plant samples indicating that in the present environmental conditions; *E. crassipes* will play an efficient role in the removal of Cr from the surface water. This is supported by the study to assess the uptake efficiencies, the uptake and bioaccumulation kinetics and the toxic effects of Cr, Ni and Zn on *Eichhornia crassipes* which showed that *E. crassipes* removed 81%, 95% and 70% of Cr, Ni and Zn, respectively from water (Hadad *et al*., 2011). Phytoremediation potential of *E. crassipes* in the contaminated creek: There was substantial bioaccumulation of Pb, Ni and Cr in the roots with most plant roots having BCF above 1. In the shoot, BCF was > 1 for Pb and Cr only, while Ni had BCF < 1 (Table 3). Except for Pb in roots of plant 2, BCF calculated for the plants sampled in 2019 showed substantial bioaccumulation of Pb, Ni, Cd and Cr metals in the roots of other plants. Ni and Cr had the highest values of BCF, 367.0430 and 810.8389 respectively. However, TF were all < 1 for every trace metal assessed (Table 4).

Table 3: Bioconcentration factor (BCF) and translocation factor (TF) for samples collected in 2018

Month	Lead	Nickel	Cadmium	Chromium
		Bioconcentration Factor (BCF) Root		
June	3.0397	25.6694	0	108.7077
July	0	5.1198	0	134.5647
August	12.3803	47.8086	0	149.9691
September	3.3593	13.416	0	123.4494
October	1.2258	0.201	0	130.1419
		Bioconcentration Factor (BCF) Shoot		
June	3.1936	0	0	25.2956
July	2.2914	0.0513	0	26.8423
August	6.8862	0.0150	0	40.9480
September	2.3416	0.5004	0	24.3908
October	0.6802	0	0	22.6436
		Translocation factor (TF)		
June	1.0506 ± 0.0027	0	0	0.2327 ± 0.0044
July	0	0.0100 ± 0.0015	0	0.1995 ± 0.0004
August	0.5562 ± 0.0003	0.0003 ± 0.0001	0	0.2730 ± 0.0009
September	0.6970 ± 0.0012	0.0373 ± 0.0004	0	0.1976 ± 0.0027
October	0.5549 ± 0.0016	0	0	0.1740 ± 0.0005

Table 4 Bioconcentration factor (BCF) and translocation factor (TF) for samples collected in 2019

Month	Lead	Nickel	Cadmium	Chromium
		Bioconcentration Factor (BCF) Root		
June	60.9778	341.4174	5.3308	810.8389
July	0.2259	1.0052	25.6337	86.4417
August	85.9069	339.4246	40.3539	368.6197
September	91.9612	338.0236	50.4140	328.2787
October	55.3266	367.0430	42.1940	272.1384
		Bioconcentration Factor (BCF) Shoot		
June	9.1320	0	0	76.1841
July	0	0	11.8310	20.6202
August	0.6774	9.3748	0	76.2376
September	6.2401	0	0.0143	26.8841
October	0.5474	0.0573	1.1181	66.6342
		Translocation factor (TF)		
June	0.1498 ± 0.0002	0	0	0.094
July	0	0	0	0.2385
August	0.0079	0.0276	0	0.2068 ± 0.0001
September	0.0679 ± 0.0001	0	0	0.0819
October	0.0099	0.0002	0	0.2449 ± 0.0001

The endodermis of plant roots is universally characterised by casparian strips which are formed during the early ontogeny of the root cell and is part of the primary cell wall. At the early stage of the development of the endodermis of plant roots, a fatty substance known as suberin is deposited in bands of radial walls and transverse walls in the longitudinal direction which forms the casparian strip. This formation makes the cell wall relatively impermeable to water, and it presents a barrier to inward movement of water and solutes in the apoplast (Kirkham, 2014). The blockage created by the casparian strips within the endodermis leads to higher accumulation of the metals in the root as compared to the shoot (Pourrut *et al*., 2011). As stated in the introductory section, the various mechanisms employed by plant physiology and anatomy to prevent certain elements from getting into the plant through the roots and translocated into the shoots and leaves are what differentiates hyperaccumulators from excluders and this defines the phytoremediation potential of a plant. Phytoremediation technology comprises of five different technologies. Rhizofiltration involves the remediation of metals such Pb, Cr, Ni, Cd, Cu, V and radionuclides like Sr, U, and Cs, by taking up the metals from water and sequestering them in their roots. Phytostabilization involves the transformation of toxic metals into a nontoxic form and so reduce the environmental risk. Phytovolatization plants are used to absorb toxic metals and transform them into a less-toxic and volatile form by the process of transpiration. Phytodegradation involves the use of plants to degrade organic pollutants and phytoextraction involves the uptake of contaminants by the roots of plants followed by translocation and accumulation in the harvestable parts of the plant (Bhattacharya and Chakraborty, 2019; Gajic *et al.,* 2018; Mishra and Pandey, 2019; Pandey *et al.,* 2016; Pandey *et al.,* 2015). Although the plants exhibited the capacity to absorb the studied elements from the, translocation into the shoot was limited. With the exception of plant 1 in 2018 (TF = 1.0506 ± 0.0027), TF calculated for the plant samples in 2018 and 2019 are < 1. These results were similar to those obtained from a study designed to investigate the phytoremediation of industrial mines wastewater using water hyacinth in the removal of Cr (III) and Cr (VI) (Saha *et al.,* 2017). BCF in the roots were significantly higher than those in the shoots of plant samples. Similarly, *E. crassipes* was tested for its ability to bioconcentrate eight toxic metals (Ag, Cd, Cr, Cu, Hg, Ni, Pb, and Zn) commonly found in wastewater from industries and the results indicated that the elements accumulated to higher concentrations in roots than in shoots (Puthenveedu *et al.,* 2017). Although the TF values calculated were < 1, results of BCF has also confirmed that *E. crassipes* in the present study is a hyperaccumulator of the metals assessed. *E. crassipes* has been endorsed by various studies for its ability to absorb contaminants such as Pt, Cr, Ni, Cu, Zn, Ag, Cd, Hg, Pb, ethion, dicofol, cyhalothrin, pentachlorophenol, phenanthrene (Bhattacharya and Chakraborty, 2019), and this has been confirmed from results of BCF obtained in the present study. The present study also confirms that the floating plant is performing rhizofiltration as a natural phytoremediation technique in Woji creek (Bhattacharya and Chakraborty, 2019; Gajic *et al.,* 2018; Mishra and Pandey, 2019; Pandey *et al.,* 2016; Pandey *et al.,* 2015).

Conclusion: This study was designed to assess metal accumulation by indigenous water hyacinth (*Eichhornia crassipes*) from surface water in the contaminated creek of Woji. To perform this study, surface water and water hyacinth from a metal-polluted site were collected from Jun to October in 2018 and 2019. The concentrations of lead (Pb), nickel (Ni), cadmium (Cd) and chromium (Cr) in surface water and plant (root and shoot) were assessed. Phytoremediation potential of the plant was also studied. Although TF was low indicating difficulty in translocation of metals from the root to the shoot of the plant, BCF calculated for the root and shoot of the plants were high.

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