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Characterization and bio modeling of weeds for industrial waste management of selected heavy metals

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Abstract

Phytoremediation is an emerging field used to clean the environment from toxic metals. This study was conducted to analyze twenty plants, water and soil samples for the presence of heavy metals (Fe, Pb, Cu, Cr, Cd and Zn) from four industries of G.I.E, Swabi, KPK, Pakistan. Based on their phytoremediation potential, plants were categorized into groups like HA, PE PS based on BCF, TF and BAC. The results declared that *E. heliscopica* is categorized as PE for all metals. *C. sativa* is HA and PE for Fe, PE for Pb, Cd and Cu while PS for Cr. *T. latifolia* is HA and PE for Fe, PS for Pb, PE for Cr, Zn and Cu. *C. chinesis* is PE for Pb, Cd, Cr, Zn while HA and PE for Fe. *S.babylonica* and *S. cinerea* are HA and PE for Fe while PE in Pb and Zn. *S. cinerea* is HA and PE for Fe. *E. charchaias* are HA for Fe while PE for Pb, Cr, Zn and Cu. *A. annua* is PE and PS for Fe, while PE for Pb, Cd, Zn and Cu. Another plant species, *M. alba* is PE for Cd, Cu, Pb and Zn while the only plant to be PS for Fe. *A. viridis* and *G. coronaria* are PS for Fe, Pb, Cu while PE for Cd, Cr and Zn. *D. sanguinalis* is PE for Cd and Zn while PS for Cu. *E. heracifolia, J. integrrina, P. somniferum* and *T. officinale* act as PE for Cd, Zn.

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Introduction

Heavy metals are considered as contaminants playing a major role in environmental pollution (Gaur and Adholeya, 2004). They are drained into the ecosystem through natural processes and industrial waste (Sinicropi *et al.*, 2010). Natural processes involve weathering of rocks and volcanic eruptions, and industrial waste is a source of industrial pollutants (Abdullahi *et al.*, 2009). Various techniques are adopted to clear the ecosystem from metal toxins, which are costly and challenging. Phytoremediation is a very aptly and costly method to remove these pollutants from polluted soil and water. Plants use unique strategies to fight metal toxins, which contributes to various mechanisms such as metal chelation, compartmentalization in certain organelles, and rejection and inactivation because of the exudation of organic ligands (Choppala *et al.*, 2014). The chelation and detoxification of heavy metals in aboveground plant parts is a key characteristic of extremely good accumulators. Phytoremediation has several purposes, that is, plant extraction absorbs pollutants from the soil through the roots and reaches the above-ground parts of the plant. Phytoremediation efficiency can be measured by employing the Bioconcentration factor (BCF) and translocation factor (TF). BCF is defined as the ratio of the metal concentration within the root to the metal concentration inside the soil and can be used to estimate the efficiency of the plant to absorb metal from the soil (Zhuang *et al.*, 2007; Ladislas *et al.*, 2012; Mahdavian *et al.* 2017). According to Yoon *et al.* (2006), vegetation with BCF and TF greater than 1 have a capacity for plant extraction, while plants with BCF more than 1 and TF less than 1 may be used for plant stabilization. Plants showing TF and BCF values much less than 1 aren't suitable for plant extraction (Fitz and Wenzel 2002). Shift factor (TF = Cshoot / Croot), which represents the migration of metal from root to shoot, is calculated as the ratio of the metal content in the bud to the metal content in the root (Malik *et al.*, 2010). Bioaccumulation factors (BAF = C shoot / C soil) are determined to quantify the metal accumulation in plant shoots in soil (Rezvani and Zaefarian 2011). Bioaccumulation coefficient (BAC = C plant / C soil) is the ratio of the metal absorption in plant parts (roots, stems and leaves) to the metal concentration in external media (such as soil), is to limit the accumulation efficiency of trace metals in plants (Sekabira *et al.* 2011). Some plants could withstand high levels of heavy metals in the soil (Solanki and Dhankhar 2011, Baker *et al.* 2000). These plants can be referred to as metal repellents, metal indicators, and super accumulators. The third category is the best because they have High tolerance and they can absorb metals from the soil and then store them in biomass, for example, Zea mays (corn) is a super accumulator that resists heavy metals and has a short time. The ability to internally absorb metals shows rapid growth rates (Cunningham *et al.* (1995), Baker *et al.*, 2000) and other non-accumulating plants (Memon *et al.*, 2001, Memon and Schroder, 2009). Super accumulators can be called "genius warriors" (Nazir *et al.*, 2011).

The present work was aimed to assess the phytoremediation potential of indigenous plants in Gadoon Industrial Estate Swabi, Pakistan. The agricultural land in the vicinity of the industrial estate is irrigated by farmers intentionally or unintentionally through the effluents of industrial setup and this practice of wastewater farming has been a usual way for decades (Gaur and Adholeya, 2004)

Materials and methods

Selected industries

Four industrial units were selected for the present study including Cherat Packing Industry (PKI), Swabi Marble Factory Gadoon (MF), Saif textile mills (STM) and Sheraz international Plastic Industry (PI) (Table 02). The effluents from each of the industry channels to the cultivable lands through several streams.

Samples collection

Water and soil samples (*n*=3) were collected from the area of the above-mentioned industries. The number of collected plants was variable. The water was collected in tagged clean and dry plastic bottles directly from the outlet of the industries. Soil (0-25 cm) was amassed from the rhizosphere of collected plants in tagged dry and clean plastic sealed bags. Plants were uprooted from the polluted area. The tagged plants from each site were taken to the laboratory in newspaper magazines in proper pressed form. Following the identification process, the collected plants were washed with tap water followed by deionized water. After that, they were oven-dried in the oven at 70 °C for two days (Wu *et al* 2009).

Sample handling and preparation

The water samples were collected from effluents of the targeted industries, passed through Whatman filter paper; the filtrate was made up to 50 ml for each sample. The soil samples were air-dried in the oven, then crushed and processed through the sieve (2 mm) to get uniform particles. The plants receiving water from industrial wastes were collected. The collected plants were first washed with tap water then with deionized water. The plants were identified with the help of specimens in the herbarium of Islamia College Peshawar as well as with the guide of taxonomists of the department of Botany, Islamia College Peshawar. The identified plants were oven-dried in the oven at 70 °C for two days (Wu *et al* 2009). The dried plants were then divided into three parts (stem, root and leaves) and crushed into powder by processing in a grinder and sieve of 1mm (Aishah *et al.* 2016).

Detection of heavy metals by Atomic Absorption Spectrometry

Preparation of soil grains for analysis of selected heavy metals: The dried soil was processed through the wet digestion method to detect heavy metals in soil (AOAC, 1984). Each tagged soil sample weighing 1 gm was left in the conical flask for 1 hour with 15 ml conc. HNO_3 followed by adding (5ml) $HCLO_4$ (3:1) and placed on the hot plate for 2-3 hours. The wet digested material was then filtered through Whatman filter paper and the volume of the filtrate was made up to 50 ml by adding distilled water. Preparation of plant parts and water for analysis of selected heavy metals: The identified and labeled plant parts were wet digested for extraction of heavy metals in the plants (AOAC, 1984).

The dried plant parts were crushed into powder with the help of mortar and pestle. Each sample weighing 1 gm was allowed to settle in HNO_3 followed by $HCLO_4$ (3:1) in a conical flask on the hot plate. 10 ml of HCl was poured into it to dissolve oxides and inorganic salts. The prepared mixture was filtered and graduated up to 50 ml volume by adding deionized water to it.

The collected water samples were simply filtered via Whatman filter paper and a 50 ml volume was attained by adding distilled water.

The prepared material (soil, water and plants) were then processed for detection of heavy metals (Iron, lead, zinc, chromium, cadmium, and copper) using Atomic Absorption Spectrophotometer in Department of Environmental Sciences, Quaid-e-Azam University, Islamabad.

Coefficients for bioaccumulation and translocation

Based on the phytoremediation potential, plants were grouped in the following categories (Raza *et al.* 2019).

$$TF = \frac{\text{Average conc. of metal in aerial tissue of plants (mgKg-1)}}{\text{Average conc. of metal absorbed by root (mgKg-1)}}$$

$$BCF = \frac{\text{Average conc. of metal in root of plants (mgKg-1)}}{\text{Average conc. of metal in soil (mgKg-1)}}$$

$$BAC = \frac{\text{Average conc. of metal in shoot of plants (mgKg}^{-1}\text{)}}{\text{Average conc. of metal in soil (mgKg}^{-1}\text{)}}$$

Statistical analysis

The data obtained were statistically analyzed using GraphPad Prism 6 and SPSS software version 20. Various Multivariate tests within the subject effects were performed, and analysis was performed to investigate that different plant parts and sites differed significantly in terms of heavy metal concentration. Other analysis such as Wilk lambda statistics, F test and ANOVA were calculated for multiple parameters.

Results and discussion

Plants take essential heavy metals like iron, copper, zinc, cadmium, lead and manganese from the soil due to concentration gradients and selective uptake of these metals (Peralta-Videa *et al.*, 2009). Metal pollution has harmful effects on biological systems and does not undergo biodegradation. Toxic heavy metals as Pb, Co, Cd cannot be biodegraded but accumulated in soil or water and thus can cause various diseases and disorders even if they are present in minute quantity (Pehlivan *et al.*, 2009).

It is a well-known factor that heavy metals cannot be degraded chemically but need to be physically removed or transformed into nontoxic compounds (Gaur and Adholeya, 2004).

Table 1. Multivariate analysis results for the investigated sites.

Multivariate Tests[a]						
Effect		Value	F	Hypothesis df	Error df	Sig.
Parts	Pillai's Trace	.974	10.924	35.000	1580.000	.000
	Wilks' Lambda	.264	13.981	35.000	1314.895	.000
	Hotelling's Trace	1.966	17.434	35.000	1552.000	.000
	Roy's Largest Root	1.512	68.265[c]	7.000	316.000	.000
Sites	Pillai's Trace	1.660	55.552	21.000	942.000	.000
	Wilks' Lambda	.051	77.467	21.000	896.446	.000
	Hotelling's Trace	7.165	105.996	21.000	932.000	.000
	Roy's Largest Root	5.690	255.247[c]	7.000	314.000	.000
Parts * Sites	Pillai's Trace	2.068	8.890	105.000	2226.000	.000
	Wilks' Lambda	.049	11.488	105.000	2006.358	.000
	Hotelling's Trace	4.856	14.351	105.000	2172.000	.000
	Roy's Largest Root	2.186	46.347[c]	15.000	318.000	.000

a. Design: Intercept + Parts + Sites + Parts * Sites

b. Exact statistic

c. The statistic is an upper bound on F that yields a lower bound on the significance level.

In the present study, the water, soil and plant samples have been analyzed for the presence of heavy metals in Gadoon Industrial Estate, Swabi, Pakistan. A total of six factories were selected and 20 plants were analyzed for iron, lead, zinc, chromium, cadmium and copper.

The potential of a plant to transport various heavy metals was also assessed by the coefficients (BAC, BCF and TF) (Table 3). The concentration of different heavy metals in water and soil samples from the studied area has been shown in Table 4 and that of plant samples in Table 5 (roots), Table 6 (stem) and Table 7 (leaves).

Multivariate analysis

Various Multivariate tests within the subject effects are performed, and analysis was performed to investigate that different plant parts and sites differed significantly in terms of heavy metal concentration. The obtained results as shown in (Table 1) indicated that a high degree of Wilk lambda statistic within plant parts (0.264). As the greater the Wilk-lambda values, the higher the group variation as a proportion of the total variation. F statistic values were used to find out the significance of means between the groups of variables.

Further Two-way ANOVA analysis was performed and results are given in (Table 2). It was observed that interaction between these independent variables is significant for heavy metal, Chromium (p=0.004). Variable site is also significantly associated with Chromium (p=0.001). Between the variables, parts and Site, significant interaction with a metal ion, copper is found (p=0.002).

Table 2. Two-way ANOVA results (test of between-subjects).

Tests of Between-Subjects Effects						
Source of variation		Type III Sum of Squares	df	Mean Square	F	Sig, p
Corrected Model	Iron (Fe)	3196354.538[a]	23	138971.900	27.585	.000
	Plant species	8154.000[b]	23	354.522	53.532	.000
	Lead	32395.932[c]	23	1408.519	16.037	.000
	Copper	82700.509[d]	23	3595.674	4.385	.000
	Zinc	282676.895[e]	23	12290.300	5.976	.000
	Chromium	15119.678[f]	23	657.377	6.370	.000
	Cadmium	282755.079[g]	23	12293.699	55.928	.000
Intercept	Iron (Fe)	1994920.690	1	1994920.690	395.973	.000
	Plant species	17634.543	1	17634.543	2662.766	.000
	Lead	14641.770	1	14641.770	166.702	.000
	Copper	16204.343	1	16204.343	19.760	.000
	Zinc	202511.829	1	202511.829	98.473	.000
	Chromium	5766.057	1	5766.057	55.871	.000
	Cadmium	35406.041	1	35406.041	161.074	.000
Parts	Iron (Fe)	1187278.026	5	237455.605	47.133	.000
	Plant species	0.000	5	0.000	0.000	1.000
	Lead	5549.520	5	1109.904	12.637	.000
	Copper	8678.628	5	1735.726	2.117	.063
	Zinc	47928.918	5	9585.784	4.661	.000
	Chromium	1836.812	5	367.362	3.560	.004
	Cadmium	36064.240	5	7212.848	32.814	.000
Sites	Iron (Fe)	924904.165	3	308301.388	61.195	.000
	Plant species	8154.000	3	2718.000	410.410	.000
	Lead	7677.744	3	2559.248	29.138	.000
	Copper	1918.615	3	639.538	.780	.506
	Zinc	42378.978	3	14126.326	6.869	.000
	Chromium	1869.331	3	623.110	6.038	.001
	Cadmium	97127.089	3	32375.696	147.288	.000
Parts * Sites	Iron (Fe)	1870332.566	15	124688.838	24.750	.000
	Plant species	0.000	15	0.000	0.000	1.000
	Lead	14494.060	15	966.271	11.001	.000
	Copper	29972.788	15	1998.186	2.437	.002
	Zinc	112553.975	15	7503.598	3.649	.000
	Chromium	10322.460	15	688.164	6.668	.000
	Cadmium	138437.305	15	9229.154	41.986	.000
Error	Iron (Fe)	1602092.958	318	5038.028		
	Plant species	2106.000	318	6.623		
	Lead	27930.554	318	87.832		
	Copper	260777.016	318	820.054		
	Zinc	653973.959	318	2056.522		
	Chromium	32818.421	318	103.203		
	Cadmium	69900.480	318	219.813		
Total	Iron (Fe)	6150636.497	342			
	Plant species	44460.000	342			
	Lead	81432.635	342			
	Copper	387183.221	342			
	Zinc	1341187.305	342			
	Chromium	60168.730	342			
	Cadmium	400846.572	342			
Corrected Total	Iron (Fe)	4798447.496	341			
	Plant species	10260.000	341			
	Lead	60326.485	341			
	Copper	343477.525	341			
	Zinc	936650.854	341			
	Chromium	47938.099	341			
	Cadmium	352655.559	341			

a. R Squared = .666 (Adjusted R Squared = .642)

b. R Squared = .795 (Adjusted R Squared = .780)

c. R Squared = .537 (Adjusted R Squared = .504)

d. R Squared = .241 (Adjusted R Squared = .186)

e. R Squared = .302 (Adjusted R Squared = .251)

f. R Squared = .315 (Adjusted R Squared = .266)

g. R Squared = .802 (Adjusted R Squared = .787)

Concentration of Iron

Iron is one of the important metal elements for plants and animals whereas its ratio above 40-500 µg/g d.w may be lethal for plants (Allen, 1989). The results declared that maximum Fe concentration was detected in the soil of packing industry which was 236 mg/Kg, whereas, the water 0.093 mg/Kg from Saif textile mills industry revealed the highest concentration of Fe. The results further declare that maximum accumulation of iron was found in the stem of *Euphorbia heliscopica* i.e, 586 mg/Kg. The next phytoextractor of iron was *Euphorbia charchaias*, where 499 mg/Kg of Fe was absorbed by its stem followed by accumulation of the maximum amount of iron by *Morus alba* stem i.e, 134 mg/Kg. Similarly, concentrations of 133 mg/Kg and 106 mg/Kg have been measured for *Salix babylonica* and *Artemisia annua* respectively.

Our results are similar to those (Nematian, 2013) who reported *Euphorbia macroclada, Reseda lutea* and *Centaurea iberica* as hyperaccumulators of Fe from the selected species growing on heavily contaminated soils of mining place in Iran.

Table 3. Plants native to the Gadoon Industrial Estate Swabi**.**

Industry/Factory	Industry/ Factory Code	Plant Species	Family name	Common Name	Plant Code
Marble Factory	MF	*Artemisia annova*	Asteraceae	sweet sagewort	I
Marble Factory	MF	*Cannabis sativa*	Cannabaceae	Bhang	II
Marble Factory	MF	*Morus alba*	Moraceae.	white mulberry	III
Marble Factory	MF	*Typha latifolia*	Typhaceae	common cattail	IV
Packing Industry	PKI	*Amaranthus viridis*	Amaranthaceae	Amarant	V
Packing Industry	PKI	*Argemone mexicana*	Papaveraceae	flowering thistle	VI
Packing Industry	PKI	*Artemisia annua*	Asteraceae	sweet sagewort	VII
Packing Industry	PKI	*Digitaria sanguinalis*	Poaceae	hairy finger-grass	VIII
Packing Industry	PKI	*Erechtites heracifolia*	Asteraceae	fireweeds	IX
Packing Industry	PKI	*Euphorbia heliscopica*	Euphorbiaceae	sun spurge	X
Packing Industry	PKI	*Glebionis coronaria*	Asteraceae	garland chrysanthemum	XI
Packing Industry	PKI	*Jatropha integrrima*	Euphorbiaceae	nettlespurge	XII
Packing Industry	PKI	*Papaver somniferum*	Papaveraceae	Opium poppy	XIII
Packing Industry	PKI	*Taraxacum officinale*	Asteraceae	common dandelion	XIV
Plastic industry	PI	*Clerodendrum chinense*	Lamiaceae	Chinese Glory Bower	XV
Plastic industry	PI	*Salix babylonica*	Salicaceae	Babylon willow	XVI
Plastic industry	PI	*Salix cinerea*	Salicaceae	common sallow	XVII
Steel mill	STM	*Euphorbia charchaias*	Euphorbiaceae	Mediterranean spurge	XVIII

Table 4. Metal content in the soil and water of surveyed industries.

		Industry/ Factory				
S. No	Heavy metals in plant medium	MF	PKI	PI	STM	Permissible limit
1	Soil (mg/Kg)					
a	Fe	4.6 ±2.77	236±3	2.8±1.53	0.8±0.05	7,000-550000
b	Pb	23.35±2.56	26.37±0.76	3.78±5.3	16.78±2.6	2-200
c	Cd	0.37±0.05	0.77±0.23	0.77±0.25	0.67±0.05	0.01-0.7
d	Cr	13.59±0.79	12±2.6	37.6±3.2	9.09±0.38	1-3000:
e	Zn	22.5±2.1	19.3±0.6	0.8±0.7	58.4±2.7	10-300
f	Cu	13.14±0.5	18.1±0.7	31.47±2.8	14.67±3.5	2-100
2	Water (mg/l)					
a	Fe	0.02±0.03	0.01±0.01	0.06±0.01	0.093±0.006	0.5
b	Pb	0.03±0.03	0.02±0.01	0.15±0.07	0.86±0.005	0.065
c	Cd	0.13±0.08	0.07±0.01	0.05±0.01	0.046±0.004	0.01
d	Cr	0.06±0.03	0.87±0.06	0.07±0.03	0.031±0.002	400
e	Zn	1.73±1.50	0.02±0.02	0.72±0.18	0.015±0.002	0.2
f	Cu	1.50±1.30	0.01±0.00	0.04±0.02	0.064±0.08	0.017

The least concentration of Fe was found in *Calotropis procera* and *Oxalis pes-caprae* collected from the soap and oil industry. The leaves of *Euphorbia heliscopica* and *Euphorbia charchaias* absorbed a maximum iron concentration of 274 and 179 mg/Kg respectively. *Quercus palustris, Salix babylonica* and *Argemone mexicana* stood next to for higher absorption of iron by their leaves i.e, 149, 144 and 127 mg/Kg respectively. The roots of *Amaranthus viridis*, *Artemisia annova* and *Cannabis sativa* accumulated 345, 119 and 82 mg/Kg of iron as shown in Fig.1.

Concentration of Lead

Maximum lead concentration of 26 and 23 mg/Kg was detected in the soil samples of the Packing industry and marble factory respectively. The maximum values of lead reported in the water sample were 0.86 mg/Kg from effluents of Saif textile mills.

The results reveal that different plant species accumulated variable amounts of lead in different parts of the plants analyzed. Roots of *Glebionis coronaria* accumulated 56 mg/Kg, *Argemone mexicana* 53 mg/Kg, *Amaranthus viridis* 43 mg/ Kg, *Artemisia annova* 39 mg/Kg and *Typha* 38 mg/Kg of Lead. Similarly, the stem of *Salix cinerea* absorbed 58 and that of *Artemisia annova* stored 20mg/Kg of lead. Our results are in agreement with the work of Badr *et al* 2012, who reported that plants having a high capacity of lead translocation will have a high concentration of lead in the shoot. 40 and 31 mg/Kg of lead were detected in leaves of *Salix cinerea* and *Cannabis sativa* respectively.

Table 5. Metal concentration in the root of analyzed plants of Gadoon Amazai Industrial estate.

	Heavy Metals					
Plant Code	Fe	Pb	Cd	Cr	Zn	Cu
I	119.7±17.6	39±1	1.97±0.05	1.67±2.08	39±1.8	28.67±2.5
II	82.6±3.8	19.47±0.7	1.13±0.15	3.33±4.9	49.3±1.10	17.97±0.2
III	5.3±2.02	12.63±2.3	3.67±0.5	7.33±0.66	13±6.08	9.1±0.2
IV	49.3±0.57	38±2.6	0.43±0.11	1.4±0.1	19.6±19.9	3.67±0.5
V	345±2.5	43±4	2.33±0.57	41.67±3.8	151±2.8	46.33±3.2
VI	77±7.2	53±20	1.67±0.57	0.33±0.5	159.7±8.9	225±02.2
VII	78±50.2	36.67±4.1	3±1	0.67±0.57	40.7±3.7	32±7.5
VIII	164.7±8.3	1±0	1±0	0.67±0.57	213±1.7	253.33±4.09
IX	1.7±0.2	1.73±0.49	6.3±1.63	1.33±0.57	3.6±0.43	5±1.3
X	4±1.05	5.6±2.2	1.9±1.01	0.77±0.11	3.8±4.3	2.93±1.3
XI	1.7±0.57	56.33±3.2	1±0	1.67±0.57	1.3±0.5	37.33±3.7
XII	2±1	2.67±9.2	1.33±0.6	1±4.07	14±10.1	3.3±6.2
XIII	54.3±5.03	3.57±0.6	1.33±0.5	37.33±2.08	1.7±1.4	3.97±5.1
XIV	69±3.60	4.23±0.41	1.17±0.76	4.93±0.7	19.5±0.5	3.27±0.6
XV	3.7±1.52	1±0	1.67±0.5	2±1	1±0	18.33±3.0
XVI	1±5.50	15±1	1.67±0.5	0.33±0.57	63±2.6	30.33±1.5
XVII	82.3±0.57	3.43±0.5	1.33±0.57	1.33±0.5	1±0	6.13±0.3
XVIII	6±1	4.53±0.4	1.8±0.26	1.90±0.1	9.6±0.6	1.67±0.5

The values are mean and ± represents standard deviation.

This indicates the transport of heavy metals via the xylem sap (Linger *et al.*, 2002). In many studies, Lead (Pb) was found to be toxic to human beings when present in large amounts. Soil and plants can be contaminated by lead from vehicle exhaust, dust and gases discharge from industrial waste. Since Pb is not biodegradable, when soil is contaminated, it becomes exposed for the long term. Lead accumulated into upper 8 inches of soil and due to its long-term contamination, remedial action is required to convert the soil to normal (Traunfeld and Clement, 2001). The toxic range of lead for plants reported by (Ross, 1994) is 30-300 µg/g.

Concentration of Cadmium

One of the most toxic metals is cadmium which exists in relation to zinc (Badr *et al* 2012). The soil of the packing industry and plastic industries showed a high range of cadmium i.e, 0.76 mg/Kg (Table 4). Maximum concentration (0.13 mg/Kg) was observed in water samples of Swabi marble factory.

The amount of cadmium in all the surveyed sites was very rare which may suggest the removal of cadmium by phytoremediation (Fig. 1). The accumulation in the roots of *Erechtites heracifolia* (6.3 mg/Kg) was maximum (Table-5). Maximum accumulation of cadmium was observed by the stem of *Artemisia annova* and *Typha* (64 mg/Kg) (Table 6) and *Cannabis sativa* (51 mg/Kg). The leaves of *Morus alba* (13mg/Kg) and *Artemisia annua* (8.8 mg/Kg) concentrated the maximum cadmium (Table 7). A similar result was displayed by (Rafati, *et al*, 2011) of accumulation of high Cd levels in the leaves i.e, (4.60 mg/kg), this result is in contrast with Wang, 2002 and Prince, 2000 who revealed that Cd accumulates more in roots of *M. alba* as compared to leaves, hence hindering its movement to the leaves.

Table 6. Metal concentration in the Stem of analyzed plants of Gadoon Amazai Industrial estate.

	Heavy Metals					
Plant Code	Fe	Pb	Cd	Cr	Zn	Cu
I	16.8±0.25	20.43±8.26	64.33±5.0	1.63±0.55	36.7±5.7	12.67±0.5
II	16.8±0.81	0.23±0.05	51.57±0.37	1.93±0.05	16.6±5.7	2.56±1.8
III	134.7±10.2	15.2±4.2	13±0.5	4.66±4.6	19±1.1	43.33±2.8
IV	18.1±1	12.33±1.5	64±1	10±0	29±5.7	19±1
V	57.7±3.21455	5±1	1.67±1.1	64.67±8.3	35.7±4.04	2.67±1.5
VI	47.3±3.7	15.73±21.0	2±1	6.53±2.8	37.3±3.7	18±2.6
VII	106.7±3.7	2.63±0.32	1.33±0.57	16.17±0.7	48.3±2.08	2±1
VIII	71±3.6	2.6±0.26	1±0	2.87±0.15	62.7±8.5	1±0
IX	39±1	6.23±0.58	1±0	1.6±0.4	29±2.6	2±1
X	586.7±14.0	7.3±0.4	1.33±0.5	5±1	103±2.6	5.33±0.5
XI	67±3	3.13±0.2	1.33±0.5	1.6±0.2	87.3±3.05	6±4.3
XII	2.9±0.1	7.93±0.15	1±0	2.05±0.7	29.2±2.2	1.47±0.1
XIII	66.7±2.08	1.6±0.17	0.67±0.57	4.33±0.5	38.3±1.5	7.67±1.5
XIV	20±32.0	1.8±0.1	0.97±0.05	6.33±1.5	15±3.6	0.03±0.05
XV	88.3±3.05	18.4±0.7	3±1	60±10	73.7±4.9	14±1
XVI	133.7±4.04	14.77±0.2	1.33±0.57	6.3±1.52	0.4±0.15	13.13±0.3
XVII	2.3±6.6	58.27±43.0	2±0	2±1.4	2±1	15.67±0.4
XVIII	499.7±10.5	12.6±2.0	3.87±0.15	3.93±0.05	47.3±3.5	12.67±0.5

The values are mean and ± represents standard deviation.

Concentration of Chromium

The toxic metal (non-essential) chromium is abundant in the environment in two ionic forms i.e, trivalent and hexavalent. The second mentioned form is more dangerous because of its properties like (high solubility, oxidation and penetration into plasma membranes) (Badr *et al.*, 2012). The lethal range of chromium in plants lies 1-10 µg.g dry weight (Macnicol and Beckett, 1985). The results show that the maximum amount of chromium was absorbed by the soil of the plastic industry (37 mg/Kg) followed by the marble factory and packing industry i.e, 13 and 12 mg/Kg respectively. Maximum Chromium concentration was observed in water samples of the packing industry i.e, 0.87 mg/Kg. The accumulation of chromium in the stem of *Amaranthus viridis* (64 mg/Kg), *Clerodendrum chinesis* (60 mg/Kg) and *Typha* (10 mg/Kg) were absorbed in maximum.

Table 7. Metal concentration in the leaf of analyzed plants of Gadoon Amazai Industrial estate.

	Heavy Metals					
Plant Code	Fe	Pb	Cd	Cr	Zn	Cu
I	58.8±0.72	12.93±0.1	0.77±0.05	1.7±0.005	27.9±1.1	5.4±0.4
II	89.1±9	40.6±2.1	2.7±0.5	3.27±0.47	5.2±0.5	36.5±5.3
III	73.3±22.8	13.53±0.85	13.67±1.1	2.9±0.1	19.5±0.7	10.03±1.7
IV	49±1	1.73±0.20	3.83±0.15	8.3±1.12	21.7±2.08	2.53±0.1
V	1.3±0.5	2.67±0.49	1.33±0.57	2.73±2.1	2.7±1.52	3.33±0.5
VI	127.3±21.0	6.93±0.05	2±1	2.5±1.3	72.3±3.5	20±10
VII	56±6.0	16.03±0.96	8.8±0.2	3.73±0.20	17.7±1.5	9.3±0.5
VIII	1.3±0.5	2.6±0.6	1.33±0.5	1.33±0.5	7±1	2±1
IX	46.7±2.5	4.9±0.1	1.33±0.5	2.8±0.2	41.7±2.08	7.6±0.6
X	274.3±22.8	0.4±0.1	1.33±0.5	1.67±0.34	123.7±4.04	15.73±0.2
XI	137.3 ±3.785939	9.3±0.6	1.33±0.5	2.87±0.15	197.7±2.5	36.33±4.6
XII	46.7±15.2	2.8±10.2	1.33±0.7	3.13±4.4	34±10.2	4.67±7.04
XIII	126.7±4.1	BDL	1.67±0.5	3.3±1.9	176.7±15.2	15.67±3.5
XIV	1.2±0.8	3.53±0.41	1.3±0.6	4.53±0.5	±3.05	6.97±1.0
XV	123±1.73	20±1	6.9±4.2	BDL	47.8±3.05	16.77±0.2
XVI	144±40.7	10.77±0.3	1±0	5.3±1.1	0.3±0.5	15.67±1.5
XVII	133.7±20.8	31.17±15.4	1.33±0.57	1.33±0.5	29.4±2.4	7.27±0.4
XVIII	179.3±17.9	7.5±0.5	7.8±0.43	7.87±0.8	86.3±4.1	15.33±3.5

The values are mean and ± represents standard deviation, BDL: Below detectable limit.

The leaves showed the following concentrations of chromium in *Typha* (8.3) and *Euphorbia charchaias* (7.8). The maximum amount of chromium was recorded in the roots of *Amaranthus viridis* (41 mg/Kg) and *Papaver somniferum* (37 mg/Kg).

Concentration of Zinc

Zinc is one of the important micronutrients but its high levels are toxic not to plants but also human beings (Badr *et al* 2012). According to Kloke the range of Zn above 300 µg/g d.w is lethal. The toxic levels of Zn for plants are from 100 to 500 µg/g d.w. The soil of the textile mill and marble factory suggested a higher amount of zinc i.e, 58 and 22 mg/kg (Table 4). The highest values (1.73 mg/Kg) of zinc was recorded in water samples of the Marble factory. Almost all plant species showed great affinity for Zinc (Fig. 1). It is confirmed by Kos *et al* 2003 that most of the plants are hyperaccumulators for Zn. The roots of *Digitaria sanguinalis* (213 mg/Kg), *Argemone Mexicana* (159 mg/Kg), *Amaranthus viridis* (151 mg/Kg) and *Mentha arvensis* (64 mg/Kg) accumulated maximum zinc (Table 5). The maximum amount of zinc was recorded in the stem of *Euphorbia heliscopica* (103 mg/Kg), *Clerodendrum chinesis* (73 mg/Kg), *Digitaria sanguinalis* (62 mg/Kg) and (47 mg/Kg) in *Euphorbia charchaias* (Table 6). The maximum zinc was absorbed by the leaves of *Papaver somniferum* (176 mg/Kg), *Euphorbia heliscopica* (123 mg/Kg), *Euphorbia charchaias* (86 mg/Kg), *Taraxacum officinale* (74 mg/Kg) and Argemone Mexicana (72 mg/Kg) (Table-7).

Table 8. Translocation and accumulation factors detected in growing plants.

	Bioconcentration factor (BCF)						Bioaccumulation coefficient (BAC)						Translocation factor (TF)					
Plant Code	Fe	Pb	Cd	Cr	Zn	Cu	Fe	Pb	Cd	Cr	Zn	Cu	Fe	Pb	Cd	Cr	Zn	Cu
I	26.01*	1.67*	5.36*	0.12	1.74*	1.37*	16.4	1.43	178	0.25	2.88	2.97	0.63-	0.86-	33.1**	2**	1.66**	2.17**
II	17.95*	0.83	3.09*	0.25	2.19*	0.69	23	1.75	148	0.38	0.97	4.06	1.28**	2.1**	47.9**	1.56**	0.44-	5.86**
III	1.14*	0.54	10*	0.54	0.58	0.28	45.2	1.23	72.7	0.56	1.72	1.64	39.5**	2.27**	7.27**	1.03**	2.96**	5.87**
IV	10.72*	1.63*	1.18*	0.1	0.87	2.56*	14.6	0.6	185	1.35	2.26	0.33	1.36**	0.37-	157**	13.1**	2.59**	0.13-
V	1.46*	1.63*	3.04*	3.47*	7.84*	12.4*	0.25	0.29	3.91	5.62	1.99	2.1	0.17-	0.18-	1.29**	1.62**	0.25-	0.17-
VI	0.33	2.01*	2.17*	0.03	8.29*	1.77*	0.74	0.86	5.22	0.75	5.69	0.62	2.27**	0.43-	2.4**	27.1**	0.69-	0.35-
VII	0.33	1.39*	3.91*	0.06	2.11*	14*	0.69	0.71	13.2	1.66	3.43	0.17	2.09**	0.51-	3.38**	29.9**	1.62**	0.01-
VIII	0.7	0.04	1.3*	0.06	11.1*	0.28	0.31	0.2	3.04	0.35	3.62	0.53	0.44-	5.2**	2.33**	6.3**	0.33-	1.92**
IX	0.01	0.07	8.22*	0.11	0.19	0.16	0.36	0.42	3.04	0.37	3.67	1.16	50.4**	6.42**	0.37-	3.3**	19.6**	7.18**
X	0.02	0.21	2.48	0.06	0.2	2.06*	3.65	0.29	3.48	0.56	11.8	2.34	213**	1.38**	1.4**	8.7**	60.2**	1.13**
XI	0.01	2.14*	1.3*	0.14	0.07	0.18	0.87	0.47	3.48	0.37	14.8	0.34	123**	0.22-	2.67**	2.68**	214**	1.86**
XII	0.01	0.1	1.74*	0.08	0.73	0.22	0.21	0.41	3.04	0.43	3.28	1.29	24.8**	4.03**	1.75**	5.18**	4.52**	5.88**
XIII	0.23	0.14	1.74*	3.11*	0.09	0.18	0.82	0.06	3.04	0.64	11.2	0.39	3.56**	0.45-	1.75**	0.2-	126**	2.14**
XIV	0.29	0.16	1.52*	0.41	1.01*	1.56*	0.09	0.2	2.96	0.91	4.64	0.78	0.31-	1.26**	1.94**	2.2**	4.57**	0.5-
XV	0.48	0.26	2.17*	0.05	1.2*	0.22	68.9	10.2	12.9	1.6	146	2.02	143**	38.4**	5.94**	30**	121**	9.36**
XVI	0.36	3.97*	2.17*	0.01	75.6*	0.19	100	6.76	3.04	0.31	0.84	0.73	278**	1.7**	1.4**	34.9**	0.01-	3.74**
XVII	29.76*	0.91	1.74*	0.04	1.2*	0.11	49.2	23.7	4.35	0.09	37.7	1.91	1.65**	26.1**	2.5**	2.5**	31.4**	16.8**
XVIII	7.83*	0.27	2.7*	0.21	0.16	0.85	886	1.2	17.5	1.3	2.29	0.08	113**	4.43**	6.48**	6.21**	13.9**	0.09-

All stated values are average (n=3), where the values of BCF >1 are significant * for phytostabalization, TF <1 are metal excluders- and TF > 1 are metal hyperaccumulators.

Concentration of Copper

Copper is one of the important metals for the process of plants and animals but its high levels may be hazardous for them (Badr *et al* 2012).

The permissible limit of copper lies 10-30 µg/g d.w for plants (Macnicol and Beckett, 1985). The soil of the plastic factory and packing industry detected a maximum concentration of copper i.e 31 and 18 mg/Kg (Table 4). Maximum Copper concentration was 1.50 mg/Kg recorded in water samples of Marble factory of the selected industrial zone. The maximum concentration of copper was observed in the roots as compared to other parts of plants. It is very similar to the results of Badr *et al* 2012, who reported maximum Cu aggregated in the roots of *Phragmite australis* The results in (Table 5) shows the maximum ratio of Cu in the roots of *Digitaria sanguinalis* (253 mg/Kg), *Argemone mexicana* (225 mg/Kg) and *Mentha arvensis* (34 mg/Kg) accumulated maximum amount of copper. This rhizo-concentration of Cu may be due to the formation of plaque (metal hydroxides) which facilitate their deposition in root surfaces. The stem of *Morus alba* (43 mg/Kg), *Typha* (19), *Argemone Mexicana* (18 mg/Kg) and *Euphorbia charchaias* (12 mg/Kg) accumulated the maximum of copper among all Analysed plants (Table 5). The maximum copper was accumulated by the leaves of *Cannabis sativa* (36), *Lantana camara* (17.6 mg/Kg) and (15.3 mg/Kg) by *Euphorbia charchaias* (Table 7).

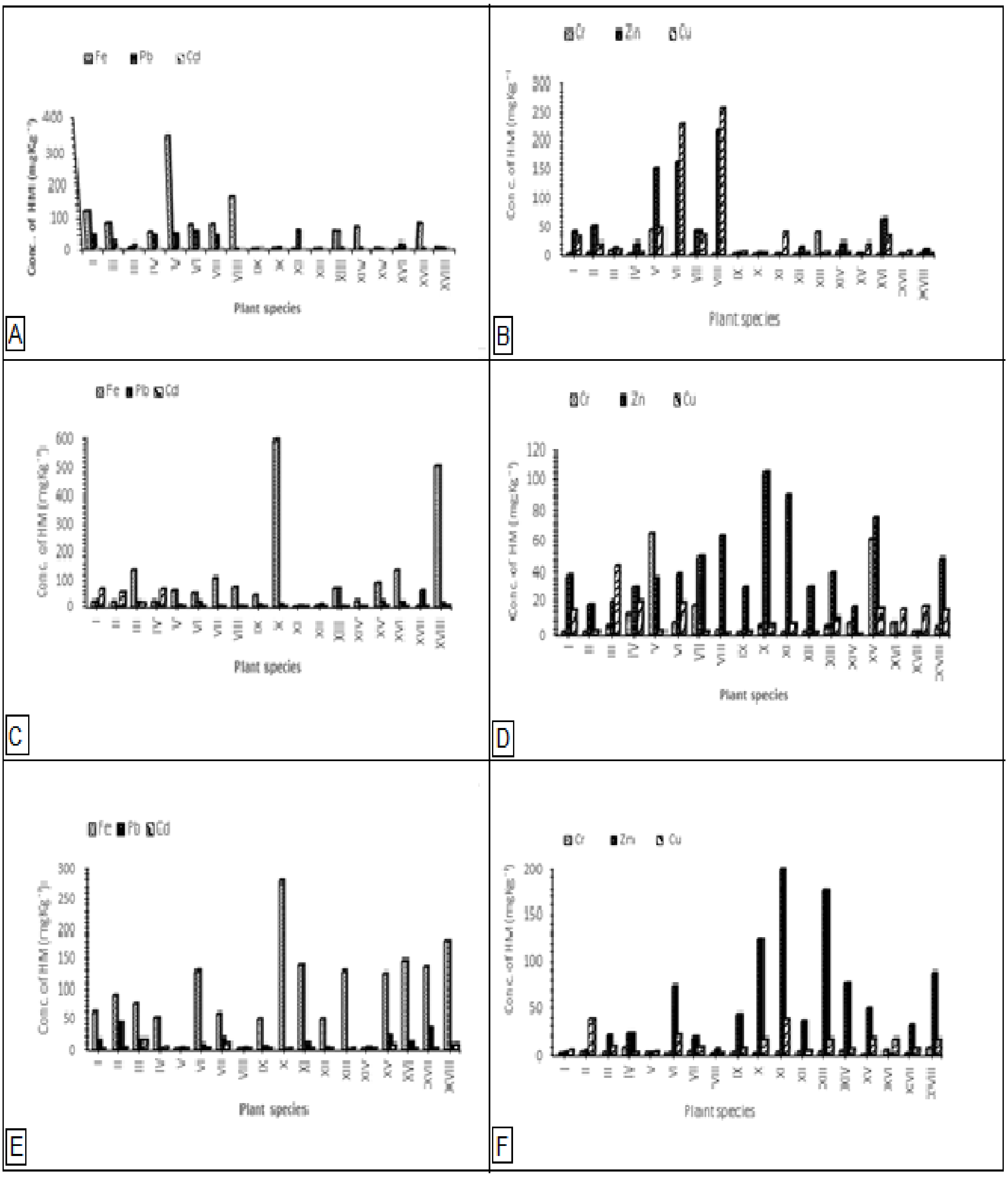

Fig. 1. Accumulation and translocation of selected heavy metals: A and B= in roots of different plants, C and D= in shoot of different plants. E and F= in leaf of different plants.

Accumulation, Biological concentration, and Translocation Coefficients (BAC, BCF and TF)

The potential of a plant to transport various heavy metals can be assessed by the coefficients (BAC, BCF and TF). Metal excluder species commonly have TF lower than 1 whereas metal accumulator species has TF above 1 (Baker, 1981). According to Saraswet and Rai 2009 and Zacchiini 2008 those Plants having shoot BCF >1 are best suited for phytoextraction while those with TF < 1 and root BCF > 1 could be utilized for Phytostabilization. There are series of factors associated with bioavailability and accumulation of metals in which prevailing climate, soil properties, the genotype of plants, redox state of metals and relation of the plant-rhizosphere system with seasonal variations (Kabata-Pendias and Pendias, 1984). Our results showed that the root to soil concentration for iron showed a decline as the values of TF and BCF raised. The phenomenon of phytoremediation starts its journey at the very early stage i.e, during the germinating period of seeds, where plants absorb metal ions with water.

The toxic metals reach the shoot through root via transpiration pull (Ximenez-Embun *et al.*, 2001). Maximum values of BAC were recorded by *Morus alba* (45), *Cannabis sativa* (23), *Artemisia annova* (16), the translocation factor for *Artemisia annova* < 1, (*Typha* (14). Highest TF was recorded by *Euphorbia heliscopica* (213), *Oxalis pescaprae* (186) and *Euphorbia charchaias* (113) for iron. The BCF values recorded for iron were highest for *Artemisia annova* (26), *Euphorbia charchaias* (7.8) and (1.4) in *Amaranthus viridis*. The TF values for lead were maximum in *Morus alba* (18), *Erechtites heracifolia* (6.4), *Euphorbia charchaias* (4.4) whereas the BCF for lead were *Lantana camara* (3.6), *Artemisia annova* (1.67), *Typha* (1.62) (Table 7).

Salix cinerea, *Cannabis sativa* showed a high range of BAC (23), (1.74) for lead, where the BCF ratio became <1, *Erechtites heracifolia* showed (6.4) shoot to root ratio where it's BAC and BCF <1. Maximum BCF was showed by *Argemone Mexicana* (2), *Artemisia annua* (1.3) for the lead. Cadmium was absorbed and presented at a very high ratio a range of 185- 3 by different plants from different industries. Almost all the collected and analyzed plants showed a high root to soil ratio.

The BAC of *Typha* was very high (185). Similarly, the TF and BCF of almost all plants were >1 which indicates that all the Analysed plants were good for phytoextraction and Phytostabilization. Maximum TF was showed by *Oxalis pes-caprae* (32), *Artemisia annua* (29) all other plants except *Papaver somniferum* (0.2), as TF values increased it reduced the BCF below 1 for chromium (Table 8).

The potential of selected plants for copper and showed that *Artemisia annua*, *Taraxacum officinale* were very appropriate for phytoextraction of zinc. According to Yoon *et al.* (2006), only plant species with both BCF and TF greater than 1 have the potential to be used for phytoextraction *Cannabis sativa* can be used for phytoextraction of copper. Shoot concentrations of Cu varied between 2.7 and 15 mg/kg, with the lowest concentrations again observed for *Z. mays*, while C. sativa exhibited the highest concentrations (Meers *et al.* 2005). Specific plant species can absorb and hyper accumulate metal contaminants or excess nutrients in harvestable root and shoot tissue, from the growth substrate through the phytoextraction process. This is for metals, metalloids, radionuclides, nonmetals, and organics contaminants in soils, sediments, and sludge's medium (Prasad and Freitas, 2003).

Conclusion

This study shows the potential of some highly accumulating plants to repair contaminated soil through plant extraction and other processes, including plant stabilization and plant volatilization. Twenty plants aggregated in the industrial zone of Pakistan were investigated for selected HM. For Phytoextraction potential, it was observed that stem and leaves of *Euphorbia (heliscopica* and *charchaias*) showed highest affinity for Fe while suitable for removal of Zn. However, stem and leaves of

Euphorbia charchaias was found best for phytoremediation of Cu.

The metal analysis of different parts of Artemisia annova revealed that Pd and Cd were accumulated maximum in stem and roots. Stem and roots of Amaranthus viridis whereas stem and leaves of Typha were suitable extractors of Cr. This study recommended that these plants can be used for minimization of heavy metals, but it should be prohibited for use as food and fodder due to health hazards involving Phyto mining for recovery of heavy metals. Further monitoring of current environmental and agricultural quality of soil in terms of heavy metal accumulation may be adopted for future soil contamination.

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