

## Uptake of metals by plants in urban areas

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**Abstract** In the present study, bulk contents of Ni, Zn, Cu, Pb and Mn in urban area of Tehran city are determined. Subsequently, the chemical bonds of metals with various soil fractions are brought out. Chemical partitioning studies revealed that various percentile of Ni, Zn, Cu, Pb and Mn is found in anthropogenic portion of soils. Zinc, Ni, Cu, Pb and Mn fall within “low pollution” class in accordance with index of pollution ( $I_{POLL}$ ). The trend of anthropogenic share of studied metals in soils of Tehran is Zn (55 %) > Cu (31 %) > Ni and Pb (30 %) > Mn (12 %). The overall potential of studied plants in metal removal from soil is *Salvia* > *Viola* > *Portulaca*. It should be pointed out that roots have higher potential in metal removal from soil when compared with leaf and stem. Lithogenic portion of metals remains intact before and after pot analysis. Thus, phytoremediation is highly dependent on the chemical bonds of metals. Present study showed that metal contents of loosely bonded ions, sulfide bonds and organometallic bonds are reduced after 90 days of plant cultivation. The overall removal trend of studied metals is Zn (16 %) > Cu (14 %) > Ni (11 %) > Pb (7 %) > Mn (6 %). The

obtained results show that the anthropogenic portion of metals is reduced after the phytoremediation practice. For instance, the initial anthropogenic portion of Zn (55 %) is changed to 39 % showing an overall reduction of about 16 %. The anthropogenic portions of Cu, Ni, Pb and Mn are also reduced by 14, 11, 7 and 6 %, respectively.

**Keywords** Soil · Contamination · Phytoremediation · Chemical fraction · Anthropogenic

### Introduction

Metals and organic materials are among essential components in soil. As a result of industrial as well as agricultural activities, the levels of metals and organic materials are increased leading to soil contamination (Subhashini et al. 2013). Subsequently, various soil cleaning techniques (biological, chemical and physical) have been examined by researchers (Sannino et al. 2013, 2016; Kristanti et al. 2011; Niazy et al. 2016). In the recent years, appropriate instrumental methods have been developed for predicting the exact toxicities of metal ion species (Ali and Aboul-Enein 2006). Many researchers opine that organic and inorganic pollutants can be treated by low cost and new generation adsorbents (Ali et al. 2012; Ali 2012, 2014; Daryabeigi Zand and Hoveidi 2016) both from wastewater as well as freshwater. Removal of metal ions from wastewater by inexpensive adsorbents can prevent soil contamination (Ali 2010). Effectiveness of electrocoagulation as well as electrodialysis of contaminated water with arsenic has received ample attention (Ali et al. 2011). It is shown arsenic removal from soils with higher moisture is much feasible (Sultana and Kobayashi 2016). In general, the inexpensive adsorbents are of immense interest to many

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researchers (Ali 2010) and therefore it is tried to bring out an appropriate protocol for experimental methodologies in this growing field (Ali and Gupta 2006). Immobilization, soil washing and phytoremediation techniques are known as the best available technologies (BATs) for remediation contaminated soils (Scanferla et al. 2012). Some metals possess inauspicious effects on the growth of plants that can be decreased (up to 46 %) by *Pseudomonas* (Kamran et al. 2016). Chen et al. (2015) found out that metal ATPase (HMA) could regulate concentrations of Cu, Ag, Zn, Cd, Co, Pb and Mn in various tissues of plants. It should be pointed out that the use of endosulfan is banned but it is still being used in several countries for cleaning up hazardous sites (Mitton et al. 2016).

Phytoremediation potential of alfalfa in co-contaminated soil was examined and to some extent increased by citric acid alfalfa (Agnello et al. 2016). Heavy metals and nutrients can be effectively removed by wetland plants possessing high aboveground biomass (Vymazal 2015, Javadi et al. 2010). It is found out that metal accumulation by various plants is not necessarily proportional to growth performance of a particular plant species phytoremediation (Wang et al. 2015). Some analysis also found out that the ability of different plant organs for absorbing metals is not the same (Li et al. 2015). Some researchers have proposed biomass pyrolysis for hyperaccumulation of metals (Dilks et al. 2016). *Betzickiana* has been successfully used for phytoremediation of Cd and Pb to lower plant stress (Tauqeer et al. 2015). Some researchers have shown bio-concentration restriction in soil-root transfer at higher zinc concentrations in the soil (Liu et al. 2006).

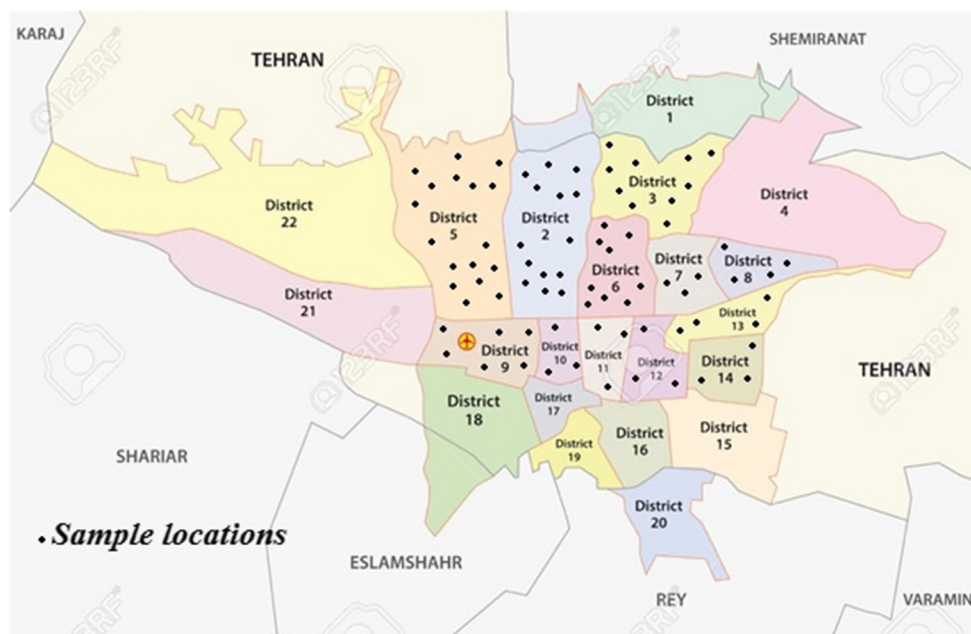
Fortunately in the recent years, more attention has been paid to various environmental aspects of urban areas including soil pollution in urban areas of Iran (Mohammadpour Roudposhti et al. 2016a). For instance, a pollution index is developed for agricultural soils adjacent to large cities (Mohammadpour Roudposhti et al. 2016b). Such pollution studies have also been of interest by researchers in the vicinity of urban areas located near industrial zone (Ghaemi et al. 2015). An overview of the spatial distribution and chemical properties of heavy metals through dust fallout in urban area is investigated. It is found out that about 70 % of metals in the deposited particulate matter were from external origin during dust fall (Tabatabaei et al. 2014, 2015).

Tehran is the capital city of Iran with a day population of 14 million. The number of cars and motor vehicles reaches to around 7 million. The overall gasoline consumption by fleet is around 3 billion liters per year. Such huge amount of gasoline consumption leads to severe air pollution that finally finds their way onto the soil. The main objective of present study is to find out the association of metals with various soil phases. It is also aimed to know about the metal bonds and their uptake by plants.

## Materials and methods

Soil samples from 0 to 55 cm depth were collected at 80 sites within Tehran metropolitan city (Fig. 1). An offset grid pattern is used in the present study (Mohammadpour Roudposhti et al. 2016b). About 80 soil samples (five samples from each grid) were collected. Subsequently, the

**Fig. 1** Map showing soil sampling location in Tehran metropolitan city



samples of each grid were mixed together to furnish about 16 composite soil samples (Fig. 1) for further analysis. Soil samples were immediately packed in airtight pre-labeled polyethylene bags and preserved at 4 °C. The samples were oven-dried at 45 °C for about 48 h. Subsequently, they were passed through 63 µm mesh size (Vaezi et al. 2015; Vesali Naseh et al. 2012).

About 0.5 g of each soil sample was digested by 5 mL of HF, and subsequently they were treated with 7 mL of aqua regia (1:3 HCl:HNO<sub>3</sub>). The volume of solution was brought out to 50 mL by 1 N HCl (Karbassi et al. 2008). Chemical partitioning study was carried out in four sequential steps. In the first step, acetic acid (25 % v/v) was used to dissolve exchangeable/carbonate fraction. In steps 2 and 3, mixture of HOAc (25 % v/v) along with 0.1 M hydroxylamine hydrochloride and 30 % (w/v) H<sub>2</sub>O<sub>2</sub> “extraction with 1 M ammonium acetate” was used to extract metals bonded with sulfides and organics, respectively. In step 4, hot 50 % HCl was used to break down the most resistant metal bonds (Mollazadeh et al. 2013).

In this study, 3 flowering plants (*Viola* sp., *Portulaca* and *Salvia*) were selected for testing their ability to absorb metals from the contaminated soil. These plant species are selected for the present study because of their common use within Tehran city. Once the chemical analysis of soil was carried, 48 pots of 4 kg capacity were used for pot analysis (16 pots for each plant species). Fresh plant samples were collected after 3 months of cultivation by carefully pulling from the soil to avoid damage to the roots. The plant samples were washed with distilled water to remove any foreign particles. Then roots, stems and leaves were separated. The separated parts were oven-dried at 100 °C for about 96 h. Dried samples of different parts of the plants were finely powdered using agate pestle and mortar. Plant samples (0.5 g) of each part (leaves, stems and roots) were digested by 5 mL of concentrated HNO<sub>3</sub>. After cooling, the solution was filtered with Whatman filter No. 42. It was then made up to 25 mL by distilled water. The metal contents (Ni, Zn, Cu, Pb and Mn) in soil samples as well as plant samples were determined by atomic absorption spectroscopy (Varian AA-30 model). Standard sediment sample (MESS-1) was used to check the accuracy (better than ±6 % for all elements) of the analysis (Biati et al. 2014).

Total organic contents of soil samples were measured by recording the loss on ignition (LOI) through heating the samples for 4 h at 450 °C in a muffle furnace. Phosphorus was measured by extracting solution (0.5 M NaHCO<sub>3</sub>, pH 8.5); total nitrogen by Kjeldahl digestion; pH was analyzed by glass electrode using a 1:1 soil/water ratio; and electrical conductivity (EC) was measured by conductivity meter in a soil–water extract (1:2 soil/water ratio). Titration method was used to measure soil lime, and Na and K were

measured by flame photometer. Total carbon (C) was measured as per the method described by Supaphol et al. (2006). Soil particle size was determined using Bouyoucos hydrometer method. The WinTal software was used to bring out the texture of soil. All reagents used were of analytical grade (Merck). Cation-exchange capacity (CEC) was also measured (Mohammadpour Roudposhti et al. 2016b). The Ca and Mg concentrations were determined by complex-metric titration.

The transfer factor (TF) of elements from soil to plant was calculated by the following equation:

$$TF = C_{\text{Plant}}/C_{\text{Soil}} \quad (1)$$

where  $C_{\text{Plant}}$  is the concentration of elements in plants and  $C_{\text{Soil}}$  is the concentration of elements in soil (Mahmood and Malik 2014).

To assess the intensity of elemental contamination in Tehran's soils, the pollution index ( $I_{\text{poll}}$ ) was calculated by the following formulae (Karbassi et al. 2008):

$$I_{\text{POLL}} = \text{Log}_2\{C_n/B_n\} \quad (2)$$

where  $C_n$  is the total elemental content in soils and  $B_n$  is background level (lithogenic portion) of element obtained by chemical partitioning technique (Karbassi et al. 2008). It should be noted that the modified scale (Salehi et al. 2014) was used to bring out soil pollution intensity (Table 1).

## Results and discussion

Generally, the soils in Iran are alkaline in nature. The organic content of soils is also very low when compared with many other countries. Table 2 depicts general characteristics of soil samples within Tehran. The higher Na contents of soil might be due to the use of salt during winter time for deicing of the roads. Organic matter has a very high CEC ranging from 250 to 400 meq/100 g (Moore et al. 1998). Generally, higher CEC is indicative of presence of higher amount of clay and organic in the soil. Figure 2 shows the texture of soil in Tehran. The soil classification falls within loam to silt loam. The lower organic matter and also rather low clay fraction of Tehran's soil may justify the lower CEC values reported in the present investigation.

In spite of various pollution sources, the metal contents of Tehran's soils show lower values when compared with the values given for mean crust (Table 3). This could be indicative of deviation among the geology of the area of study with the mean crust. Thus, chemical partitioning techniques should be used to bring out the share of lithogenous and non-lithogenous fractions of metals (Table 4).

If the lithogenic fraction (Table 4) is considered as the background values for the areas of study, then it would be

**Table 1** Terminologies for contamination classes on single and integrated indices

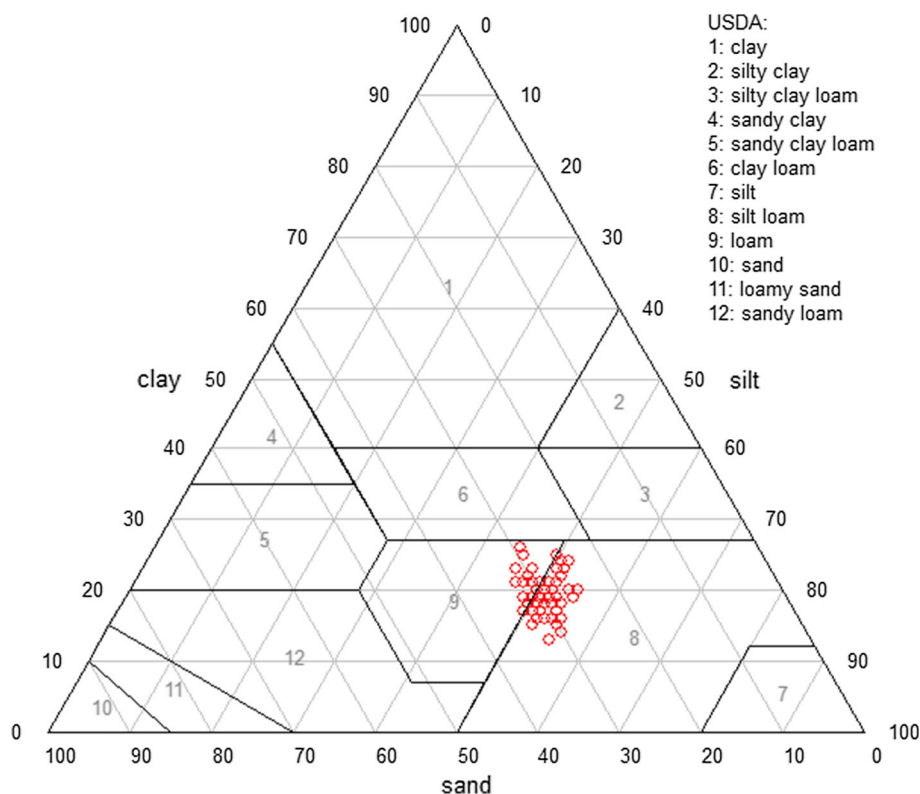
Indices	Unpolluted	Low polluted	Moderately polluted	Strongly polluted	Extremely polluted
$I_{\text{POLL}}^*$	<0.42	0.42–1.42	1.42–3.42	3.42–4.42	>4.42

\* Same terminology used for Igeo by Salehi et al. (2014) is adopted

**Table 2** Physicochemical parameters of the agricultural soils ( $N = 16$ ) in Tehran

Parameter	Unit	Minimum	Maximum	Mean	SD ( $\pm$ )*
pH	–	6.9	8.2	7.7	0.43
Organic matter	%	1.1	2.2	1.8	0.31
Total N	%	0.01	0.07	0.04	0.02
Total P	%	4.2	24.5	15.2	8.5
CEC	mol/g soil	5.3	22.8	15.5	8.2
EC	ds/cm	0.04	2.2	1.2	1.05
Ca	mg/kg	2.7	38.4	22.3	15.9
Mg	mg/kg	45.9	128.5	84.3	34.2
Na	mg/kg	14.5	59.8	35.8	20.8
K	mg/kg	8.9	44.3	23.5	17.6

\* Standard deviation

**Fig. 2** Texture analysis of Tehran's soil samples

obvious that mean metal contents (obtained in the present study) are much higher than the background values (except for Pb). The trend of anthropogenic share of studied metals in soils of Tehran is Zn (55 %) > Cu (31 %) > Ni and Pb (30 %) > Mn (12 %). The chemical partitioning of metals clearly shows the influence of man's activities on contaminating soils in urban areas. Table 5 shows soil

pollution intensity within Tehran city in accordance with  $I_{\text{POLL}}$  formulae (Karbassi et al. 2008). According to the terminology adopted (Salehi et al. 2014), the contamination class for Ni, Zn, Pb, Cu and Mn falls within low contamination. The low to moderated contamination class has been previously reported for Tehran's landfill known as Aradkuh (Salehi et al. 2014).

**Table 3** Concentration of elements (mg/kg) in the soils of Tehran city

Element	Present study (N = 16)			SD (±)*	Mean crust
	Min.	Max.	Mean		
Ni	73	85	78	7	80
Zn	74	92	80	9	95
Pb	32	39	34	3	12
Cu	38	52	42	6	45
Mn	523	640	584	61	850

\* Standard deviation

Subsequently, *Viola* sp., *Portulaca* and *Salvia* that are almost of 1-year life span were cultivated on the soils with the above-mentioned characteristics. The aim was to know about the chemical bonds of metals that are being removed by plants. As discussed earlier (Table 4), metals can be found in five different bonds and the bioavailability of each bond differs from each other. *Viola* sp. is a genus of flowering plants in the violet family *Violaceae*. It is the largest genus in the family, containing between 525 and 600 species. Most species are found in the temperate Northern Hemisphere; however, some are also found in widely divergent areas such as Hawaii, Australasia and the Andes. Some *Viola* species are perennial plants, some are annual plants, and a few are small shrubs. *Portulaca* is the type genus of the flowering plant family *Portulacaceae*,

comprising about 40–100 species found in the tropics and warm temperate regions. They are also known as moss roses. Common Purslane (*Portulaca oleracea*) is widely considered an edible plant and in some areas an invasive type of weed. Some *Portulaca* species are used as food plants by the larvae of some Lepidoptera species including the Nutmeg (*Hadula trifolii*). *Salvia* is the largest genus of plants in the mint family, Lamiaceae, with nearly 1000 species of shrubs, herbaceous perennials and annuals. Within the Lamiaceae, *Salvia* is part of the tribe Mentheae within the subfamily Nepetoideae. It is one of several genera commonly referred to as sage. The genus is distributed within three distinct regions of diversity: Central and South America (approx. 500 species); Central Asia and Mediterranean (250 species) and Eastern Asia (90 species).

Table 5 presents the metal removal by *Viola* sp., *Portulaca* and *Salvia*. It is evident that *Salvia* has the highest potential removal of Ni, Zn and Mn from soil when compared with *Viola* and *Portulaca* species. The overall potential of studied plants in metal removal from soil is *Salvia* > *Viola* > *Portulaca*. It should be pointed out that roots have higher potential in metal removal from soil when compared with leaf and stem.

Once the pot analysis was completed (Table 6); the metal contents of soils remaining in pots (bulk as well as chemical partitioning) were measured. This was done to know the amount of depletion of total metal contents as well as individual fractions. A comparison between

**Table 4** Origin of elements in Tehran soils

Element	mg/kg (N = 16)							Anthropogenic	Lithogenic
	Mean metal contents	Mean metal fractions							
		1*	2*	3*	4*	5*			
Ni	78	12 (15)	4 (5)	8 (10)	52 (67)	2 (3)	24 (30)	54 (70)	
Zn	80	18 (22)	12 (15)	14 (18)	33 (41)	3 (4)	44 (55)	36 (45)	
Pb	34	8 (24)	2 (6)	0 (0)	23 (67)	1 (3)	10 (30)	24 (70)	
Cu	42	2 (5)	7 (16)	4 (10)	27 (64)	2 (5)	13 (31)	29 (69)	
Mn	584	45 (7)	15 (3)	12 (2)	504 (87)	8 (1)	72 (12)	512 (88)	

\* Step 1. Loosely bonded ions; Step 2. Sulfides bonds; Step 3. Organometallic bonds; Step 4. Most resistant bonds and Step 5. Within lattice bonds [Step 5 = Bulk metal content—(1 + 2+3 + 4)]. Also rounded-off figures within brackets show percentile of mean metal fractions, anthropogenic and lithogenic portions while compared with mean metal contents

**Table 5** Comparison of calculated pollution indices for Tehran soils

Element	Pollution Index			Salehi et al. (2014) Contamination class
	Mean metal (Cn)	Lithogenic fraction (Bn)	Pollution index ( $I_{poll}$ )	
Ni	78	54	0.53	Low
Zn	80	36	1.15	Low
Pb	34	24	0.50	Low
Cu	42	29	0.54	Low
Mn	584	512	0.50	Low

**Table 6** Metal accumulation by selected plants ( $N = 48$  pots)

Name of plant/metal		Controlled (mg/kg)			After 90 days (mg/kg)		
		Leaf	Stem	Root	Leaf	Stem	Root
<i>Viola</i>	Ni	12	18	14	14	19	20
	Zn	22	24	20	26	30	32
	Pb	5	2	3	6	3	3
	Cu	19	17	20	22	20	22
	Mn	120	132	128	135	145	145
<i>Portulaca</i>	Ni	10	12	12	11	14	13
	Zn	15	12	18	16	16	25
	Pb	6	5	6	7	8	8
	Cu	14	14	16	19	16	18
	Mn	78	22	36	85	30	48
<i>Salvia</i>	Ni	18	12	22	22	16	31
	Zn	16	16	22	22	25	35
	Pb	4	2	3	5	2	4
	Cu	22	22	20	25	24	25
	Mn	66	80	65	72	98	95

Tables 4 and 7 shows that lithogenic portion of metals remains intact before and after pot analysis. On the other hand, the metal contents of loosely bonded ions, sulfide bonds and organometallic bonds are reduced after cultivation of plants for a duration of 90 days. The obtained results show that the anthropogenic portion of metals is reduced for all studied metals {Zn (39 %) > Pb (23 %) > Ni (19 %) > Cu (17 %) > Mn (6 %)}. It is obvious that initial anthropogenic portion of Zn (55 %) is about 39 % after the phytoremediation practice. In other words, about 16 % of anthropogenic portion of Zn is removed by phytoremediation. The overall removal trend of studied metals is Zn (16 %) > Cu (14 %) > Ni (11 %) > Pb (7 %) > Mn (6 %). It is interesting to note that loosely bonded ions are the main contributors to the phytoremediation process (except for Cu). It should be

noted that sulfide and organic bonds of Cu play a major role in phytoremediation processes. In general, the trend of various bonds in contribution of metals to the phytoremediation process can be summarized as loosely bonded ions > sulfide bonds > organometallic bonds.

## Conclusion

Phytoremediation has received ample attention as an environmentally friendly technique for treating contaminated soils. This is especially true in the urban areas where people are more concerned with environmental issues. Many plants have been studied worldwide. The potential of many plants in removal of metals from contaminated soils has been extensively discussed. The importance of CEC, pH, soil grain size, organic matters and other factors is brought out. However, the previous studies do not discuss about role of various metal bond in phytoremediation processes. In the present study, chemical partitioning technique was used to know which metal bond is more affected by phytoremediation processes. The results revealed that lithogenic portion of metals (most resistant and within lattice bonds) does not contribute any metal to the plants. The results also showed that loosely bonded ions as well as sulfides bonds are the most contributor to the phytoremediation plants. Though organometallic bond of metals do contribute to the processes of phytoremediation but their share is negligible when compared with loosely bonded ions and sulfide bonds.

The results of present investigation showed that metal contents in Tehran's soil in spite of various human activities are not higher than the mean crust. However, chemical partitioning studies revealed that various percentile of Ni, Zn, Cu, Pb and Mn are found in anthropogenic portion of soils. The trend of anthropogenic share of studied metals in soils of Tehran is Zn (55 %) > Cu (31 %) > Ni and Pb (30 %) > Mn (12 %) when compared to total metal contents of the soil. The overall potential of studied plants in

**Table 7** Concentration of metals in Tehran soils after plant cultivation

Element	mg/kg ( $N = 48$ )							Anthropogenic	Lithogenic
	Mean metal contents	Metal fractions							
		1*	2*	3*	4*	5*			
Ni	67	5 (7)	2 (3)	6 (9)	52 (78)	2 (3)	13 (19)	54 (81)	
Zn	59	8 (14)	7 (11)	8 (14)	33 (57)	3 (4)	23 (39)	36 (61)	
Pb	31	5 (16)	2 (7)	0 (0)	23 (74)	1 (3)	7 (23)	24 (77)	
Cu	35	1 (3)	3 (9)	2 (5)	27 (78)	2 (5)	6 (17)	29 (83)	
Mn	542	15 (3)	5 (1)	10 (2)	504 (92)	8 (2)	30 (6)	512 (94)	

\* Step 1. Loosely bonded ions; Step 2. Sulfides bonds; Step 3. Organometallic bonds; Step 4. Most resistant bonds and Step 5. Within lattice bonds [Step 5 = Bulk metal content—(1 + 2+3 + 4)]. Also rounded-off figures within brackets show percentile of mean metal fractions, anthropogenic and lithogenic portions while compared with mean metal contents



metal removal from soil is *Salvia* > *Viola* > *Portulaca*. It should be pointed out that roots have higher potential in metal removal from soil when compared with leaf and stem. Since CEC of soil types differs from place to place and also considering the role of enzymes in the processes of CEC, we suggest further studies of present kind to better know about the role of metals associated with various soil phases in phytoremediation processes.

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