Journal of Hazardous Materials 190 (2011) 744–754

Contents lists available at ScienceDirect

Journal of Hazardous Materials

journal homepage: www.elsevier.com/locate/jhazmat

Combined mild soil washing and compost-assisted phytoremediation in treatment of silt loams contaminated with copper, nickel, and chromium

Menghau Sung[a,*], Chi-Yi Lee[b], Suen-Zone Lee[c]

[a] Department of Environmental Science and Engineering, Tunghai University, Taichung 40704, Taiwan
[b] Guan-Cheng Environ. Tech. Protection Co., Ltd., Tainan 71066, Taiwan
[c] Department of Environmental Engineering and Science, Chia-Nan University, Tainan 71710, Taiwan

ARTICLE INFO

Article history:
Received 13 October 2010
Received in revised form 13 March 2011
Accepted 30 March 2011
Available online 8 April 2011

Keywords:
Phytoremediation
Soil washing
Heavy metals
Compost
Green remediation

ABSTRACT

A new soil remediation option, combining the soil washing process using pure water followed by the compost-assisted phytoextraction, is evaluated using silt loams contaminated with plating wastewater containing Cu, Ni, and Cr. Plants utilized in this study are the rapeseeds, sunflowers, tomatoes, and soapworts. Phytoextraction operation was carried out in pot experiments over a period of 4 months. Metal concentrations in roots and shoots of plants were analyzed upon completion of each pot experiment. Hypothesis testing was employed in assessing the significance of difference in the experimental data. Results indicated that the rapeseed, a hyperaccumulator, is most effective in extracting metals from the compost-amended silt loams. The fast-growing sunflowers and tomatoes are comparable to rapeseeds in accumulating metals despite their relatively low metal concentrations in tissues. Bioaccumulation coefficients obtained for all plants are less than one, indicating that phytostabilization rather than phytoextraction is the dominant mechanism at this simulated final-phase condition.

1. Introduction

Soil contamination by heavy metals has been a serious problem worldwide. Various techniques such as excavation, solidification, stabilization, soil washing, electroremediation, and phytoremediation have been employed to mitigate the impact of heavy metals in the soil environment [1]. Among these techniques, phytoremediation, including phytostabilization and phytoextraction, is considered to be highly cost-effective and not harmful to physical, chemical, and biological characteristics of the soil. In phytoextraction, heavy metals are removed through uptake and subsequent translocation from roots to the above-ground parts of the plants [2,3]. Although phytoextraction is an attractive alternative, it still has drawbacks emerged from recent practices, including the long treatment time to achieve specific objectives [4,5] and unfavorable soil characteristics such as highly acidic soils that can limit its performance [6]. Thus, techniques to shorten the uptake time for plants, and to add amendments to parent soils with the purpose for effective plants growth have become two important tasks in optimizing phytoremediation.

In order to speed up the phytoextraction process, various chelators have been utilized in soils to assist rapid metal translocation from soil to plants [7,8]. Although non-biodegradable chelators such as EDTA (ethylenediaminetetraacetic acid) are effective in increasing phytoextraction efficiency by solubilizing heavy metals, they also cause groundwater pollution problems since the amounts of metals leached out of the root zone are much greater than ones extracted by roots [9,10]. In recent years, less effective but biodegradable chelators such as NTA (nitrilotriacetate) and EDDS (S,S-ethylenediaminedisuccinic acid) have been used as alternatives [7,11]. In addition to chelators, composts have also been added in soils to assist phytoremediation. Their effects on properties of clay soils [12–14] as well as on plants growth [15,16] have both been examined. Compost-assisted phytoextraction in contaminated soils that are inimical to vegetation such as barren soils and mine tailings has also been conducted. For instance, in mine tailings restoration it was found that when the clay loams were amended with composted biosolids, willows growing in the medium demonstrated effective phytoextraction of Mn, Cu, and Cd [17]. Composts can not only supply nutrients to plants, but also create loose and ventilated soils for plants growing in hostile soils.

Metals in soils can distribute in various chemical pools ranging from water soluble, residual, precipitated, to various recalcitrant forms that are bound to carbonate, Fe and Mn oxides, and organic matter [18]. Metals in soluble or weakly adsorbed pools are considered as having higher phytoavailability than those in strongly adsorbed or occluded forms [19]. In fact, in modeling plant uptake of metals from soils, it has normally been assumed that the roots can only absorb ions from soil solution [20]. For adsorbed or precipitated metals, they have to dissolve to the soil solution prior to

---

* Corresponding author.
E-mail address: mhsung@thu.edu.tw (M. Sung).

0304-3894/$ – see front matter © 2011 Elsevier B.V. All rights reserved.
doi:10.1016/j.jhazmat.2011.03.113

their absorption by the roots. Consequently, in an effective field phytoextraction process the plants would first absorb soluble metals initially present in soil solution, and then extract adsorbed or precipitated metals on the soil surface. At the final-phase of a typical phytoextraction operation, the root system would be in a soil environment of minimum soluble metals. The phytoextraction efficiency at this phase is important since it determines the overall duration of the process. However, our knowledge in this aspect is still lacking since most studies of phytoextraction so far focused merely on the initial stage when soluble metals were readily available.

Soil washing with various chemical solutions has been a popular and effective technique in remediation. However, a follow-up unit designed to treat the final washing solution is always necessary. When a chelator such as EDTA is employed as the washing solution, an intense treatment unit, such as the advanced oxidation process, would be required to breakdown the complex. In this study, we proposed a new green remediation option that combined the soil washing process using pure water and the phytoremediation process. The polluted soils were washed with pure water first to remove soluble metals, and were subsequently phytoremediated. Since no chelators were added, the metal-containing washing solution can be treated by a simple unit such as metal precipitation by alkalization, or by other recent green technologies such as metal sequestration with calcite [21]. The time required to complete the entire remediation is shortened compared to a standard phytoremediation process. For clayey soils that are originally not suitable for plants, natural soil amendments such as composts could be added to assist the plants growth, further making this green remediation option viable to unfavorable soils. Although this is an attractive method, the performance of metal absorption by plants under the environment of minimum soluble metals had never been evaluated.

The goal of this study is to understand the performance of the compost-assisted phytoextraction of contaminated silt loams devoid of soluble heavy metals, obtained by mild soil washing using pure water. The washed soils are assumed to represent the late-phase soil conditions in a typical phytoextraction process. Field silt loams contaminated by plating waste water are used in this investigation. Specific objectives of this study are: (1) to understand the effects of composts on phytoextraction in inimical silt loams, (2) to mimic the phytoextraction performance at the late phase of a phytoextraction process, and (3) to determine the concentration and mass of heavy metals that plants are able to accumulate during the operations. Plants tested in this study include tomatoes (*Solanum lycopersicum*), sunflowers (*Helianthus annuus*), rapeseeds (*Brassica napus*), and soapworts (*Saponaria officinalis*). The first two are frequently used as fast-growing species, the third one is a hyperaccumulator [22], and the last one is a perennial species that has not been tested for phytoextraction before.

2. Materials and methods

2.1. Soils and composts

Field soils used in this study are from a site right next to a plating plant in southern Taiwan. This site is known to contamination with Cr, Ni, and Cu, which are all ingredients used in plating. Collected soil samples were first dried in the air for two weeks, crushed, and sieved through a 2.0 mm screen to remove stones and undesirable debris. After this pretreatment procedure, the soils were put into a tank and deionized water of pH 7 was added as mild washing solution at the soil to water mass ratio of 1:100. An impeller mixer was placed in the tank to start washing soils by mixing. The washing process was completed after 24 h. Then, the soils were separated from the water, dried in the air for another two weeks, and then saved for later pot experiments. The compost was obtained using wasted tea leaves as the main carbon source and swine manure as the nitrogen source by mixing at a mass ratio of 20 to 1. The composting process was carried out in the high rate composter maintaining at 60 °C for 30 days. The mature compost had a C/N ratio close to 9. The compost was dried in air, ground, and then passed through 2.0 mm screen prior to use.

2.2. Pot experiments

Four different test soils were prepared by mixing 0%, 5%, 10%, and 15% of compost, based on dry weight, into the washed soils. The pot used in the experiments had a diameter of 8.5 cm and a height of 7.0 cm. A total of 170 g of dry test soil was used in each pot. The experiments were carried out in triplicate pots. Seeds of sunflowers, tomatoes, and rapeseeds were first cultivated in peat moss for about one to two weeks until their seedlings emerged. Then they were transferred to pots filled with test soils. As to soapworts, they did not start from seeds, but from grown ones by transferring a single root system to each test pot. All prepared pots were placed outdoors regularly, but were kept indoors on rainy days. A total of 15 rainy days was recorded during the growing period of four months. Each pot was watered three times a day with the mist sprayer. The volume sprayed was kept at minimum so as not to cause any significant infiltration. After growing for four months, the whole plant in each pot was taken out of the soil, and the root was cleaned and cut. Subsequently, both the roots and shoots were drying in a 50 °C oven for three days, weighed on the balance, and were then ground into powders for further chemical analyses. Pot experiments using uncontaminated garden soils were also conducted as controls to understand the background accumulation levels of these metals in plants.

2.3. Chemical analysis

Conventional aqua regia digestion method [23] was used to determine concentrations of heavy metals in test soils, roots, and shoots. In digestion, a well-mixed sample of 3 g was first mixed with 28 mL of aqua regia in a 250 mL beaker. Then the beaker was connected to a reflux system, which was kept at the room temperature for 16 h and then under boiling for 2 h to complete the extraction. After the digestion, the supernatant was filtered and the filtrate was analyzed by FAA spectrophotometer (Z-5300, Hitachi Co., Japan) for Cu, Ni, and Cr. For the organic matter determination using the Walkley–Black method [24], 0.5 g of the sample was mixed with 5 mL of 0.5 N $K_2Cr_2O_7$ plus 5 mL of concentrated H_2SO_4 in a 250 mL beaker for oxidation. The concentration of organic matter was then determined by back titration of the remaining $K_2Cr_2O_7$ with 0.5 N ferrous sulphate. The cation exchange capacity (CEC) was determined by the standardized method of extraction with ammonium acetate [25]. The total nitrogen was determined by the Kjeldahl method [26]. The available phosphate and potassium were determined by the colorimetric method [27] and the FAA spectrophotometer [28], respectively. Extractants used for phosphate and potassium were concentrated H_2SO_4 and Bray's reagent, respectively.

2.4. Statistical analysis

Once the means as well as standard deviations of metal concentrations accumulated in plants from the aforesaid triplicates were obtained, the inter-species and intra-species difference between two selected means was statistically assessed. The two-sample *t*-test for independent samples was used for the hypothesis testing. Prior to performing the *t*-test, the equality of the two variances was assessed by the *F*-test. If the two variances were equal, the *t*-test scheme with equal variances would be employed; otherwise the scheme with unequal variances would be adopted. In *t*-test, we test the hypothesis H_0: $\Delta = 0$ versus H_1: $\Delta \neq 0$, where Δ represents the difference between two means. For a selected type of plant, the *t*-test was first conducted between a control pot and a pot with a specific content of compost. Then, the test was continued between other selected pairs until all possible pairs of comparisons were made. Since there were three different compost contents (i.e., 5%, 10%, and 15%), the entire intra-species comparisons would include: (i) control vs. 5%, (ii) control vs. 10%, (iii) control vs. 15%, (iv) 5% vs. 10%, (v) 5% vs. 15%, and (vi) 10% vs. 15%. These six comparisons were carried out for three different metals and four different plant species. For inter-species comparisons, different types of plants growing in identical soil conditions were compared. All of the hypothesis testing was performed using the OriginPro 8 software (OriginLab Corp., USA).

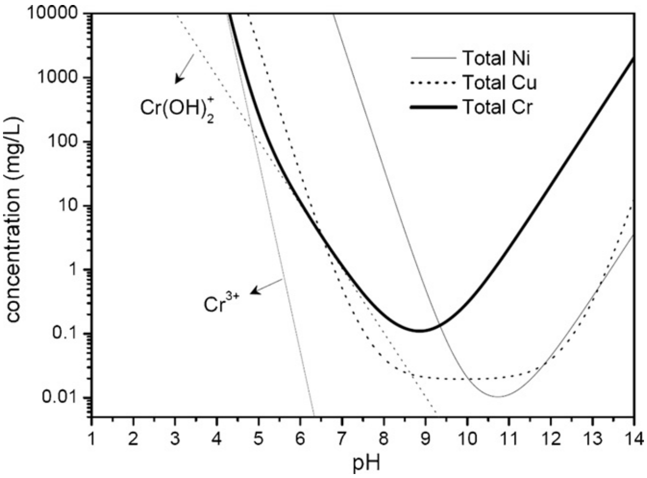

Fig. 1. Solubility plot of Cu, Ni, and Cr as a function of pH. Concentrations of two Cr species (Cr^{3+} and $Cr(OH)_2{}^+$) are also shown.

3. Results and discussion

3.1. Test soil properties

Table 1 shows results of physical and chemical properties of the control, original, washed, and test soils, plus the pure compost. It is seen that the original soils contained 2% clay, 64% silt, and 34% sand. Their texture thus belongs to silt loam. They are severely contaminated with heavy metals of Cu (783 mg/kg), Cr (2033 mg/kg), and Ni (626 mg/kg). The soils also have low nutrient contents of available phosphorous (14 mg/kg) and potassium (106 mg/kg). After soil washing using pure water, readily soluble metals are removed and concentrations of Cu, Cr, and Ni remained in the soils are 467, 2009, and 383 mg/kg, respectively. It is evident that there is a high removal efficiency of approximately 40% for Cu and Ni, but nearly none removal of Cr, by mild soil washing. It is also seen in Table 1 that the garden soils used for controls also contain these three heavy metals. But their concentrations are all within the reasonable ranges of uncontaminated soils since average Cu, Cr, and Ni concentrations in natural soils are 30, 100, and 40 mg/kg, respectively [29]. As to the compost, it contains a relatively high amount of Cu when compared with the control/garden soils, whereas the Ni and Cr contents are much lower. Since the concentrations of Cu, Ni, and Cr in tea leaves are generally in the μg/kg range [30], most of these metals are assumed to come from the manure. The Cu content found in some poultry manure could be as high as 300 mg/kg [31], which supports our assumption for the origin of metals in compost. The contribution of metals from the compost in test soils can be calculated using data in Table 1. For Cu under the 15% of compost addition, less than 1% of Cu in test soils comes from the compost. Thus, it is safe to neglect the contribution of metals from the compost in various test soils. Moreover, it should be noted that the original silt loams are acidic (pH 3.6). After soil washing, their pH increases to about 5.1. The addition of compost, having a pH of 7.1, further brings alkalinity to the final test soils to raise the pH values to between 5.4 and 6 as shown in Table 1. The effects of pH are twofold. In one part, plants can only grow healthy in their optimal pH range. In the other part, soil pH can affect species of metals available for extraction. The addition of compost also adds potassium, phosphorous, and nitrogen to the soils, which are all essential nutrients for plants.

Although the total metal contents of Cu, Ni, and Cr in the washed soils are determined, their speciation still needs to be elucidated. For Cu and Ni, they are quite stable in the forms of Cu^{2+} and Ni^{2+} under normal soil conditions. However, for Cr it could exist in both trivalent, Cr(III), and hexavalent, Cr(VI), forms. In an oxidizing environment, Cr(VI) occurs as dichromate ($Cr_2O_7{}^{2-}$) and $HCrO_4{}^-$ when pH > 5.8, and as chromate ($CrO_4{}^{2-}$) in neutral or alkaline solutions. Cr(VI) is more mobile than Cr(III) since it is much more soluble than Cr(III) and is often repelled by negatively charged soil particles [32]. Consequently, the slight removal of Cr from soil washing implies that most of the Cr is in the Cr(III) oxidation state. The removal by washing could become much higher if it is in the Cr(VI) state. A solubility plot (Fig. 1) considering Cu^{2+}, Ni^{2+}, Cr^{3+}, plus their hydroxide complexes (e.g., Cu^{2+}, $CuOH^+$, $Cu(OH)_2{}^0$, $Cu(OH)_3{}^-$, $Cu(OH)_4{}^{2-}$, Ni^{2+}, $NiOH^+$, $Ni(OH)_2{}^0$, $Ni(OH)_3{}^-$, Cr^{3+}, $CrOH^{2+}$, $Cr(OH)_2{}^+$, $Cr(OH)_3{}^0$, and $Cr(OH)_4{}^-$) and precipitates (e.g., $Cu(OH)_{2(s)}$, $Ni(OH)_{2(s)}$, and $Cr(OH)_{3(s)}$) was constructed using stability constants of Cu and Ni from Martell's handbook [33] and Cr from the literature [34]. As shown in Fig. 1, when the pH is between 5 and 6 it is evident that Ni is very soluble, concentrations of its hydroxide complexes are extremely low, and the dominant species is Ni^{2+}. As to Cu and Cr, they are much less soluble than Ni. At the pH of 5.5, the solubility of Cu is around 400 mg/L, and that of Cr is about 40 mg/L. Using the above data of Cu (467 mg/kg) and Cr (2009 mg/kg) concentrations in the washed soils and assuming a hypothetical water content of 10% (w/w) in soils when they are used in growing plants, we estimate concentrations of Cu and Cr in the soil solution to be 4670 mg/L and 20,090 mg/L, respectively, if they are all in the soluble forms. These estimates are significantly higher than the calculated solubility. Therefore, Cu and Cr in the silt loams would exist mainly as their precipitates (i.e., $Cu(OH)_{2(s)}$ and $Cr(OH)_{3(s)}$), and their maximum soluble concentrations would be their solubility as indicated above. For Cu, the dominant species in the soluble form is still Cu^{2+} between pH 5 and 6. As to Cr, the dominant species in this pH range include Cr^{3+} and $Cr(OH)_2{}^+$, whose pH dependent distribution is also shown as light dashed lines in Fig. 1. In fact, pH 5 is the border line for these two species. When pH is greater than 5, $Cr(OH)_2{}^+$ is the most important soluble species of Cr.

Although a rigorous sequential extraction procedure was not carried out, the soil pools these metal ions are associated with could still be inferred. With respect to Ni, suppose 383 mg/kg of Ni in the washed silt loams are all in the form of soluble Ni^{2+}. It is equal to a concentration of 38.3 mg/100 g or 1.07 meq/100 g by dividing the molecular weight of Ni (58.7 g/mol) and multiplying its equivalence (2 eq/mol). It is evident that the CEC of the washed silt loams, which is 10.1 meq/100 g, is much greater than the Ni^{2+} concentration of 1.07 meq/100 g. Thus, the potential for Ni^{2+} to constitute parts of the CEC is high. In other words, Ni^{2+} in the silt loams can be reasonably assumed to be in the exchangeable form. As to Cu and Cr, after completing calculations analogous to Ni just above by using the previously simulated soluble concentrations (i.e., 400 mg/L for Cu

Table 1
Physical and chemical properties of the control, original, washed, and test soils used in this study.

Parameter	Control soil	Original soil	Washed soil	COM[a]	5% COM[a]	10% COM[a]	15% COM[a]
Clay (<0.002 mm), %	7	2	1	–	–	–	–
Silt (0.002–0.05 mm), %	42	64	58	–	–	–	–
Sand (0.05–2 mm), %	51	34	41	–	–	–	–
CEC, meq/100 g	11.3	12.4	10.1	229	17.4	25.9	63.1
pH (H_2O)	8.4	3.59	5.13	7.1	5.67	5.42	5.95
Total N, %	0.137	0.164	0.055	3	0.232	0.382	0.538
Available P, mg/kg	24.9	13.9	10.2	410	24.9	55.2	78.2
Available K, mg/kg	34.3	106	107	10,223	709	1129	1320
C/N ratio	–	–	–	9	–	–	–
Total Cu, mg/kg	10.9	783	467	23.4	445	438	419
Total Cr, mg/kg	24.4	2033	2009	6.56	1980	1953	1929
Total Ni, mg/kg	22.3	626	383	6.47	346	327	295
Organic matter, %	0.875	0.174	0.40	94	3.43	5.31	9.21

[a] COM stands for compost.

and 40 mg/L for Cr), their equivalent concentrations in the silt loams become 1.26 meq/100 g and 0.23 meq/100 g, respectively. Both of these are also much less than the CEC value, suggesting that soluble Cu and Cr ions could also be in the exchangeable forms.

Preliminary pot experiments using the washed silt loam alone (i.e., 0% of compost addition) to grow sunflowers, tomatoes, soapworts, and rapeseeds all failed after two weeks of trial test. These plants withered and died mainly as a result of improper medium, characterized by water-logged and low-ventilation conditions. After the washed silt loam was amended with 5%, 10%, and 15% (w/w) of compost to form the test soils, plants growing in them were all healthy over the two weeks of trial test. These recipes were then employed in the following long-term pot experiments. Table 2 shows the final dried biomass of each plant after harvesting. In general, plants are able to produce higher biomass under higher compost ratios. For the rapeseeds, they produce a larger biomass when growing in compost-amended soils than in the control soils. The sunflowers produce a comparable mass as the control under the highest compost ratio of 15%. As to tomatoes and soapworts, the biomass they produce in compost-amended soils is much less than the control soils. The production of less biomass when growing in the test soils implies that metal toxins have some effects on the growth of these three plants (i.e., sunflowers, tomatoes, and soapworts). The rapeseeds, a hyperaccumulator, are the only one that can withstand the toxins during growth. In fact, compost amendments are effective measures of soil modification by creating a ventilated soil structure, raising the pH values, and supplying additional nutrients, which are all critical to plants growth. Although the growth of plants in terms of biomass behaved differently, compost-amended soils are able to sustain plants growth so that they could extract or stabilize contaminants.

3.2. Heavy metal concentrations in plant tissues

Figs. 2–4 show the concentrations of Cu, Ni, and Cr, respectively, accumulated in the entire plant tissues, including shoots and roots, of four different plants growing in the controlled soils, i.e., soils free of contaminants, and in three test soils after four months. Data in these figures are the mean value of triplicates, shown together with their standard errors as error bars. In general, plants in compost-amended soils can accumulate higher concentrations of metals than plants in the control soils, an indication that phytoextraction is working to some degrees. The ranges of total metals in these four different plants are: (i) 15–60 mg/kg for Cu, (ii) 25–90 mg/kg for Ni, and (iii) 25–150 mg/kg for Cr. From Table 1, it is seen that both the CEC and the organic matter increase in the test soils after adding the compost. A higher CEC could lead more metal ions to be in the exchangeable sites. A higher organic matter content essentially adds more ligands to form metal complexes. Both of these two effects have the potential to promote the dissolution of metal hydroxide precipitates.

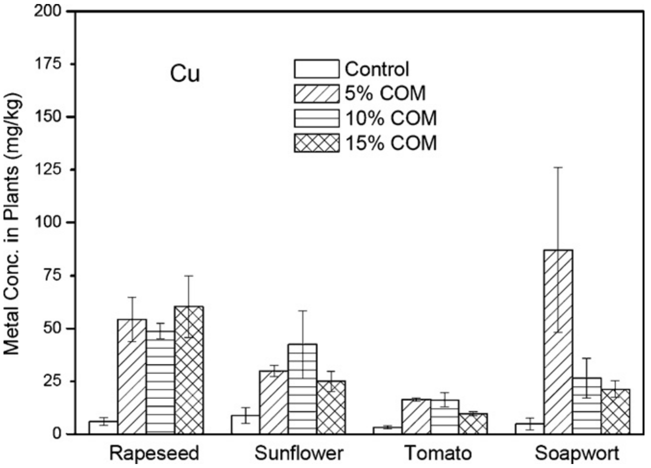

Fig. 2. Cu concentrations (mg/kg) measured in the tissues (roots and shoots) of four different types of plants growing in uncontaminated controlled soils and in three compost-amended silt loams in triplicate pots. The growing times for each plant are shown in Table 2.

The higher mean concentration of Cr in plants implies that Cr is extracted more efficiently than the other two metals. Several reasons contribute to Cr's high extraction efficiency. First, due to the relatively high charge state of Cr^{3+}, once they are in the

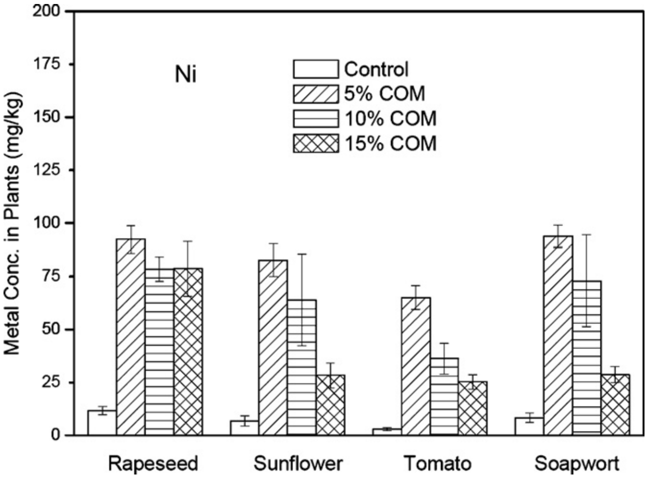

Fig. 3. Ni concentrations (mg/kg) measured in the tissues of four different types of plants growing under various conditions.

Table 2
Average biomass of plants and percentage of metals accumulated in roots and shoots of plants under various soil conditions.

		Biomass (g)[a]	Cu		Ni		Cr	
			Root	Shoot	Root	Shoot	Root	Shoot
Rapeseed (162 days)	Control	0.55	45	55	37	63	0	0
	0% Compost	0	0	0	0	0	0	0
	5% Compost	1.07	80	20	56	44	87	13
	10% Compost	1.26	75	25	50	50	100	0
	15% Compost	1.14	74	26	55	45	91	9
Sunflower (120 days)	Control	2.40	25	75	31	69	0	0
	0% Compost	0	0	0	0	0	0	0
	5% Compost	1.02	96	4	71	29	100	0
	10% Compost	2.17	84	16	64	36	100	0
	15% Compost	2.20	84	16	48	52	100	0
Tomato (150 days)	Control	4.68 (97 days)	37	63	30	70	0	0
	0% Compost	0	0	0	0	0	0	0
	5% Compost	1.92	79	21	44	56	96	4
	10% Compost	3.13	81	19	38	62	100	0
	15% Compost	3.20	72	28	43	57	100	0
Soapwort (102 days)	Control	2.41 (138 days)	90	10	75	25	0	0
	0% Compost	0	0	0	0	0	0	0
	5% Compost	0.53	91	9	69	31	85	15
	10% Compost	1.27	93	7	77	23	100	0
	15% Compost	1.52	84	16	70	30	98	2

[a] This is the averaged dry mass of a whole plant, including its root and shoot, after growing for a specific period of time, which is indicated in the parenthesis of the first column unless specified together with the biomass itself.

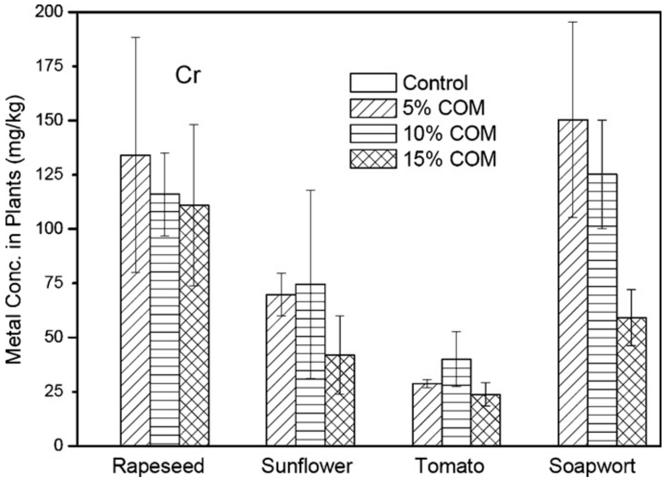

Fig. 4. Cr concentrations (mg/kg) measured in the tissues of four different types of plants growing in various conditions.

exchangeable sites it is not easy to remove them by mild soil washing. As seen in Table 1, the soil washing process removes about 18% of CEC from the original contaminated soils. The other 82% of ions retained are those strongly adsorbed, and the Cr^{3+} ions could occupy a significant portion of them. The second reason is that some Cr(III) could be oxidized by oxygen or Mn oxide in soils to become Cr(VI), which is much more soluble. It has been found that with the presence of a high concentration of K in soils, the Cr uptake for plants can be promoted significantly [35]. This is mainly because the K salts of Cr(VI) have a very high solubility. As shown in Table 1 that the K contents in soils increase drastically as a result of compost addition, these K ions can effectively promote the dissolution of Cr(VI) so that they become extractable. Additionally, it is also observed that data for Cr generally have higher standard errors than Cu and Ni. This is probably because the Cr uptake is complicated by aforesaid dissolution mechanisms, which create more uncertainties. For Ni and Cu, they have more soluble ions ready for uptake by plants. Thus, the dissolution mechanism is not critical and less uncertainty is involved. This is why smaller error bars are found for the data of Ni and Cu.

3.3. *Statistical assessments*

Tables 3–5 compile, in matrix form, the results of hypothesis testing for Cu, Ni, and Cr, respectively. Each value in the table represents the comparison between a specific experimental condition in the column and in the row. Both the *t*-value as well as the *p*-value (in parenthesis) are listed in the tables. For example, the value for the first column (i.e., RC) and first row (i.e., R5) in Table 3 is the testing between the rapeseed in the control soils and the rapeseed in contaminated silt loams amended with 5% compost. The *p*-value is the probability to accept the null hypothesis (i.e., two means are equal or $\Delta = 0$). Thus, a high *p*-value suggests the acceptance of the null hypothesis, meaning the two means are equal. On the other hand, a low *p*-value suggests the rejection of the null hypothesis, and implies that the two means are significantly different. In the following assessments, *p*-values of 0.9 and 0.1 are used as the basis for acceptance and rejection of the null hypothesis, respectively.

3.3.1. *Test soils vs. control soils*

As mentioned above from Figs. 2–4 that plants grown in various compost-amended soils are able to accumulate a higher metal concentrations in tissues than plants grown in control soils, this point is further confirmed by the hypothesis testing. In Table 3 for the metal of Cu, its concentration in rapeseeds grown in control soil (i.e., RC) is significantly lower than in test soils with three different compost additions (i.e., R5, R10, and R15) since all of the *p*-values are much smaller than 0.1. Such trends are generally true for the other three types of plants. However, it should be pointed out that the *p*-values for some conditions (i.e., SFC vs. SF10, and SW5 vs. SWC) are slightly greater than 0.1.

3.3.2. *Intra-species comparisons*

From Table 3 and Fig. 2 for Cu, it is seen that there is no significance for the following comparisons in the rapeseeds' group: R10 vs. R5, R15 vs. R5, and R15 vs. R10. In analogous comparisons for the sunflowers (SF) and soapworts (SW), there is also no significance. But for tomatoes (T), the following results are valid: T5 = T10, and

Table 3
Statistical t-values and the corresponding p-values (in parentheses) from hypothesis testing between various pairs of data in Fig. 2 (Cu concentrations in plants).

	Rapeseed				Sunflower				Tomato				Soapwort			
	RC	R5	R10	R15	SFC	SF5	SF10	SF15	TC	T5	T10	T15	SWC	SW5	SW10	SW15
R5	−4.54 (0.09)[c]		0.49 (0.649)	−0.34 (0.754)												
R10	−11.37 (3.4e−4)[c]			−0.767 (0.486)												
R15	−3.719 (0.021)[c]															
SF5		2.236 (0.089)[c]			−6.136 (3.6e−3)[c]		0.77 (0.484)	−0.892 (0.423)								
SF10			0.387 (0.718)		−2.069 (0.107)[c]			−1.039 (0.357)								
SF15				2.302 (0.083)[c]	−3.071 (0.037)[c]											
T5		2.77 (0.069)[c]				3.83 (0.031)[c]			−16.53 (4.8e−4)[c]		0.0458 (0.966)[d]	−4.94 (0.039)[c]				
T10			6.65 (2.7e−3)[c]				1.595 (0.186)		−3.94 (0.017)[c]			−1.52 (0.226)				
T15				2.69 (0.075)[c]				2.45 (0.091)[c]	−6.899 (0.006)[c]							
SW5		−0.817 (0.459)				−1.473 (0.2146)				−1.41 (0.252)			−2.122 (0.101)[c]		−1.517 (0.204)	−1.69 (0.166)
SW10			2.21 (0.092)[c]				0.849 (0.4436)				−1.043 (0.356)		−2.295 (0.083)[c]			−0.529 (0.625)
SW15				2.59 (0.061)[c]				0.603 (0.579)				−2.25 (0.109)[c]	−3.872 (0.018)[c]			

Note: R = rapeseed; SF = sunflower; T = tomato; SW= soapwort; C = control; the number following the plant abbreviation represents the compost content.

[c] Two means are significantly different.

[d] Two means are the same.

Table 4

Statistical t-values and the corresponding p-values (in parentheses) from hypothesis testing between various pairs of data in Fig. 3 (Ni concentrations in plants).

	Rapeseed				Sunflower				Tomato				Soapwort			
	RC	R5	R10	R15	SFC	SF5	SF10	SF15	TC	T5	T10	T15	SWC	SW5	SW10	SW15
R5	−12.27 (2.5e−4)[c]		−1.605 (0.184)	−0.948 (0.397)												
R10	−11.187 (3.6e−4)[c]			−0.0197 (0.9852)												
R15	−5.157 (6.7e−3)[c]															
SF5		0.9736 (0.3854)			−9.741 (6.2e−4)[c]		−0.817 (0.459)	−5.603 (4.9e−3)[c]								
SF10			0.648 (0.552)		−2.656 (0.056)[c]			−1.597 (0.185)								
SF15				3.539 (0.024)[c]	−3.557 (0.024)[c]											
T5		2.79 (0.068)[c]				1.579 (0.2124)			−12.153 (1.2e−3)[c]		−2.707 (0.073)[c]	−5.932 (9.6e−3)[c]				
T10			4.53 (0.011)[c]				1.225 (0.287)		−4.579 (0.010)[c]			−1.36 (0.245)				
T15				3.996 (0.016)[c]				0.453 (0.674)	−6.58 (2.7e−3)[c]							
SW5		−0.173 (0.871)				−1.205 (0.2946)				−3.388 (0.043)[c]			−15.76 (9.5e−5)[c]		−0.942 (0.399)	−10.08 (5.4e−4)[c]
SW10			0.245 (0.818)				−0.294 (0.783)				−1.614 (0.182)		−2.989 (0.040)[c]			−2.021 (0.1133)
SW15				3.716 (0.021)[c]				−0.043 (0.968)[d]				−0.672 (0.539)	−5.139 (6.8e−3)[c]			

Note: R = rapeseed; SF = sunflower; T = tomato; SW= soapwort; C = control; the number following the plant abbreviation represents the compost content.

[c] Two means are significantly different.

[d] Two means are the same.

Table 5

Statistical t-values and the corresponding p-values (in parentheses) from hypothesis testing between various pairs of data in Fig. 4 (Cr concentrations in plants).

	Rapeseed				Sunflower				Tomato				Soapwort			
	RC	R5	R10	R15	SFC	SF5	SF10	SF15	TC	T5	T10	T15	SWC	SW5	SW10	SW15
R5	(−)[c]		−0.315 (0.768)	−0.351 (0.742)												
R10	(−)[c]			−0.1197 (0.911)[d]												
R15	(−)[c]															
SF5		1.168 (0.307)			(−)[c]		−0.105 (0.921)	−1.354 (0.247)								
SF10			0.877 (0.43)		(−)[c]			−0.693 (0.527)								
SF15				1.67 (0.171)	(−)[c]											
T5		1.51 (0.229)				3.22 (0.049)[c]			(−)[c]		0.688 (0.541)	−0.71 (0.529)				
T10			3.313 (0.036)[c]				0.763 (0.488)		(−)[c]			−1.188 (0.30)				
T15				2.317 (0.081)[c]				0.966 (0.389)	(−)[c]							
SW5		−0.23 (0.829)				−1.749 (0.155)				−2.092 (0.128)			(−)[c]		−0.488 (0.651)	−1.947 (0.123)
SW10			−0.293 (0.784)				−1.015 (0.367)				−3.04 (0.038)[c]		(−)[c]			−2.349 (0.079)[c]
SW15				1.314 (0.259)				−0.775 (0.481)				−2.541 (0.064)[c]	(−)[c]			

Note: R = rapeseed; SF = sunflower; T = tomato; SW= soapwort; C = control; the number following the plant abbreviation represents the compost content.

[c] Two means are significantly different; some t- and p-values are unavailable due to the occurrence of zero concentrations in the controls.

[d] Two means are the same.

T5 > T15. Also, from Table 4 and Fig. 3 for Ni, it is observed that R15 = R10, SF5 > SF15, T5 > T10, T5 > T15, and SW5 > SW15; from data in Table 5 and Fig. 4 for Cr, it is observed that R15 = R10, SF10 = SF5, and SW5 > SW10. A common trend found in the above series of comparisons is that plants quite often can have the highest metal concentrations in their tissues when growing under the lowest compost ratio (i.e., 5%). Due to the effect of dilution, the soil metal concentration decreases when the compost ratio in the test soil increases as shown earlier in Table 1. On the contrary, the nutritional level as well as the degree of metal dissolution increases as the compost ratio increases. Thus, plants growing in the soil with a low compost ratio are, in fact, exposed to an environment of relatively high total metal concentration, low nutritional level, and low degree of dissolution. Presumably, plants would accumulate more metals in a soil with a high metal concentrations, high nutrition level, and high degree of dissolution. However, when the compost is added to a soil, the nutritional level and degree of dissolution is raised but the metal concentration in the soil is inevitably diluted. Consequently, these pertinent factors have opposite effects on the performance of metal uptake. As seen above that several plants have the highest uptake under the lowest compost ratio of 5%, this suggests that the soil metal concentration in these groups is the controlling factor. In other words, the minimum compost ratio of 5% is enough to improve the soil structure, to provide enough nutrition, and to solubilise metal precipitates, so that plants can perform effective extraction. Any more addition of the compost only further dilutes the metal concentration in the soils, resulting in less effective extraction. This is particularly true for Ni since except for the rapeseeds all other three plants reach their highest concentrations at the 5% compost ratio (Fig. 3 and Table 4).

3.3.3. *Inter-species comparisons for Cu*

With respect to Cu, the following inter-species comparisons for the rapeseeds are of significance: R5 > SF5, R15 > SF15, R5 > T5, R10 > T10, R15 > T15, R10 > SW10, and R15 > SW15. Thus, rapeseeds generally have better performance over the other three plants. As to the sunflowers, the only two comparisons that are of significance are: SF5 > T5, and SF15 > T15. The *p*-value for the comparison between SF10 and T10 is 0.186 (Table 3), a little greater than the critical value of 0.1. Thus, in most conditions sunflowers outperform the tomatoes. Finally, it is significant that SW15 > T15. Consequently, for all plants under the 15% compost addition, the tomatoes have the lowest Cu concentrations.

3.3.4. *Inter-species comparisons for Ni*

From Table 4, it is seen that the rapeseeds at a 15% compost ratio outperform the other three plants at the same ratio: R15 > SF15, R15 > T15, and R15 > SW15. Therefore, if the compost is added at the highest ratio, the rapeseeds are the most favourable plant with respect to Ni uptake. On the other hand, at the lowest ratio of 5%, soapworts have a significantly higher Ni concentration than the tomatoes (i.e., SW5 > T5), which have fast-growing characteristics. In fact, at the ratio of 5% and 10% the *p*-values found for the null hypothesis are 0.871 and 0.818, respectively, which are both close to the critical value of 0.9. Consequently, at these low and middle ratios (i.e., 5% and 10%) soapworts are as effective as the rapeseeds, which is a hyperaccumulator. However, soapworts are not that competitive as the Ni concentration in soils drops since R15 > SW15 as described above.

3.3.5. *Inter-species comparisons for Cr*

From Table 5 with respect to Cr, the following comparisons are valid for the rapeseeds: R10 > T10, and R15 > T15. Meanwhile, the *p*-values to accept the equality of Cr concentrations in soapworts and rapeseeds at the ratio of 5% and 10% are 0.829 and 0.784, respectively, which are close to 0.9. This behaviour is very close to that for the Ni uptake observed above. Thus, the soapworts also have the potential to compete with rapeseeds in the uptake of Cr. Moreover, at the 10% and 15% ratios, soapworts have significantly higher Cr concentrations than tomatoes (i.e., SW10 > T10, and SW15 > T15).

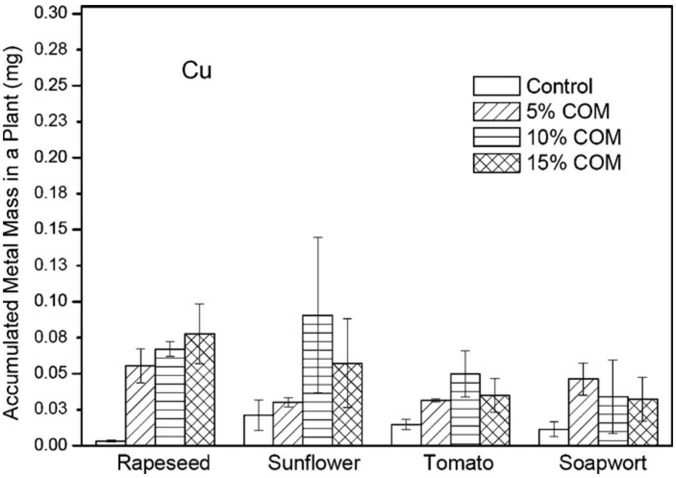

Fig. 5. Average mass (mg) of Cu extracted by various plants in a pot.

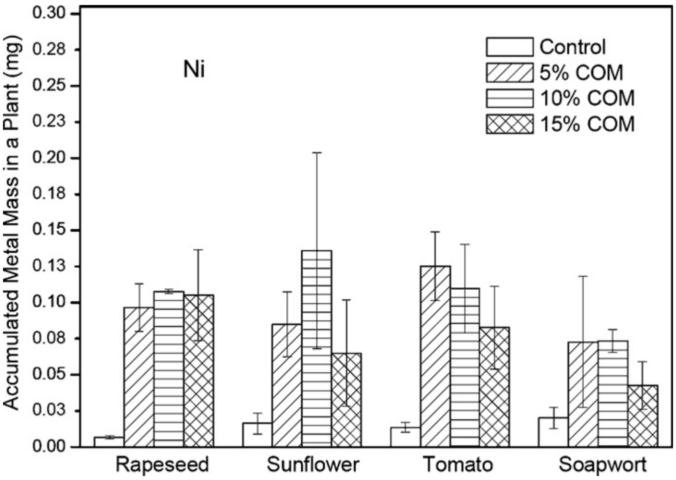

Fig. 6. Average mass (mg) of Ni extracted by various plants in a pot.

3.4. *Mass of heavy metals in plants*

As mentioned in the experimental section, the plant tissue weight is also an item we recorded for each sample during experiment. Thus, the total mass of each metal that each plant is able to accumulate can be calculated. Figs. 5–7 show results of the final mass of Cu, Ni, and Cr, expressed as mg per pot, in an entire plant. Unlike data for metal concentrations in plants (Figs. 2–4), standard errors in these figures are large. This is primarily because plants produce different body weights during growth. This adds more uncertainty to these data and generates large standard errors. A rule of thumb in estimating statistical significance is to check the gap between the top and the bottom of two error bars. If the gap equals two times the means of two error bars, the *p*-value is approximately 0.05 in the case of triplicates [36]. Using this method as a quick check, we find that most comparisons in these data are of low significance. Thus, the rigorous hypothesis testing is not conducted on these data.

Recall from the inter-species comparisons that the rapeseeds generally are able to accumulate a higher Cu concentration in their

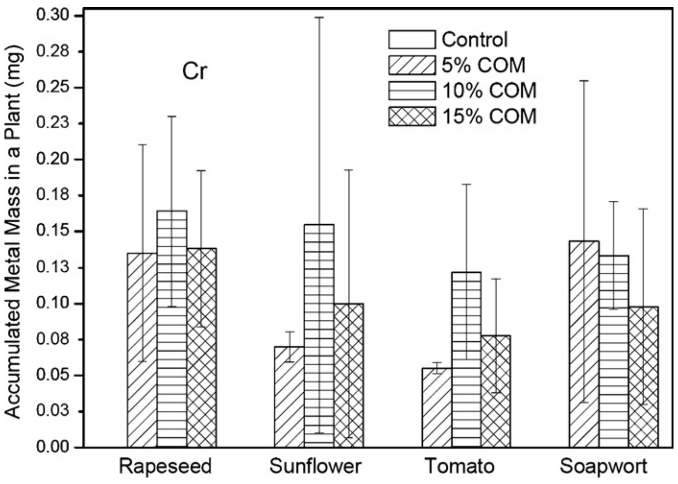

Fig. 7. Average mass (mg) of Cr extracted by various plants in a pot.

tissues than the tomatoes and sunflowers. But such advantage of the rapeseeds no longer exists when the total mass of accumulation is used as the basis of comparison as shown in Fig. 5. This trend is also valid for Ni, and some cases of Cr. The major difference, in terms of metal extraction behaviour, between rapeseeds and the other two plants (i.e., tomatoes and sunflowers) is that rapeseeds are a type of hyperaccumulator, whereas tomatoes and sunflowers are both fast-growing species. Thus, fast-growing plant species do have the capability to increase their biomass fast enough to extract a comparable amount of metals that a hyperaccumulator can extract despite their lower metal concentrations in the tissues. As to the soapworts, although their extraction capability, in terms of plant tissue concentration, is comparable to the hyperaccumulator (i.e., rapeseeds) with respect to Ni and Cr (Figs. 3 and 4), the overall masses of Cr accumulation fall to the same range of the other three plant species. As to the mass of Ni, its mean value is generally lower than the other three plants. This low accumulation by soapworts is mainly due to their slow growth behaviours. Although this is a drawback of soapwort, it should be reminded that it is a perennial plant and is capable of performing the long-term phytoextraction operation.

3.5. Distribution of heavy metals in plants

Whether accumulated metals are translocated to the shoots or remained in the roots of the plants is also a subject of importance. Table 2 shows the average percentage of distribution of various metals in the shoots and roots of four plants growing in the compost-amended soils. From observing data in Table 2, it is evident that the percentage of metals accumulated in the roots is highly dependent on both metal and plant species. The empirical metal order of Cr > Cu > Ni in the roots can be generalized. In the phytoextraction of Cr, over 95% of the metal is concentrated in the roots for nearly all conditions. Seven of these samples even have accumulated all of the Cr in their roots, as shown in the columns for Cr in Table 2. Among them, five samples are from the sunflowers and tomatoes, which are both fast growing plant species. In the phytoextraction of Cu, most root accumulations are over 80%. Rapeseeds and tomatoes demonstrate relatively lower Cu accumulation in the roots than sunflowers and soapworts. As to Ni, a significantly higher shoot accumulation is observed compared to Cr and Cu for most plants. For example, Ni distributions in the shoots for the rapeseeds and tomatoes are approximately 50% and 40%, respectively. For sunflowers, the percentage of Ni in the shoots essentially increased from 30% at the 5% compost ratio to about 50% at the 15% compost ratio. Thus, metal contents in plant shoots have a strong dependence on the compost ratio. The high nutritional level under a high compost ratio condition could stimulate more metal distribution in the shoots.

Table 6
Bioaccumulation coefficients of Cu, Ni, and Cr for four plant species under various compost contents.

	Compost content	Cu	Ni	Cr
Rapeseed	5%	0.12	0.27	0.068
	10%	0.11	0.24	0.059
	15%	0.14	0.27	0.058
Sunflower	5%	0.067	0.24	0.035
	10%	0.097	0.20	0.038
	15%	0.060	0.096	0.022
Tomato	5%	0.037	0.19	0.015
	10%	0.037	0.11	0.021
	15%	0.026	0.086	0.012
Soapwort	5%	0.030	0.27	0.076
	10%	0.061	0.22	0.064
	15%	0.051	0.097	0.031

As mentioned earlier, the fast growing species (i.e., sunflowers and tomatoes), could be as competitive as the hyperaccumulator (i.e., rapeseeds) in terms of the extraction of the mass of heavy metals. However, in field operations, the heavy metal content in the shoots is an important parameter to consider as well since shoots but not roots are to be harvested after a crop cycle. Thus, the competitiveness of the sunflowers becomes lowered since heavy metals in their shoots are relatively low. On the contrary, the competitiveness of the tomatoes is raised as a result of its capability to extract more heavy metals to the shoots. Between the two fast growing species, tomatoes would have better performance than sunflowers in field operations. Undoubtedly, the rapeseeds still outperform other types of plants after taking into accounts of all pertinent factors.

3.6. Bioaccumulation coefficients

The bioaccumulation coefficient is defined as the ratio of the heavy metal concentration in the plant tissues to the heavy metal concentration in the soil medium. Table 6 shows the bioaccumulation coefficients of Cu, Ni, and Cr for four plant species under various compost contents. All these coefficients are less than one, implying a very low efficiency of phytoextraction. In fact, all of the coefficients for Cr are even lower than 0.1 despite of the relatively high uptake of around 100 mg/kg in some plants. In addition, from Table 6 it is evident that the rapeseeds, a known hyperaccumulator, have larger bioaccumulation coefficients for all metals under various compost contents than other plants. These low bioaccumulation coefficients observed characterize the final phase of a phytoremediation process. Although phytoextraction at this phase is still active, the amount of metals plants can extract is relatively low. Consequently, the process that has become more important at this phase is phytostabilization rather than phytoextraction.

4. Conclusions

Compost amendments are found to be effective in assisting the growth of rapeseeds, sunflowers, tomatoes, and soapworts in silt loams, and in performing the phytoextraction of Cu, Ni, and Cr from water-washed silt loams that are initially too hostile for plants to grow. The addition of composts has the advantages in creating a better soil structure, raising the pH, solubilising metal precipitates, and supplying nutrients so that plants could start growing and extracting heavy metals. All of the four plants we tested are able to accumulate three heavy metals to various degrees beyond their background levels. From intra-species comparisons, it is found that the 5% compost ratio is the most favourable condition to accumulate a high metal concentration in plants. In addition, from inter-species comparisons, it is found that the rapeseeds outperform most other plants in maintaining high metal concentrations in tissues, and soapworts, which have not been tested before, can be as effective as the rapeseeds. When the total mass of metals in plants is compared, it is found that the two fast-growing plants we tested (i.e., sunflowers and tomatoes) are as competitive as the hyperaccumulator (i.e., rapeseeds). During field operations when the heavy metal contents in the shoots are of importance, tomatoes are more prominent than the sunflowers since they are able to translocate more metals to the shoots. Moreover, the relatively small bioaccumulation coefficients obtained from this simulated late-phase phytoremediation test suggest that phytostabilization rather than phytoextraction is more important. In summary, washing contaminated silt loams with pure water removes most soluble metals and quickly transformed soils into a late-phase condition of a typical phytoremediation process so that the treatment time was significantly shortened. In future field operations, other environmentally benign treatment processes for the waste solution, generated from mild soil washing, can be incorporated.

Acknowledgments

This study was partially funded by the National Science Council of Taiwan (Grant no. 96-2221-E-041-005). The authors would like to thank Mr. Chan-Ruey Chou from the environmental laboratory of the Taiwan Sugar Company for his assistance in chemical analysis, Prof. Li-Juie Tsai from the Chia Nan University for supplying the compost, and anomalous reviewers for their valuable suggestions and comments.

References

[1] C.N. Mulligan, R.N. Yong, B.F. Gibbs, Remediation technologies for metal-contaminated soils and groundwater: an evaluation, Eng. Geol. 60 (2001) 193–207.
[2] M. Barbafieri, The importance of nickel phytoavailable chemical species characterization in soil for phytoremediation applicability, Int. J. Phytoremediat. 2 (2000) 105–115.
[3] B.E. Pivetz, Phytoremediation of contaminated soil and ground water at hazardous sites, in: Ground Water Issue, Environmental Protection Agency, EPA/540/S-01/500, Washington, DC, 2001.
[4] J. Japenga, G.F. Koopmans, J. Song, P. Romkens, A feasibility test to estimate the duration of phytoextraction of heavy metals from polluted soils, Int. J. Phytoremediat. 9 (2007) 115–132.
[5] G.F. Koopmans, P. Romkens, J. Song, E.J.M. Temminghoff, J. Japenga, Predicting the phytoextraction duration to remediate heavy metal contaminated soils, Water Air Soil Pollut. 181 (2007) 355–371.
[6] F. Pedron, G. Petruzzelli, M. Barbafieri, E. Tassi, Strategies to use phytoextraction in very acidic soil contaminated by heavy metals, Chemosphere 75 (2009) 808–814.
[7] C.L. Luo, Z.G. Shen, X.D. Li, A.J.M. Baker, Enhanced phytoextraction of Pb and other metals from artificially contaminated soils through the combined application of EDTA and EDDS, Chemosphere 63 (2006) 1773–1784.
[8] S. Doumett, L. Lamperi, L. Checchini, E. Azzarello, S. Mugnai, S. Mancuso, G. Petruzzelli, M. Del Bubba, Heavy metal distribution between contaminated soil and *Paulownia tomentosa*, in a pilot-scale assisted phytoremediation study: influence of different complexing agents, Chemosphere 72 (2008) 1481–1490.
[9] F. Madrid, M.S. Liphadzi, M.B. Kirkham, Heavy metal displacement in chelate-irrigated soil during phytoremediation, J. Hydrol. 272 (2003) 107–119.
[10] Y.H. Chen, Z.G. Shen, X.D. Li, The use of vetiver grass (*Vetiveria zizanioides*) in the phytoremediation of soils contaminated with heavy metals, Appl. Geochem. 19 (2004) 1553–1565.
[11] B. Kos, D. Lesˇtan, Induced phytoextraction/soil washing of lead using biodegradable chelate and permeable barriers, Environ. Sci. Technol. 37 (2003) 624–629.
[12] S.M. Aggelides, P.A. Londra, Effects of compost produced from town wastes and sewage sludge on the physical properties of a loamy and a clay soil, Bioresour. Technol. 71 (2000) 253–259.
[13] F. Pedra, H. Domingues, A.B. Ribeiro, A. Polo, O. Monteiro, Relationship between Cu and Zn extractable foliar contents and BCR sequential extraction in soil treated with organic amendments, Environ. Technol. 27 (2006) 1357–1367.
[14] J. Nyamangara, J. Mzezewa, Effect of long-term application of sewage sludge to a grazed grass pasture on organic carbon and nutrients of a clay soil in Zimbabwe, Nutr. Cycl. Agroecosyst. 59 (2001) 13–18.
[15] S. Mbarki, N. Labidi, H. Mahmoudi, N. Jedidi, C. Abdelly, Contrasting effects of municipal compost on alfalfa growth in clay and in sandy soils: N, P, K, content and heavy metal toxicity, Bioresour. Technol. 99 (2008) 6745–6750.
[16] H.S. Chen, Q.Y. Huang, L.N. Liu, P. Cai, W. Liang, M. Li, Poultry manure compost alleviates the phytotoxicity of soil cadmium: influence on growth of pakchoi (*Brassica chinensis* L.), Pedosphere 20 (2010) 63–70.
[17] M.J. Boyter, J.E. Brummer, W.C. Leininger, Growth and metal accumulation of geyer and mountain willow grown in topsoil versus amended mine tailings, Water Air Soil Pollut. 198 (2009) 17–29.
[18] A. Tessier, P.G.C. Campbell, M. Bisson, Sequential extraction procedure for the speciation of particulate trace metals, Anal. Chem. 51 (2002) 844–851.
[19] V.H. Kennedy, A.L. Sanchez, D.H. Oughton, A.P. Rowland, Use of single and sequential chemical extractants to assess radionuclide and heavy metal availability from soils for root uptake, Analyst 122 (1997) R89–R100.
[20] P. Verma, K.V. George, H.V. Singh, R.N. Singh, Modeling cadmium accumulation in radish, carrot, spinach and cabbage, Appl. Math. Model. 31 (2007) 1652–1661.
[21] G. Montes-Hernandez, R. Perez-Lopez, F. Renard, J.M. Nieto, L. Charlet, Mineral sequestration of CO_2 by aqueous carbonation of coal combustion fly-ash, J. Hazard. Mater. 161 (2009) 1347–1354.
[22] L. Marchiol, P. Sacco, S. Assolari, G. Zerbi, Reclamation of polluted soil: phytoremediation potential of crop-related Brassica species, Water Air Soil Pollut. 158 (2004) 345–356.
[23] ISO 11466, Soil quality – extraction of trace elements soluble in aqua regia, in: TC 190/SC3 Chemical Methods and Soil Characteristics, International Organization for Standardization, Geneva, Switzerland, 1995.
[24] WalkleyF A., I.A. Black, An examination of Degtjareff method for determining soil organic matter and a proposed modification of the chromic acid titration method, Soil Sci. 37 (1934) 29–37.
[25] B.M. Tucker, Laboratory Procedures for Cation Exchange Measurement on Soils, CSIRO Division of Soils Technical Paper No. 23 (1974).
[26] ISO 11261, Determination of total nitrogen – modified Kjeldahl method, in: TC 190/SC3 Chemical Methods and Soil Characteristics, International Organization for Standardization, Geneva, Switzerland, 1995.
[27] R.H. Bray, L.T. Kurtz, Determination of total, organic, and available forms of phosphorus in soils, Soil Sci. 59 (1945) 39–45.
[28] E.O. McLean, M.E. Watson, Soil measurements of plant available potassium, in: R.D. Munson (Ed.), Potassium in Agriculture, ASA/CSSA/SSSA, Madison, WI, 1985, pp. 277–308.
[29] Hazardous Waste Land Treatment SW-874, USEPA Office of Solid Waste and Emergency Response, vol. 273, 1983.
[30] X. Cao, G. Zhao, M. Yin, J. Li, Determination of ultratrace rare earth elements by inductively coupled plasma mass spectrometry with microwave digestion and AG50W-X8 cation exchange chromatography, Analyst 123 (1998) 1115–1119.
[31] E. Guerra-Rodrıguez, J. Alonso, M.J. Melgar, M. Vaĭzquez, Evaluation of heavy metal contents in co-composts of poultry manure with barley wastes or chestnut burr/leaf litter, Chemosphere 65 (2006) 1801–1805.
[32] S.E. Fendorf, R.J. Zasoski, Environ. Sci. Technol. 26 (1992) 79.
[33] A.E. Martell, R.M. Smith, Critical Stability Constants, Plenum Press, New York, 1974.
[34] D. Rai, B.M. Sass, D.A. Moore, Chromium(III) hydrolysis constants and solubility of chromium(III) hydroxide, Inorg. Chem. 26 (1987) 345–349.
[35] K.M. Shams, G. Tichy, A. Fischer, M. Sager, T. Peer, A. Bashar, K. Filip, Aspects of phytoremediation for chromium contaminated sites using common plants *Urtica dioica*, *Brassica napus* and *Zea mays*, Plant Soil 328 (2010) 175–189.
[36] G. Cumming, F. Fidler, D. Vaux, Error bars in experimental biology, J. Cell Biol. 177 (2007) 7–11.