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Modeling Phytoextraction of Heavy Metals at Multiply Contaminated Soils with Hyperaccumulator Plants

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ABSTRACT

Soils and waters contaminated with heavy metals pose a major environmental and human health problem that needs an effective and affordable technological solution. Phytoextraction offers a reasonable technology which uses plants to extract the heavy metals from soils. However, the effectiveness of this new method needs to be demonstrated by means of mathematical modeling. The phytoextraction models also are needed to manage the contaminated soils. A thorough literature review indicates that very few models have yet been developed for phytoextraction due to complexities involved within the soil-water-chemicals-plant system, even for a single metal contamination in the laboratory scale. Furthermore, the complexity increases in the field scale problems where the soils are multi-contaminated and also are with high heterogeneity involved in soil physico-chemical properties. On the other hand, in the case of hyperaccumulator plants there are a great deal of data spread worldwide because of the attentions that have been made to test the phytoextration technology in the last years. Consequently, analysis of the existing database of measured phytoextraction data for hyperaccumulators may result in simple models. The objective of this study was to develop a simple model for phytoextraction of heavy metals at multi-contaminated soils. The more preferable input parameters to derive the phytoextraction models were selected by reviewing the literature. Using the published data of Cd and Zn phytoextraction with *Thlaspi caerulescens*, some reasonable models were derived. The model calculations suggest that phytoextraction using *T. caerulescens* is not feasible even when the soil is only moderately contaminated with both Cd and Zn.

Keywords: Heavy Metal, Hyperaccumulator, Modeling, Multi-Contaminated Soils, Phytoextraction

INTRODUCTION

Soil pollution has recently been attracting considerable public attention since the magnitude of the problem in our soils calls for immediate action (Garbisu and Alkorta, 2003). Soils may be polluted by a wide range of contaminants from industrial activities, sewage sludge disposal, agricultural inputs, mining, metal processing, and energy production. Among these contaminants, heavy metals are primarily a concern because of their immutable nature (Garbisu and Alkorta, 2003).

Soils contaminated with heavy metals create major environmental and human health problems that need effective and affordable technological solutions. More often, conventional remediation approaches that mostly resort to excavation and either landfilling or soil washing followed by physical or chemical separation of the contaminants are both expensive and intrusive to the ecosystem. Phytoextraction has been proposed as a suitable alternative to those destructive and high-cost engineer-based techniques. It involves growing plants that hyperaccumulate heavy metals on contaminated sites, harvesting the plants, recycling the biomass both for energy and metal, or disposing of them as hazardous waste (Cunningham et al., 1995). While the cost of conventional remediation methods range from \$10 to \$1000 m^{-3} of treated soil material, phytoextraction is estimated to cost about \$0.05 m^{-3} of treated soil material (Cunningham et al., 1997). Although phytoextraction offers cost advantages and is comparable to in situ bioremediation and natural attenuation, but the trade off is the time needed to achieve the treatment. Furthermore, the technology has not been demonstrated conclusively at many sites to date, and it remains to be seen if it is effective at full scale. Therefore, mathematical or statistical modeling is necessary to demonstrate the effectiveness of the technology to regulatory agencies. Phytoextraction models also could be used to calculate the time needed to soil remediation, economical assessment of biomass recycling for metals, and to manage the contaminated soils.

A thorough literature review indicates that very few models have yet been developed for phytextraction due to the complexities involved within the soil-water-chemicals-plant system. Plant uptake models that originally have been developed for nutrients are well established for the supply of solutes from soils (Barber, 1995; Tinker and Nye, 2000), have been used to provide a quantitative knowledge of the effect of the plant on metal concentrations in adjacent soil (Whiting et al., 2003; Mullins and Sommers, 1986; Adhikari and Rattan, 2000; Schnepf, 2002; Lehto et al., 2006). Plant uptake models have evolved from simple diffusion and mass flow based models (Bouldin, 1961; Barber and Cushman, 1981; Olsen et al., 1962; Lehto et al., 2006) to more complex models that incorporate quantifiable processes in the rhizosphere for both nutrients and even for heavy metals (Barber and Cushman, 1981; Kirk et al., 1999, Puschenreiter et al., 2005; Klepsh et al., 2006). A list of these models and two samples of their mathematical equations have been published in Lehto et al. (2006). Although, this modeling has been useful in quantitative understanding the relevant rhizosphere processes, however, as they have not consider the plant yield changes as a result of soil metal concentration, they are of less help in management uses. Furthermore, the soil/plant-oriented parameters in the models are somehow hard and time-consume to be measured immediately for urgent management needs.

Attempts have been made, so far, to developed a model for coupled transport of water, heat, and solutes in the soil–plant–atmosphere continuum (Boersma et al., 1988a,b and 1991; Lindstrom et al., 1990) or to simulate uptake of contaminants into plants (Trapp and McFarlane, 1995) and also for Pb and Cd uptake in agricultural lands (Jorgensen, 1988). However, most of these models are to predict the nutrient uptake or to predict the contamination of agricultural products and there are just a few simulation models for phytoremediation process. Although the current realistic or mechanistic simulation models almost exclusively discuss uptake of minerals or metals (Silberbush, 1996; Rengel, 1993), but for the purpose of phytoextraction the mechanistic models are not well developed and the realistic models are not reasonably efficient (Tudoreanul and Phillips, 2004).

Zhao et al. (2003) assessed the potential for Zn and Cd phytoextraction by *Thlaspi caerulescens*. They provided some regression models to predict the shoot concentration and bioaccumulation factor of Zn and Cd with soil total concentration of the metals. They assumed the potential for phytoextraction to be dependent on plant biomass, the bioaccumulation factor and the soil mass that requires remediation. Assuming the average yield of the plant to be 5 (an achievable average biomass with optimized agronomic inputs) and 10 (an ideal average biomass expected to be achieved by plant breeding) t ha^{-1}, they calculated the number of crops needed to achieve the remediation targets. But, they did not consider the effect of heavy metal stress and also the other soil parameters on the plant biomass yield and plant metal uptake and the model does not suit the multi-contaminated soils.

Yanai et al. (2006) investigated the effect of soil characteristics on Cd uptake by *T. caerulescens.* They provided some regression equations to predict the Cd and Zn concentration of shoots and their uptake by the plant based on the total soil Cd or Zn concentration and some other soil parameters, such as pH, OC and soil clay content. However, the models were not aimed in phytoextrction at multi-contaminated soils. Furthermore, they did not consider the possible effect of other metals on the uptake of metal of interest by plant.

In spite of all the attempts have been made to develop a phytoextraction model, so far, there is no model to serve reasonably for multi- and even for single-contaminated soils. Indeed, the high-variable nature of soil physico-chemical properties prevents scientists to develop a general phytoextraction model for soils. However, due to the fact that in the two last decades a great concerns have been made to assess the potential phytoextraction of multi-contaminated soils in field trials with hyperaccumulator plants, there are a great deal of data for these kind of plants spread worldwide (e.g. Hammer and Keller, 2003, Zhao et al. 2003, Yanai et al., 2006, Kaysar et al, 2000, Felix, 1997). Therefore, as an alternative for other modeling approaches it is rewarding to analyze the existing database of measured phytoextraction data in multi-contaminated soils to derive some simple regression models. These models will quantify the relationships between available and missing phytoextraction data. The models will finally translate data *we have* to data *we need*. However, to derive such models it is necessary to overcome the problem of selecting more preferable or necessary input parameters which are needed to be included in a heavy metal phytoextraction model.

Soil properties have a large influence on metal bioavailability to plants. Matter of fact, the metal uptake by plants and the magnitude of stress expected to be risen from a given metal is dependent on a fraction of the total concentration of metal exists in the soil solution, more commonly known as bioavailable concentration, rather than the total soil metal concentration. However, neglecting the difficulties associated with detecting the metal available fraction in the soil, it is not a routine parameter to measure in the phytoextraction experiments and also it may be determined by different methods. On the other hand, the soil total metal concentration is not only available more readily in the publications but also the methods to its measurements are more unique.

In the soil, metals undergo reactions with ligands in soil solution and with surface sites on the solid material. Metal sorption to the solid matrix results in a reduction in the dissolved concentration of metal and this affects the overall rate of metal availability to plants. For a given soil, the soluble and adsorbed contaminants are related by the soil sorption distribution coefficient K_{SD}. For a particular metal, K_{SD} values in soil are dependent upon various geochemical characteristics of the soil and its pore-water. The main soil characteristics which affect the K_{SD} are soil pH and organic carbon content (Drgryes et al., 2006).

Soil pH significantly influences heavy metal concentrations in both soil and plant tissues. The effect of soil pH on mobility of heavy metals is a well-researched topic (Cataldo *et al.* 1981; Chen *et al.* 1997; Peles *et al.* 1998; Li and Wu 1999). Robinson et al. (1998) found an inverse correlation between plant metal content and soil pH. Brown et al. (1994) found the soil pH as a major factor controlling heavy metal bioavailability in soil, so that decreasing the soil pH increases the uptake of Zn by *T. caerulescens*. As the soil pH decreases, metals are desorbed from organic and clay particles, enter the soil solution and, become more mobile (Li and Wu 1999). When the pH is higher (i.e., >7), metals remain adsorbed and what metals in solution precipitate out in the form of salts (Chen *et al.* 1997). Variability in pH also affects the amount of Cd assimilated by the plant. John and VanLaerhoven (1972) showed that higher pH resulted in lower Cd uptake. Peles *et al.* (1998) concluded that the addition of lime to contaminated soils (essentially increasing the pH) decreased the uptake of heavy metals. However, increased levels of soil soluble Cd in low pH soils may adversely affect plant development, led to low total uptake of metal at low pHs. Khan and Frankland (1983) reported that extremely high concentrations (180 $\mu g\ g^{-1}$) of Cd in soil adversely affected plant development. Increasing in heavy metal uptake by plants will also led to trace metal deficiencies in plants (Khan and Frankland 1983) that may decreases the plant yield production. Furthermore, increased levels of Ca^{2+} (as in high ph soils) can decrease the amount of Cd that is assimilated by plants (Larlson *et al.* 2000). A higher affinity for the essential trace metal Ca results in the decreased uptake of Cd into the plant.

Yanai et al. (2006) found the soil pH, soil OC, soil clay content and soil metal concentration to be the most important factors affecting the metal uptake by plant.

Khan and Frankland (1983) reported that extremely high concentrations (180 µg g-1) of Cd in soil adversely affected plant development. Therefore, it sounds to be reasonable to use a combination of soil total concentration of metal of interest, soil pH, soil OC and also the concentration of other metals exist in the soil to derive the model for each metal in a multi-contaminated soil.

The objective of this study was to develop a simple model to account for phytoextraction of heavy metals at multi-contaminated soils.

MATERIALS and METHODS

A literature survey was conducted to obtain the data for phytoextraction of Cd and Zn in multi-contaminated soils by hyperaccumulator plants. The published data (26 data points) for phytoextraction of Cd and Zn by *T. caerulescens* ecotype *Ganges* (southern France) was used to derive the models (Lombi et al., 2001; Yanai et al., 2006). *T. caerulescens* ecotype *Ganges* known for both Zn and Cd hyperaccumulation (Cosio et al., 2005).

Stepwise multiple regression analysis (MINITAB, Release 14.20) was performed to obtain the optimal models for predicting plant relative yield and Cd and Zn concentration in *T. caerulescens*. Combining plant yield model with those of plant concentration of Cd and Zn, a model was derived to predict the total metal uptake by each crop of *T. caerulescens*. The accuracy of the model was tested, quantitatively. Using the model, then the number of crops needed to remediate the Cd and Zn below the remediation targets was simulated at a multi-contaminated soil for an initial concentration of soil Cd of 20 mg kg^{-1} and soil Zn of 1000 mg kg^{-1}, and soil Cd of 5 mg kg^{-1} and soil Zn of 500 mg kg^{-1}.

RESULTS and DISCUSSIONS

Table 1 shows the range of some soil physical and chemical properties used to derive the models. The values in Table (1) can be used to avoid the extrapolation while we are using the derived models to predict the phytoextraction data needed for other sites.

Table 1- The range of some soil physical and chemical properties§ used to derive the models

pH	OC (%)	Zn_t (mg kg^{-1})	Cd_t (mg kg^{-1})
4.4-7.7	1.5-14.6	53-27413	0.5-314.8

§ pH: soil pH, OC: soil organic carbon content, Zn_t: soil total Zn concentration, Cd_t: soil total Cd concentration.

A set of the regression equations were obtained to estimate the plant relative yield and Cd and Zn concentration in *T. caerulescens*. A number of 26 data points were used to derive all the equations. The most important soil factors affecting the plant yield and Cd and Zn uptake by *T. caerulescens* were selected among soil pH, soil OC and soil total concentration of Cd and Zn by stepwise regression analysis in such a way that the largest R_{adj}^2 and the smallest standard deviation of the error term in the model, *S*, were obtained (MINITAB, Release 14.20). According to the stepwise regression analysis the most important factors affecting the relative yield of *T. caerulescens* are the soil pH and Soil total Zn concentration. However, the most important factors determining the shoot concentration of Cd and Zn were the soil total Cd and Zn concentrations and soil total Zn concentration, respectively. Soil OC was not entered in any model. The derived regression equations and their statistics are given below:

$$\frac{Y}{Y_{\max}} = -0.106 + 0.0577\,pH + 1.8\times10^{-5}\,Zn_t \qquad (1)$$

$R^2_{adj} = 69.5, \qquad S = 0.1$

$$Cd_{shoot} = 75.4 + 6.69Cd_t - 0.0367Zn_t \qquad (2)$$

$Zn_{shoot} = 854 + 0.150Zn_t$

$R^2_{adj} = 80.7, \qquad S = 104.9$

(3)

$R^2_{adj} = 58.0, \qquad S = 918.8$

where Y and Y_{max} are the plant yield at a given concentration of Cd or Zn in the soil (t ha^{-1}) and maximum yield of plant (in this study it assumed to be 5 t ha^{-1}), respectively, $\frac{Y}{Y_{\max}}$ is the relative yield, Zn_t and Cd_t are the soil total concentration of Zn and Cd (mg kg^{-1}), respectively, and Cd_{shoot} and Zn_{shoot} are the plant shoot concentration of Cd and Zn (mg kg^{-1}), respectively. R^2_{adj} is a modified R^2 that has been adjusted for the number of terms in the model. If unnecessary terms been included in the model, R^2 can be artificially high. Unlike R^2, R^2_{adj} may get smaller by adding terms to the model (MINITAB, Release 14.20). All the obtained regression equations appeared to be significantly correlated at $p = 0.001$.

Combining Eq. (1) with Eqs. (2) and (3) and assuming Y_{max} to be 5 t ha^{-1}, the plant uptake of Cd and Zn by one crop of *T. caerulescens* was predicted, respectively. Fig. (1) shows the comparison between measured total uptake of Cd and Zn by each crop of *T. caerulescens* with those predicted by the models. The models predictions showed the significant correlation with measurements ($p = 0.001$) both for Cd and Zn uptake with *T. caerulescens*.

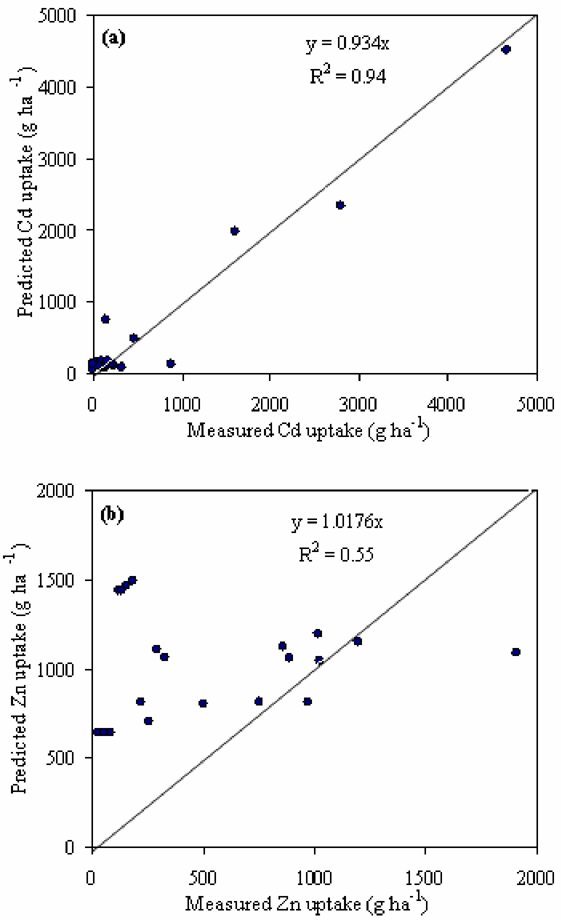

Figure 1. Comparison of measured total uptake of Cd (a) and Zn (b) by each crop of *Thlaspi caerulescens* with those predicted by combining Eq. (1) with Eq. (2) for Cd and with Eq. (3) for Zn and assuming Y_{max} to be 5 t ha^{-1}. The solid lines indicate the 1:1 diagonal.

Using the models then the number of crops needed to remediate the Cd and Zn below the remediation targets was simulated in different pHs at a multi-contaminated soil. Fig. (2) shows the Simulated concentrations of Cd and Zn in a multi-contaminated soil with pH values of 4.5 and 7.5 for an initial concentration of soil Cd of 20 mg kg^{-1} and soil Zn of 1000 mg kg^{-1} and soil Cd of 5 mg kg^{-1} and soil Zn of 500 mg kg^{-1} after successive crops of *T. caerulescens*. For an initial concentration of soil Cd of 5 mg kg^{-1} and soil Zn of 500 mg kg^{-1}, it would take 32 and 16 crops of *T. caerulescens* to phytoremediation of soil Cd to 3 mg kg^{-1} with soil pH of 4.5 and 7.5, respectively (Fig. 2a). At the same level of soil Cd and Zn contamination, it would take 299 and 145 crops of the plant to reduce the soil Zn to 300 mg kg^{-1} with soil pH of 4.5 and 7.5, respectively (Fig. 2b).

However, when the soil is more contaminated with an initial concentration of soil Cd of 20 mg kg^{-1} and soil Zn of 1000 mg kg^{-1}, it would take 200 and 100 crops of *T. caerulescens* to phytoremediation of soil Cd to 3 mg kg^{-1} with soil pH of 4.5 and 7.5, respectively (Fig. 2a).

Phytoremediation of soil Zn to soil Zn concentration of 300 mg kg^{-1} at the same level of soil Cd and Zn contamination would take 975 and 477 crops of the plant with soil pH of 4.5 and 7.5, respectively (Fig. 2b).

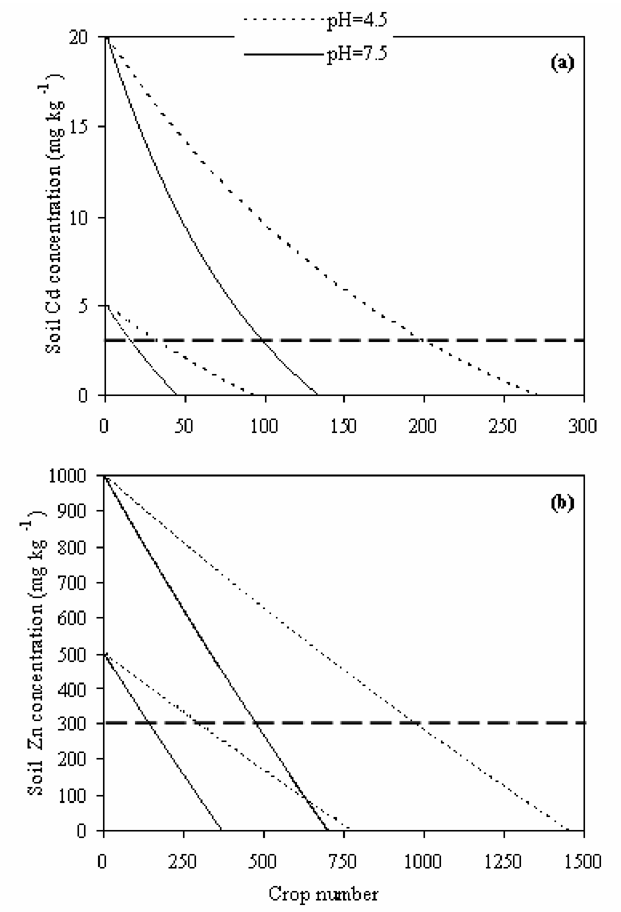

Figure 2. Simulated concentrations of Cd (a) and Zn (b) in multi-contaminated soils with different pH values (for an initial concentration of 1- soil Cd of 20 mg kg^{-1} and soil Zn of 1000 mg kg^{-1}, and 2- soil Cd of 5 mg kg^{-1} and soil Zn of 500 mg kg^{-1}) after successive crops of *Thlaspi caerulescens*. Horizontal dashed lines represent the targets for remediation.

The results showed that the number of crop needed to remediate the both soil Cd decreases by a factor of ≈ 2 with increasing soil pH from 4.5 to 7.5. The reason may be relied upon the fact that, although the Cd and Zn bioavailability to plant decreases with increasing of soil pH (Yanai et al., 2006; Degryse et al., 2006) in the case of *T. caerulescens* the increasing of the yield as a result of soil pH increasing (Yanai et al., 2006) may preponderate to result in a more total metal uptake. The results also showed that the number of crops needed to reduce the unit concentration of soil Cd is between 5.9-16 (Crop/ $mg_{Cd}\ kg^{-1}{}_{Soil}$) and for Zn is between 0.7-1.5 (Crop/ $mg_{Zn}\ kg^{-1}{}_{Soil}$). No matter how much is the magnitude of hazard risen from a unit level of contamination of soil Cd and Zn, the results revealed the more ability of *T. caerulescens* to extract the soil Zn contamination than that of Cd. However, owing to the fact that the absolute concentrations of Cd in soil are generally two orders of magnitude lower than those of Zn (Zhao et al., 2003), the phytoremediation of Cd seems to be more feasible than that of Zn.

Comparing the results above with those of Zhao et al. (2003) for the very same initial concentrations of soil Cd and Zn revealed that in a soil contaminated with both Cd and Zn, it may take 1.8-5 times more crops to soil Cd remediation to a same target than that of a single-contaminated soil. In the case of soil Zn decontaminations it is 4-9 times more crops in compare to a soil contaminated only with Zn.

The above model simulations suggest that phytoremediation using *T. caerulescens* is not feasible even when the soil is only moderately contaminated with both Cd and Zn, simultaneously. It calls more attempts to improve the metal hyperaccumulation and biomass production of *T. caerulescens* by means of plant breeding and/or genetic engineering to overcome the globally increasing problem of soil heavy metal pollution.

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