Water Air Soil Pollut (2007) 181:355–371
DOI 10.1007/s11270-006-9307-7

Predicting the Phytoextraction Duration to Remediate Heavy Metal Contaminated Soils

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Received: 8 December 2005 / Accepted: 2 November 2006 / Published online: 3 January 2007

Abstract The applicability of phytoextraction to remediate soils contaminated with heavy metals (HMs) depends on, amongst others, the duration before remediation is completed. The impact of changes in the HM content in soil occurring during remediation on plant uptake has to be considered in order to obtain a reliable estimate of the phytoextraction duration. To simulate the decrease in the HM content in soil and to assess the resulting decrease in the uptake of HMs by plants, contaminated soil was mixed with uncontaminated, but otherwise similar soil. Uptake of Cd, Pb, and Zn by the indicator plant *Lupinus hartwegii* and the Zn hyperaccumulator *Thlaspi caerulescens* (La Calamine ecotype) was a log-linear function of the in-situ measured HM soil solution concentrations. Over a wide range in dissolved Cd and Zn concentrations, uptake of these HMs by *T. caerulescens* was (much) greater than by *L. hartwegii*. Experimentally derived regression models describing the relationships between soil, soil solution, and plant were implemented in a HM mass balance model used to obtain estimates of the phytoextraction duration. For our target soils, estimates of the Cd phytoextraction duration using *L. hartwegii* or *T. caerulescens* increased significantly by more than 100 or 50 years when experimental soil—soil solution—plant relationships were used instead of the assumption of constant plant uptake of Cd. The two approaches gave similar results for phytoextraction of Zn by *T. caerulescens*.

Keywords heavy metals · hyperaccumulator · leaching · phytoextraction · phytoextraction duration · plant uptake · *Thlaspi caerulescens*

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1 Introduction

Phytoextraction has been advocated as a cost-effective and environmentally-friendly alternative to conventional engineering technologies for the remediation of soils contaminated with heavy metals (HMs) (Baker, McGrath, Sidoli, & Reeves, 1994; Cunningham, Berti, & Huang, 1995). The objective of phytoextraction is to decrease the HM content of contaminated soils to an environmentally safe and legally acceptable level. For a fast remediation, plant species with both a high potential to accumulate

HMs in the harvestable, above-ground plant parts and a high biomass production are needed. Early phytoextraction research mainly focused on plants with a high HM uptake, so-called 'hyperaccumulating' plant species. These are defined as higher plants capable of accumulating >100 mg Cd kg^{-1}, >1000 mg Cu, Ni, and Pb kg^{-1}, and >10 000 mg Zn kg^{-1} dry matter (dm) in their shoots when grown in HM-rich soils (Baker & Brooks, 1989; Baker et al., 1994). However, hyperaccumulators often accumulate only a specific HM and have a low biomass production leading to long duration times before completion of remediation (Cunningham et al., 1995). Alternatively, the use of high biomass plants in combination with the application of synthetic chelates has been suggested (Blaylock et al., 1997; Huang, Chen, Berti, & Cunningham, 1997; Grčman, Vodnik, Velikonja-Bolta, & Leštan, 2003). However, disadvantages of chelates (e.g., increased risk of HM leaching and negative impacts on soil life) often outweigh the benefits (Grčman et al., 2003; Lombi, Zhao, Dunham, & McGrath, 2001; Römkens, Bouwman, Japenga, & Draaisma, 2002; Wang, et al., in press).

Phytoextraction is a promising technology for the remediation of moderately HM contaminated soils (Robinson et al., 1998; Zhao, Lombi, & McGrath, 2003). In contrast to many conventional engineering technologies, however, the land has to be set aside for a relatively long time before phytoextraction is completed (Cunningham et al., 1995). Especially in urban areas, the economic costs of setting land aside can be high (Robinson et al., 2003). To evaluate the applicability of phytoextraction, it is important to have a practical tool allowing the user to obtain a good estimate of the phytoextraction duration. Estimates of the phytoextraction duration to realize the desired HM contents in soil have often been made assuming constant rates of HM uptake into plant shoots during remediation (e.g., Baker et al., 1994; Puschenreiter, Stöger, Lombi, Horak, & Wenzel, 2001). In the latter studies, plant uptake of HMs was determined in short-term experiments with only a limited number of cropping cycles. The outcome of such studies can be used to predict the phytoextraction duration as long as the HM uptake rates into plant shoots remain constant during remediation. However, the decrease of the HM contents in soil during phytoextraction may lead to reduced HM uptake by plants which results in an extended phytoextraction period to reach the target levels set at the beginning. Extrapolation of results from such short-term experiments based on constant plant uptake rates may lead to underestimation of the phytoextraction duration.

One of the keys to a solution is to consider the dynamics of HM uptake by plants during phytoextraction. In several pot and field experiments, uptake of HMs was demonstrated to be related to the HM concentration in soil solution (e.g., Hamon, Holm, Lorenz, McGrath, & Christensen, 1999; Chaudri et al., 2001; Weng, Lexmond, Wolthoorn, Temminghoff, & van Riemsdijk, 2003; Song, Zhao, Luo, McGrath, & Zhang, 2004). In the study of Song et al. (2004), Cu uptake by roots of *Silene vulgaris* and *Elsholtzia splendens* was predicted from regression models relating the Cu content in roots to the Cu concentration in soil solution in combination with pH and dissolved organic carbon (DOC). Hence, such regression models based on the dissolved HM concentration and other relevant soil solution properties (e.g., pH and DOC) can in some cases be used to predict HM uptake by plants in the field. In addition to the soil solution – plant relationship, information on the partitioning of HMs between soil and soil solution is needed. To predict the solubility of HMs in soil, regression models relating the HM concentration in soil solution to soil properties such as the HM content, pH, and organic matter have been established (e.g., McBride, Sauvé, & Hendershot, 1997; Sauvé, Hendershot, & Allen, 2000; Tipping et al., 2003). For Cd and Zn, this approach has provided reasonably accurate predictions of their solubility in a wide range of soils (R^2 between 0.6 and 0.9 [see aforementioned studies]). Once the relationships between the HM content in soil and soil solution on the one hand and between soil solution and plant on the other have been established, the resulting soil—soil solution—plant model is capable to predict changes in HM uptake with time.

To obtain reliable estimates of the phytoextraction duration to realize the target levels of HMs in soil, the aforementioned soil—soil solution—plant relationships have to be established in a range of soils reflecting the entire span of HMs reached during phytoextraction. It is, however, not practical to perform a small-scale experiment with multiple crop

cycles before field application of phytoextraction. On the other hand, the removal of HMs from soil and its effect on plant uptake of HMs cannot be artificially accelerated. To overcome this problem and to obtain a good estimate of the phytoextraction duration, an approach called 'fading out' is tested in this study. This approach involves a pot experiment in which contaminated soil is mixed and equilibrated with uncontaminated, but otherwise similar soil to obtain a range in HM contents reflecting the decrease which otherwise would have been realized by phytoextraction. Once the soil mixtures are obtained, one cropping cycle is performed with the plant species of interest. Once this is achieved, the soil—soil solution—plant relationships can be established which then can be implemented in a HM mass balance model to assess the time required to reach the HM targets levels in soil.

In this study, a Cd, Pb, and Zn contaminated soil sampled from the Waryński smelter site near Katowice in Poland was mixed and equilibrated with uncontaminated, but otherwise similar soil. Under natural conditions without soil amendments to decrease the availability of HMs, plant growth in the soil from Katowice is severely hampered due to phytotoxic levels of HMs (Kucharski et al., 2005). To create a moderate degree of HM contamination, a relatively small amount of contaminated soil was mixed with a relatively large amount of uncontaminated soil. This 'target' soil was further diluted with uncontaminated soil to obtain a range in HM contents. Although both the contaminated and uncontaminated soils used in this study are real soils, the range in HM contamination used in the pot experiment is a fictive one, because the 'target' soil as such does not exist. However, this experiment was performed solely with the intention to describe and test the applicability of the fading out approach. To illustrate the different behaviour of a so-called 'indicator' plant species (McGrath, Dunham, & Correll, 2000) versus a HM hyperaccumulator, we used two plant species: *Lupinus hartwegii* was used as an indicator plant species whereas *Thlaspi caerulescens* (La Calamine ecotype) was used as an example of a Zn hyperaccumulator (Assunção et al., 2003). Our first objective was to test whether HM uptake by *L. hartwegii and T. caerulescens* could indeed be predicted from the HM concentration in soil solution, and, in turn, whether the solubility of HMs could be predicted from the HM content in soil. Our second objective was to use the regression models, which describe the soil—soil solution and soil solution—plant relationships, in combination with a HM mass balance model to demonstrate the potential of the fading out approach as a practical tool to estimate the phytoextraction duration of HM contaminated soils.

2 Material and Methods

2.1 Soils

A loamy sandy soil collected from the 0–20 cm soil layer at the Waryński smelter site, an abandoned industrial site near Katowice located in the south-central part of Poland, was used as a source of Cd, Pb, and Zn contaminated soil (see Kucharski et al. (2005) for a site description). An uncontaminated, sandy soil was sampled from the plough layer (0–25 cm) of arable land cropped with forage maize (*Zea mays* L.) near Sellingen located in the north of the Netherlands. The field-moist soil samples were sieved through a 2-mm sieve and stored at 5°C until further use.

2.2 Fading out experiment

The pot experiment consisted of eight treatments (in duplicate): contaminated soil was mixed with uncontaminated soil in a ratio of 0:100, 0.1:99.9, 0.2:99.8, 0.5:99.5,1.0:99.0, 1.5:98.5, 3.0:97.0, and 8.0:92.0% (based on dry weight). To avoid changes in the physical and chemical characteristics of the soils induced by drying (Koopmans, Chardon, Dekker, Römkens, & Schoumans, 2006), soils were mixed field-moist (i.e., about 60% of the water holding capacity [WHC]). Pots with a volume of 8 l were filled with 6 kg of mixed field-moist soil and left outside to incubate for 81 d. The pots were covered to prevent the soil from desiccation and to avoid weed proliferation. After incubation, soil was taken out of the pots. Before refilling of the pots, 1,765 mg of a fertilizer containing 27% NH_4NO_3 and 63% $CaCO_3$ (w/w) and 1,980 mg K60 containing 60% KCl (w/w) were mixed with the soil from each pot to achieve an optimal plant growth. An anti-rooting mat was placed

Table 1 Properties of the uncontaminated soil from Sellingen and the contaminated soil from Katowice

Soil	pH (KCl)	OM[a] (%)	Clay (%)	Sorbed HMs (mg kg^{-1})		Total HMs (mg kg^{-1})			
				Cd	Pb	Zn	Cd	Pb	Zn
Sellingen	6.6	6.5	5.0	0.07	3.9	9.0	0.12	9.3	13.0
Katowice	6.7	8.5	6.8	460	8,134	6,067	548	11,564	12,691

[a] Organic matter.

on the bottom of each pot to prevent roots from growing out of the pots. Four rhizon soil solution samplers were installed in each pot; two samplers at 7 cm and two samplers at 14 cm below the soil surface (Rhizon Research Products, Wageningen, the Netherlands). This resulted in four sampling points in each pot. These samplers consist of a porous polymer (average pore size 0.1 μm) with a length of 10 cm and were attached to a polypropylene tube. Soil solution was obtained by attaching vacuum blood extraction vessels to the end of the tube. Approximately 20 seeds of *L. hartwegii* were sown on the surface of each pot. The pot experiment was performed in a greenhouse where temperature was kept at 13°C at night and at 20°C during day time. In the winter, a 12-h day was provided through the use of artificial light to supplement natural light. Soils were irrigated on a daily basis up to about 60% of the WHC. At two sampling events (after 85 and 107 d), young plant leaves were collected from the plants of each pot. The entire plant shoots were harvested after 133 d by cutting the stems just above the soil surface. Plant material was washed with demineralised water before drying. Dry weight of the plant material was determined after drying at 70°C for 48 h. Soil solution was collected at the same three sampling events at which plant material was sampled. To collect a sufficient volume of soil solution, soils were irrigated up to field capacity 24 h before sampling. In a following pot experiment with *T. caerulescens*, the soil mixtures used for *L. hartwegii* were used again. This experiment was performed under the same conditions and using the same methods as those described for *L. hartwegii*. The soil was taken out of the pots and root residues of *L. hartwegii* were removed from the soil. The soil was again mixed with the same fertilizers and amounts as those used for *L. hartwegii*. On the surface of each pot, 0.5 g of a mixture containing 0.5 g seed of *T. caerulescens*, 19 g quartzitic sand, and 2 ml water was applied. Seeds of *T. caerulescens* were collected from a Zn ore waste deposit near La Calamine in the north-east of Belgium. This is close to the site where seeds of *T. caerulescens* from the Le Prayon ecotype were collected, which has often been studied before. Plant shoots were harvested after 206 d and soil solution samples were collected.

2.3 Analyses

The pH (KCl), organic matter, and clay content of the uncontaminated and contaminated soils were determined according to Houba, van der Lee, and Novozamsky (1995). The pH was measured in a settling 1:5 (w/v) suspension of soil in 1 M KCl. Organic matter was determined by loss-on-ignition. Clay content was determined by the sieve and pipette method. Sorbed HM contents of the uncontaminated soil and contaminated soil were determined by extraction with 0.05 M NH_4EDTA and 0.43 M HNO_3, respectively (Houba et al., 1995). According to results reported by Tipping et al. (2003) for a set of soils with widely varying properties, amounts of Cd, Zn, and Pb extracted with EDTA are very similar to those extracted with HNO_3. Total extractable HM contents were determined by digestion with aqua regia (Houba et al., 1995). Concentrations of Cd, Pb, and Zn in all extracts and digests were analyzed by inductive coupled plasma spectroscopy (ICP-AES). Sorbed and total HM contents of the soil mixtures were obtained by interpolation. Heavy metals extracted with EDTA and HNO_3 are considered as estimates of sorbed HMs reacting with binding sites located on the surface of the soil and control the concentrations of HMs in soil solution whereas HMs extracted with aqua regia include the more occluded forms (Tipping et al., 2003). In Table 1, selected

properties of the uncontaminated and contaminated soils are presented. The soil solution samples were analyzed for pH, total carbon (TC) and inorganic carbon (IC) (on a Shimadzu TC5000), and major cations (by ICP-AES). DOC was calculated as the difference between TC and IC. No additional filtration of the soil solution samples was necessary before analysis, because the porous polymer of the rhizon soil solution samplers acts as a 0.1 μm-filter. Soil solution samples were diluted using demineralised water when the volume was insufficient to perform all analyses. For the analysis of soil solution samples from the pot experiment with *L. hartwegii*, samples of the four samplers were pooled. For *T. caerulescens*, however, pooled samples of the two upper and two lower samplers were analyzed separately. No consistent trends were found. Thus, for further processing, data of the upper and lower soil solution samples were averaged. Approximately 1 g of dried plant material was ground in a platinum-coated grinder. Total Cd, Pb, and Zn contents of the plant material were determined by digestion in hot concentrated HNO_3 and analysis of the digests by ICP-AES. The quality of the analyses in our laboratory was monitored regularly with standard solutions and with an interlaboratory exchange program.

2.4 Derivation of plant—soil solution and soil solution—soil relationships

Multiple linear regression analyses were performed using Genstat 5, Release 7.1 (Genstat, 2003) to derive the soil—soil solution and soil solution—plant relationships. All data were log-transformed. Significance of R^2_{adj} values was determined using *F*-tests. Significance of each variable in the regression models was assessed by *t* tests. Duplicate pots of each treatment were treated as two individual samples. Hence, the maximum number of soil solution and plant shoot samples used in the regression analyses for the pot experiments with *L. hartwegii* and *T. caerulescens* amounted to 48 and 16, respectively. Soil solution and plant shoot samples with concentrations of HMs below the detection limit were omitted from the data set. For the soil solution samples, the detection limits were 0.69 μg Cd, 13.0 μg Pb, and 5.0 μg Zn l^{-1}. The detection limits in the plant shoot samples were 0.04 mg Cd, 0.85 mg Pb, and 1.5 mg Zn kg^{-1} dm.

2.5 Estimation of phytoextraction duration

The regression models were implemented in a HM mass balance model (de Vries, Römkens, van Leeuwen, & Bronswijk, 2002). The model includes HM input to the soil resulting from atmospheric deposition and HM outputs in terms of plant uptake and losses from soil caused by leaching. The model allows for the prediction of the changes in the HM content in soil with time by adding the HM input and by relating the HM outputs via the implemented regression models to the HM content in soil. In the regression models describing the soil—soil solution relationships, equilibrium was assumed between HMs sorbed to the soil solid phase and HMs dissolved in soil solution. Transformation of HMs in the sorbed form to more occluded forms was assumed to be negligible, in line with previous work of de Vries et al. (2002). For the HM content in soil, we used the sorbed HM pool as input similar to Tipping et al. (2003). Also, plant uptake of HMs was assumed to be in equilibrium with desorption of HMs from the soil solid phase. The HM mass balance model was applied to estimate the phytoextraction duration of our target soil, i.e., the soil mixture with 8% contaminated soil using *T. caerulescens* for remediation. In the case of *L. hartwegii*, the time required to realize the target levels was estimated only for the soil mixture with 3% contaminated soil, because the shoot dry matter produced by this plant species decreased to almost zero in the soil mixture with the highest degree of HM contamination (Fig. 1). The HM contamination was assumed to occur only in the active rooting zone, i.e., the 0–25 cm soil layer. Obviously, phytoextraction would be less effective when HM contamination also occurs in the subsoil (Zhao et al., 2003). For soil density, we used 1.4 kg l^{-1}. Input of HMs was assumed to occur only via atmospheric deposition, which was set at 0.2 g Cd, 7.5 g Pb, and 27.7 g Zn ha^{-1} $year^{-1}$ (Delahaye, Fong, van Eerdt, van der Hoek, & Olsthoorn, 2003). The decrease of the HM content in soil with time was predicted with and without leaching as an output term. Leaching losses were calculated as the HM concentration in soil solution multiplied by the downward water flux from the 0–25 cm soil layer. For the downward water flux, we used 300 mm $year^{-1}$, which is similar to the average annual precipitation surplus in the Netherlands. The dry matter production of plants grown in

pot experiments is often much higher than under field conditions (e.g., Delorme, Angle, Coale, & Chaney, 2000). For this reason, we decided to use data on dry matter production from field experiments reported elsewhere in the literature. The dry matter production by *L. hartwegii* was set at 5,200 kg dm ha^{-1} $year^{-1}$ (Davis, 1991). This author reported results on the dry matter production by *Lupinus arboreus* in a field experiment in which different amounts of P were applied. For *T. caerulescens*, a dry matter production of 5,835 kg dm ha^{-1} $year^{-1}$ was used. This number was calculated from the annual dry matter production by *T. caerulescens* (Le Prayon and Whitesike Mine ecotypes) in two consecutive years in a field experiment at the Woburn Market Garden Experiment in England (McGrath et al., 2000), and is in good agreement with yield estimates used by Robinson et al. (1998) and Zhao et al. (2003) for phytoextraction duration predictions by this plant species. With current optimized agricultural management practices, it should be possible to achieve a dry matter production roughly equal to this level (Robinson et al., 1998; Zhao et al., 2003). In addition to the model calculations described previously, the phytoextraction duration was also estimated assuming a constant HM uptake into the shoots of *L. hartwegii* and *T. caerulescens* during remediation. For this purpose, the HM contents of these plant species grown in the soil mixtures with 3 and 8% contaminated soil were used, respectively.

3 Results and Discussion

3.1 Growth and heavy metal contents of *Lupinus hartwegii* and *Thlaspi caerulescens*

The shoot dry matter produced by *L. hartwegii* varied considerably over the different soil mixtures and decreased to almost zero in the soil mixture with 8% contaminated soil (Fig. 1). This was probably due to phytotoxic levels of HMs in soil. Without the result of the soil mixture with the highest degree of HM contamination, the shoot dry matter of *L. hartwegii* was between 1.3 and 3.7 times higher than the amount produced by *T. caerulescens*. However, the latter plant species, a Zn hyperaccumulator, grew well on all soil mixtures and showed no symptoms of phytotoxicity. The shoot dry matter produced by *T. caerulescens* was independent of the percentage of contaminated soil (Fig. 1). Apparently, this plant species exhibits a high tolerance to high levels of Cd, Pb, and Zn in soil. Large differences were found between the two plant species in accumulation of Cd and Zn (Table 2). The HM contents of *T. caerulescens* were between 2.4 and 5.2 (Cd) and 2.9 and 23.2 (Zn) times higher than those of *L. hartwegii*. The Cd and Zn contents of *T. caerulescens* were lower than those reported by Lombi et al. (2001) and Hammer and Keller (2002). In these studies, the HM contents of *T. caerulescens* (Ganges ecotype) grown in soils varying widely with regard to total HM contents, pH, organic matter, and clay content, ranged from 34.3 to 576 mg kg^{-1} dm for Cd and from 1,791 to 14,399 mg kg^{-1} dm for Zn. Differences in HM contents of *T. caerulescens* between our study and those of Lombi et al. (2001) and Hammer and Keller (2002) can, in part, be explained by a lower pH and higher total Cd and Zn contents in some of the soils used in the latter

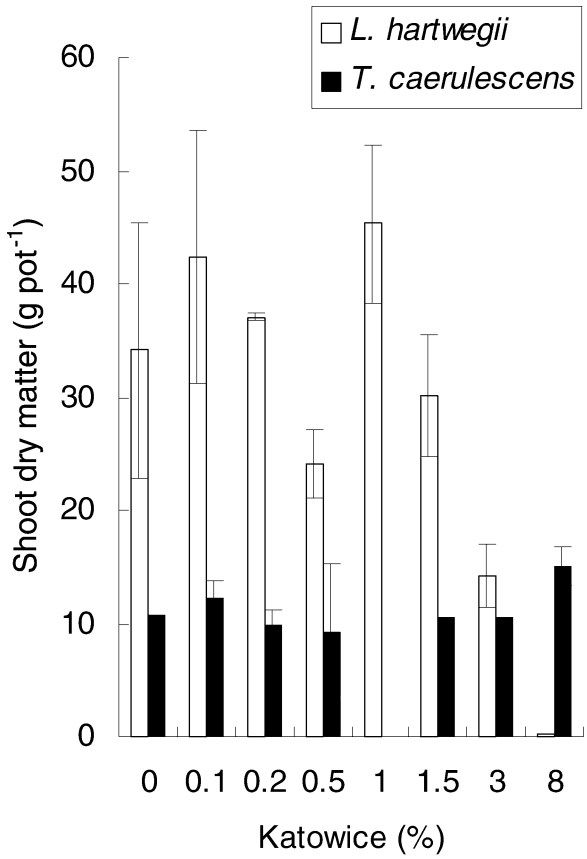

Fig. 1 Shoot dry matter of *L. hartwegii* (determined at the third, final sampling event) and *T. caerulescens*. Values represent average ± standard error calculated over treatment (*duplicate pots*). There was no growth of *T. caerulescens* in the soil mixture with 1% contaminated soil

Table 2 Heavy metal contents in the shoot dry matter (dm) of *L. hartwegii*[a,b] and *T. caerulescens*[a]

Katowice (%)	Cd (mg kg^{-1} dm)		Pb (mg kg^{-1} dm)		Zn (mg kg^{-1} dm)	
	L. hartwegii	*T. caerulescens*	*L. hartwegii*	*T. caerulescens*	*L. hartwegii*	*T. caerulescens*
0.0	0.22±0.00	0.70	bd[c]	bd	95.7±7.7	1,437
0.1	0.83±0.13	2.0±0.2	bd	bd	143±12	3,324±146
0.2	1.9±0.2	8.1±0.5	1.5±0.1	bd	198±19	3,599±19
0.5	3.2±0.2	15.6±3.1	2.0±0.1	bd	240±8	2,828±81
1.0	7.5±2.1	na[d]	6.4±2.0	na	444±120	na
1.5	9.8±0.5	44.3	7.9±1.2	6.3	548±28	3,729
3.0	21.4±1.7	111.4	19.1±3.0	13.0	1,114±122	6,157
8.0	65.1±5.5	275±33	91.4±13.4	43.0±0.5	1,722±175	5,018±422

[a] Values represent average ± SE calculated over treatment (duplicate pots).

[b] Results of the final harvest.

[c] Below detection limit.

[d] No plant material was available for HM analysis, because there was no growth of *T. caerulescens* in the soil mixture with 1% contaminated soil.

studies. Plant-specific factors, however, play a role as well. The La Calamine ecotype used in our study, which originates from the north-east of Belgium, is known to lack a constitutive Cd hyperaccumulation trait (Assunção et al., 2003) whereas the Ganges ecotype from the south of France used by Lombi et al. (2001) and Hammer and Keller (2002) is a hyperaccumulator of both Cd and Zn. Although the shoot dry matter produced by *T. caerulescens* was lower than the amount produced by *L. hartwegii* (Fig. 1), total removal of Cd and Zn was much higher (Table 3). This is due to the higher Cd and Zn contents in *T. caerulescens* (Table 2), which compensated for the effect of a lower shoot dry matter production.

3.2 Relationship between heavy metal concentration in soil solution and heavy metal soil content

In Table 4, pH and concentrations of DOC and HMs measured in the soil solution samples from the pot experiments with *L. hartwegii* and *T. caerulescens* are presented. For *L. hartwegii*, these properties were measured in samples collected at three consecutive sampling events. No consistent trends in the soil

Table 3 Total removal[a] of HMs from soil by harvesting of the *L. hartwegii* and *T. caerulescens* shoots

Katowice (%)	Cd (μg pot^{-1})		Pb (μg pot^{-1})		Zn (mg pot^{-1})	
	L. hartwegii	*T. caerulescens*	*L. hartwegii*	*T. caerulescens*	*L. hartwegii*	*T. caerulescens*
0.0	7.5±2.4	7.5	bd[b]	bd	3.4±1.3	15.5
0.1	36.6±14.8	24.2±0.7	bd	bd	6.2±2.1	41.3±6.6
0.2	70.5±6.5	81.3±14.5	55.4±6.0	bd	7.3±0.8	35.7±4.0
0.5	77.8±15.1	127±63	48.6±7.4	bd	5.8±0.9	26.8±17.5
1.0	354±149	na[c]	304±135	na	20.9±8.5	na
1.5	299±69	469	244±79	66.2	16.7±3.8	39.5
3.0	311±84	1,180	282±97	137	16.3±4.9	65.3
8.0	15.5±7.1	4,213±968	19.8±5.1	651±81	0.41±0.20	76.6±14.9

[a] Total removal of HMs from soil was calculated by multiplying the HM contents of the plant shoots with the shoot dry matter. Values represent average ± SE calculated over treatment (duplicate pots).

[b] Below detection limit.

[c] No plant material was available for HM analysis, because there was no growth of *T. caerulescens* in the soil mixture with 1% contaminated soil.

Table 4 Properties of the soil solution samples obtained from the pot experiments with *L. hartwegii*[a] and *T. caerulescens*[b]

Katowice (%)	pH		DOC (mg C l^{-1})		Cd (µg l^{-1})		Pb (µg l^{-1})		Zn (mg l^{-1})	
	L. hartwegii	*T. caerulescens*	*L. hartwegii*	*T. caerulescens*	*L. hartwegii*	*T. caerulescens*	*L. hartwegii*	*T. caerulescens*	*L. hartwegii*	*T. caerulescens*
0.0	5.7±0.2	5.8±0.1	50.8±6.4	62.0±17.6	1.4±0.2	2.0	bd[c]	bd	0.2±0.1	0.2±0.1
0.1	5.4±0.1	6.2±0.6	65.9±8.7	72.6±22.3	4.2±1.6	1.2	bd	bd	0.3±0.1	0.1
0.2	5.8±0.3	6.0±0.2	82.0±7.3	51.1±9.2	34.9±19.9	9.4±7.2	13.2	bd	1.4±0.5	0.3±0.2
0.5	5.7±0.2	6.4±0.4	65.7±8.4	68.8±4.4	40.6±9.6	16.2±10.2	14.9±1.2	bd	2.0±0.3	0.6±0.1
1.0	5.6±0.1	5.6±0.3	64.7±11.3	37.7±5.4	81.8±28.8	129±75	48.0±7.7	31.3±13.3	3.9±1.1	5.9±1.9
1.5	5.6±0.1	5.8±0.5	46.8±6.0	41.7±11.0	116±37	316±250	60.5±7.3	51.0±2.1	4.9±1.4	6.3±3.3
3.0	6.5±0.2	6.4±0.5	47.8±12.3	42.8±16.6	994±290	367±247	bd	79.6±11.6	36.0±8.5	11.9±8.5
8.0	5.8±0.1	6.8±0.1	39.6±11.1	67.0±11.0	2,670±342	1,315±87	399±66	136±4	68.3±8.2	20.5±1.5

[a] Values represent average ± SE calculated over treatment and three sampling events.

[b] Values represent average ± SE calculated over treatment (duplicate pots).

solution properties were found. Hence, data from these sampling events were averaged.

In a fading out experiment, the properties of the uncontaminated soil used to dilute the contaminated soil should be as similar as possible to those of the latter one in order to avoid changes in the solubility of HMs. With constant soil properties, the HM concentration in the soil solution of the soil mixtures depends only on the sorbed HM content in soil. Since we mixed relatively small amounts of contaminated soil with relatively large amounts of uncontaminated soil, properties of the soil mixtures are dominated by those of the uncontaminated soil resulting in little variation in organic matter and clay content. The reasonably small differences in organic matter and clay content between the uncontaminated and contaminated soils (Table 1) further minimised variation in these properties. However, soil solution properties such as pH and especially DOC varied considerably (Table 4), and can thus affect the solubility of HMs (Temminghoff, van der Zee, & de Haan, 1997). For *L. hartwegii* and *T. caerulescens*, pH varied between 5.4 and 6.8 whereas DOC was in the range of 37.7 to 82.0 mg C L^{-1}. To test whether pH and DOC should be taken into account in addition to the sorbed HM content in soil for predicting the HM concentration in soil solution, we used the following equation:

$$\log\left[\mathrm{HM}_{\text{soil solution}}\right] = a + b\ \log\left[\text{sorbed HM}_{\text{soil}}\right] + c\ \mathrm{pH} + d\ \log \mathrm{DOC} \qquad (1)$$

with: the dissolved HM concentration in µg l^{-1}, the sorbed HM content in mg kg^{-1}, and DOC in mg C l^{-1}; *a*, *b*, *c*, and *d* are regression coefficients. Overall, the sorbed HM content was the most important soil property (Table 5). All *b*-coefficients were larger than 1. Hence, the HM concentration in soil solution increases with the sorbed HM content in a non-linear manner. For the regression models of Pb and Zn, pH contributed significantly (Table 5). The negative sign of the *c*-coefficient is consistent with findings reported in the literature; with an increase in pH, the solubility of HMs in soil decreases due to increased HM binding resulting from an increased net negative surface charge on organic matter and metal oxides at higher pH levels (McBride, 1994). In most soil solution samples from the pot experiment with *T. caerulescens*, the Zn concentration was lower than in the samples from the corresponding soil mixtures of the pot experiment with *L. hartwegii* (Table 4).

Table 5 Summary of multiple regression analyses on soil properties controlling the solubility of HMs (μg l^{-1}) in the pot experiments with *L. hartwegii* and *T. caerulescens* (Eq. 1)

HM	*a*	*b*	*c*	*d*	R^2_{adj} [a] (%)	*n*
Cd	1.10±0.08***	1.25±0.09***	ns[b]	ns	79.5***	51
Pb	0.79±0.36*	1.27±0.07***	−0.42±0.06***	0.43±0.12**	93.6***	29
Zn	2.04±0.65**	1.57±0.09***	−0.25±0.12*	ns	84.4***	56

[a] Statistical significance: *for $P<0.05$, **for $P<0.01$, and ***for $P<0.001$.

[b] Not significant.

This is due to the higher pH of the soil solution samples from the pot experiment with *T. caerulescens* leading to a lower Zn solubility (Table 4). In contrast to studies of McBride et al. (1997), Sauvé et al. (2000), and Tipping et al. (2003), however, no significant pH effect was found for Cd. Apparently, variation in pH was too small to contribute significantly to the regression model for Cd. Moreover, DOC was an important property for Pb (Table 5). Since the sign of the *d*-coefficient was positive, the solubility of Pb increases with DOC. This is not surprising, because of the dominance of Pb-organic complexes generally found in soil solution (Stevenson, 1994).

3.3 Relationship between plant uptake and heavy metal concentration in soil solution

The Cd and Pb contents of *L. hartwegii* and *T. caerulescens* clearly increased with the HM concentration in soil solution (Fig. 2a and b). This behaviour is very typical for indicator plant species (McGrath et al., 2000). The results found for Cd are not surprising, because both plant species are known to lack a constitutive Cd hyperaccumulation trait (Assunção et al., 2003). With regard to uptake of Zn, however, *L. hartwegii* and *T. caerulescens* showed a very different behaviour (Fig. 2c). In the shoots of *L. hartwegii*, Zn uptake clearly increased with the Zn concentration in soil solution. In contrast, the Zn content of *T. caerulescens* depended much less on the Zn concentration in soil solution. Enabled by a high-affinity uptake mechanism for Zn in the roots, *T. caerulescens* can accumulate large amounts of Zn at a relatively constant rate from soil solution over a wide range of Zn concentrations (Pence et al., 2000). This trait is very typical for Zn hyperaccumulators (McGrath et al., 2000), and has been reported many times before for different ecotypes of *T. caerulescens* (La Calamine and Le Prayon) originating from the north-east of Belgium (Assunção et al., 2003; Baker et al., 1994; Hutchinson

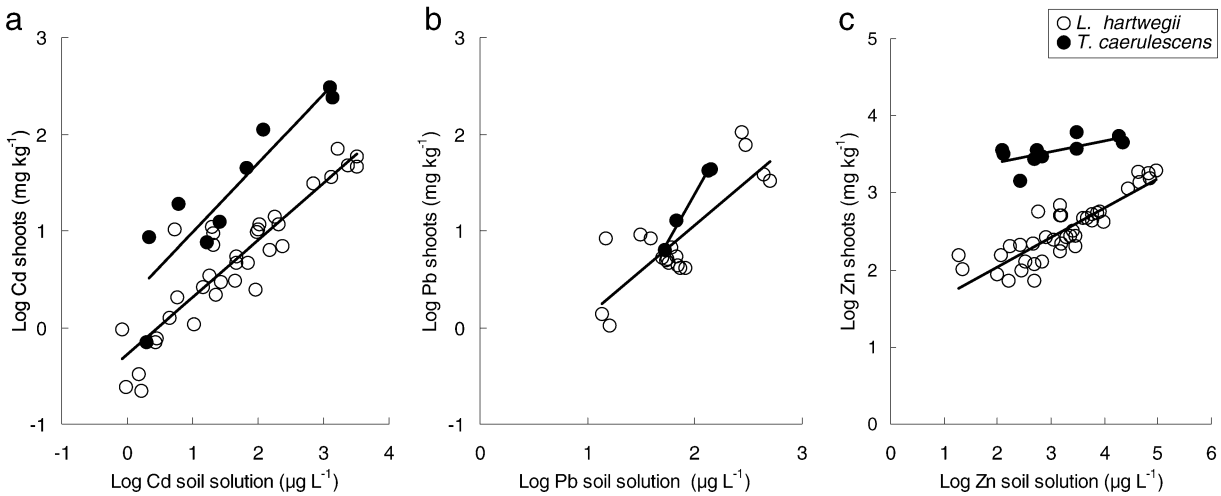

Fig. 2 Contents of Cd (**a**), Pb (**b**), and Zn (**c**) in the shoots of *L. hartwegii* and *T. caerulescens* plotted against the HM concentrations in soil solution. To guide the eye, lines fitted to the results using linear regression analysis have been added

Table 6 Summary of multiple regression analyses on soil solution properties controlling HM uptake (mg kg^{-1} dm) into the shoots of *L. hartwegii* and *T. caerulescens* (Eq. 2)

Plant species	HM	*a*	*b*	*c*	*d*	R^2_{adj} [a] (%)	*n*
L. hartwegii	Cd	−0.28±0.09**	0.59±0.05***	ns[b]	ns	81.5***	37
	Pb	0.91±0.49 ns	0.88±0.12***	ns	−0.98±0.25**	81.7***	21
	Zn	1.93±0.29***	0.35±0.04***	ns	−0.33±0.14*	77.3***	41
T. caerulescens	Cd	0.27±0.19 ns	0.72±0.11***	ns	ns	83.3***	11
	Pb	−3.53±0.08*	1.67±0.03*	0.23±0.02*	ns	100.0*	4
	Zn	3.12±0.18***	0.14±0.06*	ns	ns	33.7*	11

[a] Statistical significance: *for $P<0.05$, **for $P<0.01$, and ***for $P<0.001$.

[b] Not significant.

et al., 2000; Lombi, Zhao, Dunham, & McGrath, 2000; McGrath et al., 2000).

Uptake of HMs by plants can be predicted from the solubility of HMs. However, since pH and DOC varied considerably (Table 4), as was mentioned previously, it was tested whether these soil solution properties should be taken into account in addition to the HM concentration in soil solution for predicting uptake of HMs by *L. hartwegii* and *T. caerulescens*. We used the following equation:

$$\log\left[\mathrm{HM}_{\text{plant shoots}}\right] = a + b\ \log\left[\mathrm{HM}_{\text{soil solution}}\right] + c\ \mathrm{pH} + d\ \log \mathrm{DOC} \qquad (2)$$

with: the HM content in the plant shoots in mg kg^{-1} dm. As expected, the HM concentration in soil solution was the most important soil solution property in predicting the HM contents of *L. hartwegii* and *T. caerulescens* (Table 6). In most cases, the *b*-coefficient was smaller than 1. Hence, the HM content in the plant shoots increases with the HM concentration in soil solution in a non-linear manner. For Cd, the *b*-coefficients found for both plant species were reasonably similar. For Zn, however, the *b*-coefficient for *T. caerulescens* was much lower than for *L. hartwegii*, due to the Zn hyperaccumulation trait of *T. caerulescens*. The pH contributed only significantly to the regression model of the Pb content in *T. caerulescens* (Table 6). The sign of the *c*-coefficient was positive. For plants grown in a system with both soil and roots, pH usually has a negative effect on uptake of HMs (e.g., Smith, 1994). For plants grown in water cultures, however, the opposite has been found (Lexmond & van der Vorm, 1981;

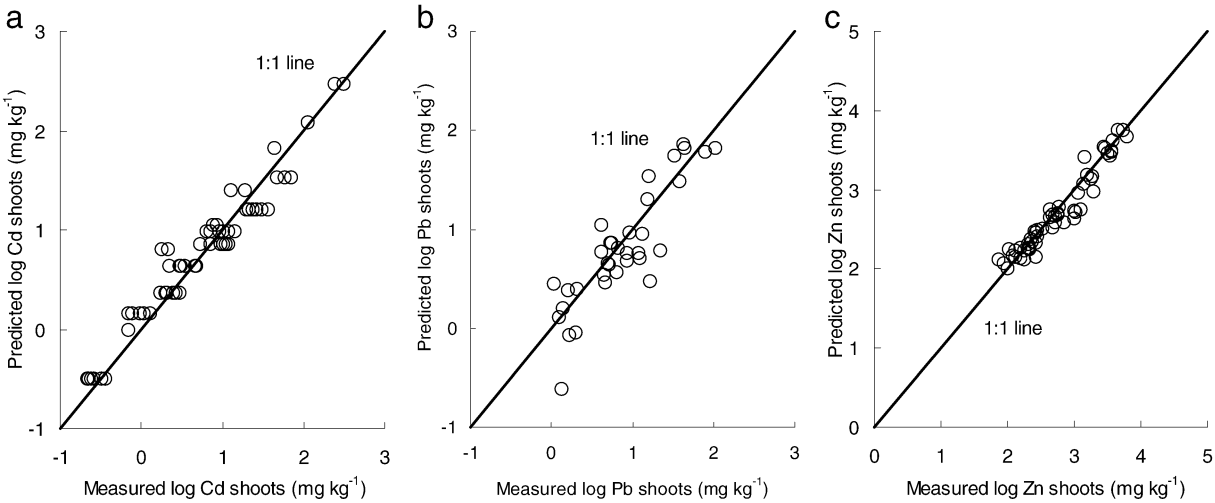

Fig. 3 Measured contents of Cd (**a**), Pb (**b**), and Zn (**c**) in the shoots of *L. hartwegii* and *T. caerulescens* plotted against predicted HM contents. Predictions were made using the regression models derived for the relationships between the HM concentrations in soil solution and soil properties (Table 5) and the HM contents in plant shoots and the solubility of HMs (Table 6)

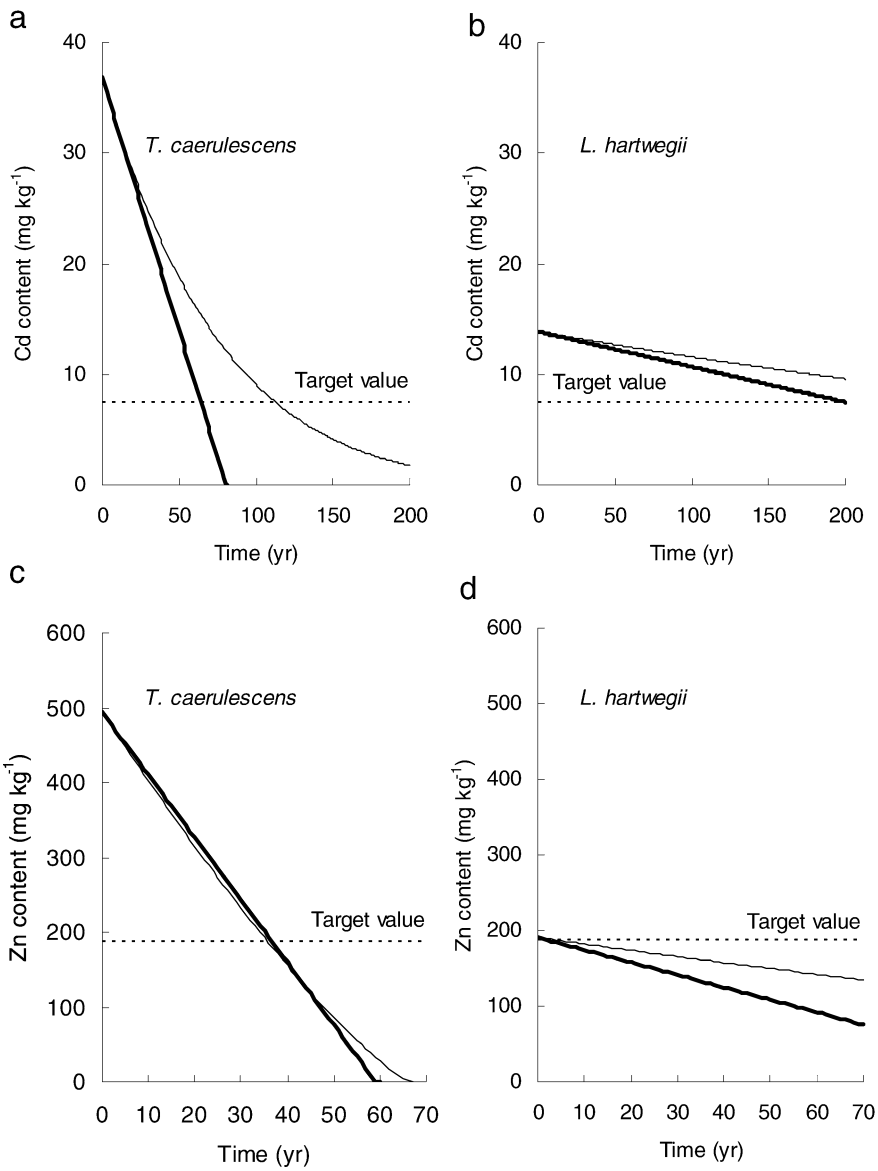

Fig. 4 Modelled decrease of the sorbed contents of Cd (**a** and **b**) and Zn (**c** and **d**) with time, predicted by either assuming a constant HM content in the plant shoots (*thick line*) or by calculating the HM content in the plant shoots as a function of the HM concentration in soil solution (*thin line*), both in the absence of HM leaching. The number of harvests required to complete phytoextraction can be read from the *x*-axis of the figure as the number of years assuming one annual harvest. The target levels represent the Dutch intervention values for HMs above which soil remediation is required

Weng et al., 2003). These contrasting effects of pH on plant uptake of HMs may be the result of competition for HM binding by different reactive surfaces, including those of the soil and plant roots (Plette, Nederlof, Temminghoff, & van Riemsdijk, 1999). In a system with both soil and plant roots, the reactive soil surfaces may out compete the plant root surface for HM binding, so the overall effect of pH on plant uptake of HMs will be negative. When only the relationship between the HM content in plants and HM concentration in soil solution is taken into consideration, the pH effect will be positive (Plette et al., 1999). For the regression models of the Pb and Zn contents in *L. hartwegii*, a significant and negative contribution was found for DOC (Table 6). Complexation of HMs with DOC usually decreases HM availability for plants (Kalis, Temminghoff, Weng, & van Riemsdijk, 2006; Song et al., 2004).

3.4 Estimation of phytoextraction duration

Based on the fading out approach, we established soil—soil solution and soil solution—plant relationships (Tables 5 and 6), and compared predicted HM contents

in the shoots of *L. hartwegii* and *T. caerulescens* with measured HM contents (Fig. 3). The sorbed HM contents and pH and DOC concentrations were used as input in the regression models describing the soil—soil solution relationships (Table 5) to calculate the HM concentrations in soil solution. In turn, the calculated dissolved HM concentrations and soil solution properties were used as input in the regression models describing the soil solution—plant relationships (Table 6) to calculate the shoot HM contents. For all HMs, agreement between predicted and measured values was reasonably good for most samples.

The regression models were implemented in a HM mass balance model to estimate the time required to realize the target levels for HMs in the soil mixtures with 3 and 8% contaminated soil using *L. hartwegii* and *T. caerulescens* for phytoextraction, respectively. In Fig. 4, the predicted decrease of the sorbed HM content in soil has been plotted against time. These calculations were done without considering leaching of HMs from soil as an output term so we can clearly show the effect on the predicted phytoextraction duration of using the experimental soil—soil solution—plant relationships instead of constant plant uptake. For *T. caerulescens*, the Cd content decreased in a linear manner with constant uptake whereas the decrease was non-linear when uptake was dependent on the Cd concentration in soil solution (Fig. 4a). The non-linearity of the decrease in the Cd content can be explained when the soil—soil solution and soil solution—plant relationships established for *T. caerulescens* (Tables 5 and 6) are combined in a single equation:

$$\log\left[\mathrm{Cd}_{T.\ caerulescens}\right] = 1.06 + 0.89\ \log\left[\text{sorbed Cd}_{\text{soil}}\right] \quad (3)$$

This relationship has a non-linear character, which results in a non-linear decrease of the Cd content in soil during phytoextraction. Using HM concentration-dependent uptake, the time required to realize the target level for Cd was much longer (114 year) than the estimate based on constant uptake (64 year). For *L. hartwegii*, the target level was realized not earlier than after 332 year using HM concentration-dependent uptake whereas the duration was 205 year based on constant uptake (Fig. 4b). Our results clearly illustrate the non-linear effect of the decrease in uptake of HMs by plants once the HM content in soil starts to decrease. This aspect of the non-linear relationship between soil and plant is crucial in the evaluation of phytoextraction as a tool to remediate HM contaminated soils. This aspect has been explored before in studies performed by Brown, Chaney, Angle, and Baker (1994), McGrath et al. (2000), Robinson et al. (1998), and Zhao et al. (2003).

Zhao et al. (2003) combined data sets from different field surveys and field and pot experiments published in the literature to derive a regression model which describes Cd uptake into *T. caerulescens* shoots as a log-linear function of the Cd content in soil, analogous to our Eq. 3. The model relates to the Le Prayon and British ecotypes which lack a constitutive Cd hyperaccumulation trait, similar to the La Calamine ecotype. Using the model of Zhao et al. (2003) in combination with our input parameters (see Materials and Methods for details), the estimated time required to realize the target level for Cd in the soil mixture with 8% contaminated soil was much longer (>300 year) than the duration estimated from our model. Although the slope of our model was in good agreement with the value found by Zhao et al. (2003) (0.89 versus 0.83), our intercept was higher (1.06 versus 0.28). Measured and modelled uptake of Cd by *T. caerulescens* was higher in our pot experiment (Table 2) explaining why our estimate of the phytoextraction duration was much shorter. This is likely the result of a higher solubility of Cd in our soil mixtures (Table 4) whereas Cd may have been present in the more occluded forms in the soils used by Zhao et al. (2003). A comparison of the results obtained by Zhao et al. (2003) with the outcome of this study clearly demonstrates the need for a soil-specific tool in order to obtain a reliable estimate of the phytoextraction duration for HM contaminated soils.

For *T. caerulescens* and *L. hartwegii*, the Pb content showed a very slight decrease over a period of 200 year (≈3 and ≈1%, respectively) using HM concentration-dependent or constant plant uptake (not shown). The low effectiveness of phytoextraction for Pb is due to the relatively low solubility of Pb in our soil mixtures (Table 5) and, in turn, the low Pb uptake by both plant species (Table 2). The problem of a long phytoextraction duration for remediation of Pb contaminated soils has been recognized before and this is the reason why there is so much interest in the application of synthetic chelates to increase the solubility and plant uptake of Pb in order to decrease the phytoextraction duration (e.g., Blaylock et al.,

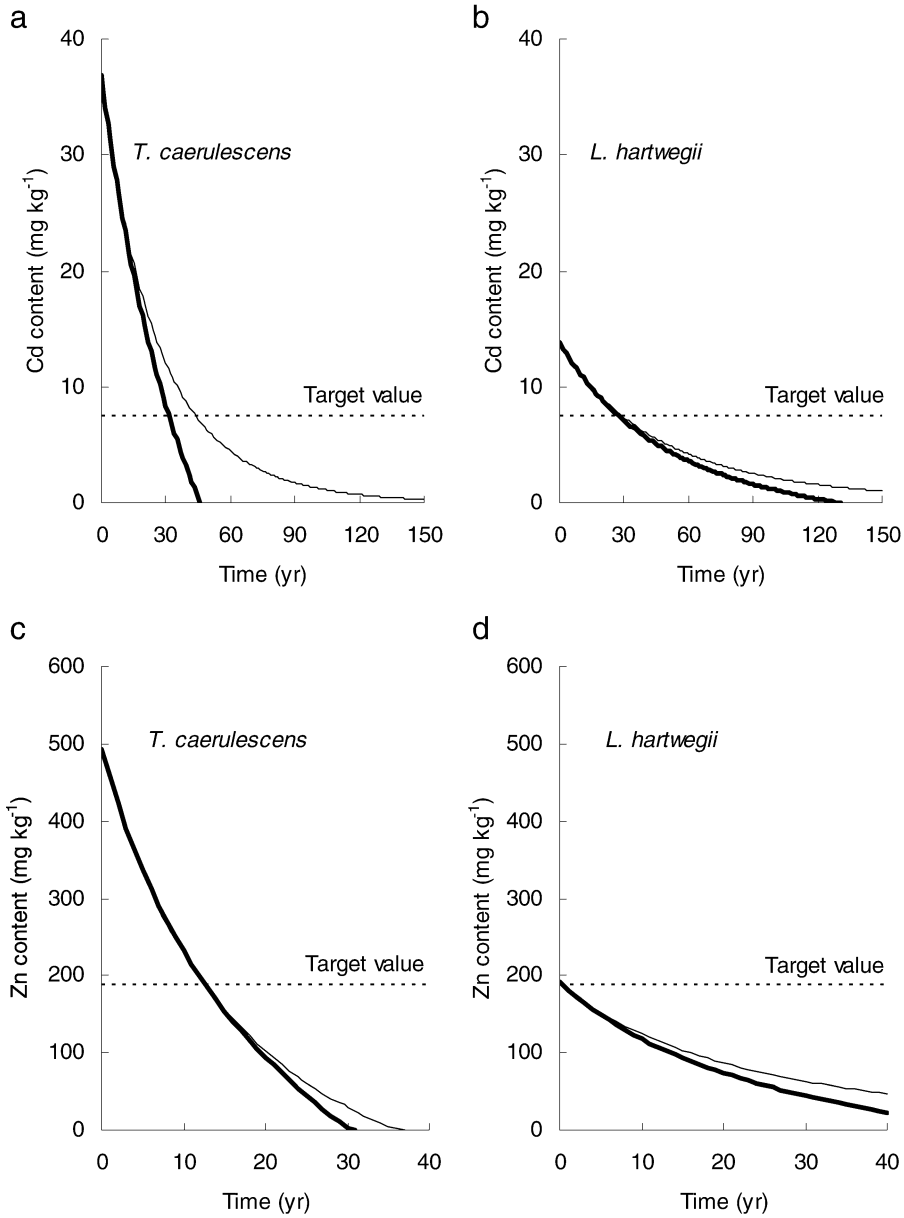

Fig. 5 Modelled decrease of the sorbed contents of Cd (**a** and **b**) and Zn (**c** and **d**) with time, predicted by either assuming a constant HM content in the plant shoots (*thick line*) or by calculating the HM content in the plant shoots as a function of the HM concentration in soil solution (*thin line*), both in the presence of HM leaching. The number of harvests required to complete phytoextraction can be read from the *x*-axis of the figure as the number of years assuming one annual harvest. The target levels represent the Dutch intervention values for HMs above which soil remediation is required

1997; Grčman et al., 2003; Huang et al., 1997; Wang et al., in press).

The difference between the decrease in the Zn content in soil with time calculated using Zn concentration-dependent or constant plant uptake is very small for *T. caerulescens* (Fig. 4c). After about 37 year, the target level for Zn was realized for both approaches. This can be explained by the relative constant rate at which *T. caerulescens* accumulates Zn from soil solution (Fig. 2c). Hence, when the uptake behaviour is typical for hyperaccumulators, the decrease of the HM content in soil can also be predicted using constant uptake. Using the regression model of Zhao et al. (2003) in combination with our input parameters, the target level was realized not earlier than after 66 year which again demonstrates the need for a soil-specific tool. For *L. hartwegii*, distinct trends in the decrease of the Zn content were found when the model calculations were performed using both approaches (Fig. 4d). However, the Zn content in the soil mixture with 3% contaminated soil was only slightly above the target level explaining why there was almost no difference

between both approaches in the time required to realize the target level (≈4 year).

The data presented in Fig. 4 have been modelled without considering leaching of HMs. However, long-term dynamic model calculations (10 to 500 year) performed by de Vries et al. (2002) demonstrated the quantitative importance of leaching for Cd and Zn. In Fig. 5, the predicted decrease of the sorbed HM content in soil has been plotted against time, with HM leaching included in the model calculations. For *T. caerulescens*, the Cd target level was realized after 45 year with Cd concentration-dependent uptake whereas it took 32 year to realize the target level assuming constant uptake (Fig. 5a). Using *L. hartwegii* for phytoextraction, the time required to realize the Cd target level estimated by both approaches was almost the same (≈30 year) (Fig. 5b). For *T. caerulescens*, the Zn target level was reached after 13 year using Zn concentration-dependent or constant uptake (Fig. 5c). For Cd and Zn, the phytoextraction duration was much shorter when leaching was included in our model calculations. Hence, leaching of Cd and Zn contributed significantly to the decrease of the HM contents in soil with time. Leaching of HMs is a serious concern because of potential HM contamination of ground- and surface waters and drinking water, leading to negative impacts on the aquatic ecosystem and human health risks (de Vries et al., 2002). Since HM leaching during phytoextraction cannot be avoided, this output term should be included in model calculations to obtain a better estimate of the phytoextraction duration.

3.5 Applicability of the fading out approach

Our fading out approach enables the user to construct a soil-specific tool to predict uptake of HMs by several plant species of interest. The coefficients in the regression models describing the plant—soil solution relationships are highly plant-specific. The methodology described and tested in our study renders an effective tool yielding the coefficients of these relationships, which can then be used to feed models for estimating the phytoextraction duration of HM contaminated soils. However, some considerations can be made regarding the applicability of the fading out approach.

Soil properties such as pH and organic matter content were assumed to remain constant during phytoextraction in our model calculations. However, pH and organic matter content may change during long-term phytoextraction and these changes obviously alter the solubility of HMs, which may affect the predicted duration before remediation is completed. For example, natural soil acidification or unbalanced nitrogen fertilization increase the availability of HMs for plant uptake due to a lower pH, but this may also reduce the biomass production (e.g., Brown et al., 1994). The combined effect of a higher bioavailability of HMs and a lower biomass production either shortens or prolongs the predicted phytoextraction duration. When designing a phytoextraction scheme, however, it can be decided to maintain the pH at a constant and agriculturally, desired level via lime application. Changes in organic matter are difficult to predict and vary depending on soil properties (e.g., soil aggregation and pH), soil biota (e.g., fungi, bacteria, and earth worms), and agricultural management practices (e.g., soil tillage and application of organic amendments) (e.g., Stevenson, 1994; Pulleman, Bouma, van Essen, & Meijles, 2000; Six, Bossuyt, Degryze, & Denef, 2004). For example, an increase of the organic matter content resulting from plant and root residues remaining in soil after harvest can prolong the predicted phytoextraction duration, because of a decrease in the availability of HMs for plant uptake due to increased HM binding to organic matter (McBride, 1994). On the other hand, a higher organic matter content can stimulate plant growth in poor soils, because it is favourable to soil structure improving rooting patterns and soil aeration and providing a higher nutrient and water supply to crops (Schmidt, 2003).

Our model predictions were based on continuous cropping of our soil mixtures by *L. hartwegii* and *T. caerulescens*. In practice, however, crops have to be rotated, because proliferation of weeds, predators, and diseases can cause a significant reduction of the biomass production (Lasat, 2000). Based on experience from crop science, short-term monocultures (2 to 3 years) are expected to be acceptable for phytoextraction before crops should be rotated (Lasat, 2000). With phytoextraction duration times such as those calculated for our soil mixtures, it is impossible to complete remediation with one plant species in monoculture. The effect of crop rotation on the phytoextraction duration depends on the plant species used for rotation and is difficult to predict. This problem, however, can be solved by carrying out

fading out experiments for all scheduled rotation crops.

In pot experiments, plant uptake of HMs usually is greater than under field conditions, because plants explore potted soil more intensely (e.g., Delorme et al., 2000). Hence, the use of our soil solution—plant relationships for model predictions in the field may have underestimated the phytoextraction duration. Further testing of the fading out approach in the field is thus necessary. On the other hand, pot experiments enable and simplify the measurement of all relevant outputs needed for HM mass balance calculations, such as the HM concentrations in soil solution. In our case, Cd and Zn leaching losses contributed significantly to the decrease of the HM contents in soil with time (Fig. 5).

In our regression models describing the soil—soil solution—plant relationships, sorbed HM pools were assumed to be in equilibrium with the HM concentrations in soil solution. However, some doubt may exist whether the incubation time of our soil mixtures was sufficient to achieve equilibrium. In our soil mixtures, surface-bound HMs form the major pool of HMs (Table 1). Similar to phosphorus bound at surface sites of metal oxides (e.g., Koopmans, McDowell, Chardon, Oenema, & Dolfing, 2002; Rietra, Hiemstra, & van Riemsdijk, 2001; van der Zee, Fokkink, & van Riemsdijk, 1987), surface-bound HMs are assumed to exhibit fast exchange kinetics with soil solution, possibly leading to a fast redistribution of sorbed HMs and a fast establishment of equilibrium between the different HM pools in our soil mixtures during incubation. Our statistically good soil—soil solution and soil solution—plant relationships support this idea (Fig. 3 and Tables 5 and 6). In calcareous soils, however, equilibrium may be more difficult to achieve due to slow dissolution kinetics of HM-carbonates. Moreover, the applicability of the fading out methodology is limited to soils with a relatively low clay content, such as those used in our experiments (Table 1). Thorough mixing of soils with a high clay content is practically not feasible without completely destroying the soil structure. Probably the most difficult part of the fading out methodology is the need for uncontaminated soil with properties similar to those of the HM contaminated soil. For example, for soils contaminated with HMs via atmospheric deposition of HMs emitted by smelters, a suitable, uncontaminated soil can be found relatively easy. However, for soils directly affected by mine and ore processing waste, this is more difficult, because these matrices can in fact not be considered as soil, and comparable, uncontaminated matrices are difficult to find. On the other hand, these matrices are usually heavily contaminated with HMs (e.g., Kucharski et al., 2005) and less appropriate for phytoextraction, due to the very long phytoextraction duration needed to complete remediation (Robinson et al., 1998; Zhao et al., 2003).

Despite the considerations previously discussed, there is a need to obtain a better insight in the expected duration of a phytoextraction scheme. In most cases, the phytoextraction duration is a crucial factor and a better estimate of the duration before remediation is completed can be of great help to decide whether or not phytoextraction is indeed a solution for a specific HM contaminated soil. As such, the fading out approach can be considered as a practical and realistic tool.

4 Conclusions

In our pot experiment, uptake of Cd, Pb, and Zn by *L. hartwegii* and *T. caerulescens* could be predicted from log-linear relationships with the in-situ measured HM concentration as the most important soil solution property. Uptake of Zn by *T. caerulescens* was, however, less dependent on the HM concentration and remained relatively constant. In turn, the HM concentration in soil solution could be predicted from log-linear relationships with the sorbed HM content as the most important soil property. Significant pH and DOC effects were found for Pb and Zn. Using the soil—soil solution—plant relationships for *L. hartwegii* and *T. caerulescens*, the phytoextraction duration to realize the Cd target level in soil was much longer than with constant uptake. Using constant uptake, the phytoextraction duration will be underestimated. With respect to uptake of Zn by *T. caerulescens*, however, the phytoextraction duration obtained by both approaches was almost the same, due to the Zn hyperaccumulating uptake behaviour of this plant species. In this case, constant uptake can be used. Including losses of Cd and Zn from soil caused by leaching in the model calculations led to a much shorter phytoextraction duration. Leaching should be accounted for when estimating the time required to remediate a HM contaminated soil using phytoextraction.

Acknowledgements The authors thank Rafał Kucharski for providing contaminated soil from Katowice and Henk Schat for providing seeds of *Thlaspi caerulescens*. This project was financed by the Chinese Ministry of Science and Technology (contract no. 2004CB720403) and the Royal Dutch Academy of Sciences (contract no. 04-PSA-E-05).

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