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Original Research

The Possibility of Using Crops as Metal Phytoremediants

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Abstract

The possibilities of using nine crops (*Beta vulgaris*, *Cichorium intybus*, *Cucurbita pepo*, *Phaseolus vulgaris*, *Hordeum vulgare*, *Brassica oleracea var. capitata*, *Zea mays*, *Medicago sativa*, and *Pastinaca sativa*) in removing metals from soil were investigated in field trials from 1999 to 2001. The aim of the study was to determine the efficiency of nine cultivated plant species in removing cadmium, chromium, copper, iron, manganese, nickel, lead, and zinc from soil. The most effective ones in cadmium, manganese, copper, nickel, lead and zinc remediation were - *Cucurbita pepo*; chromium - *Zea mays*; iron - *Medicago sativa*. The phytoremediation efficiency of the investigated crops depended both on biomass production and on the possibility of metal accumulation in tissues.

Keywords: phytoremediation, metals, biomass

Introduction

According to Brooks et al. [1] phytoremediation can be defined as the use of natural or modified plants to remove, destroy or sequester contaminants from the environment. Salt et al. [2], together with Flathman and Lanza [3], separated from phytoremediation, among other things, induced and continuous phytoextraction - defined as the use of pollutant-accumulating plants to remove metals from soil by concentrating them in harvestable parts.

According to Salt et al. [2], continuous phytoextraction is based on the genetic and physiological capacity of specialized plants to accumulate, translocate and resist high amounts of metals without symptoms of toxicity. Among plants there are differences in resistance to heavy metals, the decrease of yield being the most usual plant reaction to a high level of trace elements in soil [4]. Baker [5] suggested three types of plant-soil relationships: accumulators (where metals are concentrated in above-ground plant parts from low or high soil levels), excluders (where metal concentration in the shoot remains constant and low over a wide range of soil concentration, up to a critical soil value above which the mechanism breaks down and unrestricted transport results), and indicators (where uptake and transport of metals to the shoot are regulated so that internal concentration reflects external levels). Baker et al. [6] and Raskin et al. [7] defined hyperaccumulators which accumulate more than 0.01% Cd, 0.1% Ni, Co, Cu, Cr, Pb, and more than 1% Zn.

The small biomass and slow growth characteristics of hyperaccumulators may limit their utility for phytoremediation. Ebbs et al. [8] has suggested that a greater shoot biomass of crops can more than compensate for lower shoot metal concentration in phytoextraction techniques. The total amount of metal removed from soil is the result of the metal content in the harvestable tissues and of the plant biomass per area unit. For phytoextraction to be successful, crops should possess a sufficient accumulation of the metal intended to be extracted, fast growth with a large biomass; suitable plant phenotype for easy harvest, treatment and disposal; and tolerance to site conditions. These characteristics are common for many commer-

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Table 1. Physical and chemical characteristics of studied soil profiles.

Depth (cm)	Organic Carbon (%)	pH_{KCl}	Hh*	S**	T***	Metal concentration ($mg\cdot kg^{-1}$)							
			($me\cdot 100g^{-1}$)			Cd	Cr	Cu	Fe	Mn	Ni	Pb	Zn
0-20	1.2	4.8	0.43	29.2	29.6	0.58	1.05	7.44	1272.9	177.3	2.32	8.21	43.00
20-40	0.0	4.3	0.43	12.7	13.1	0.40	1.16	12.98	1233.7	107.2	2.16	5.13	26.81

* Hh - exchangeable acidity, ** S - total exchangeable alkalis, *** T - sorption capacity of soil

cially grown species. Some experiments were conducted to select crops suitable for phytoremediation [9, 10]. The obtained results allowed the selection of some species particularly prone to extract metals from soil, i.e. sunflower, corn, mustard, barley, and pumpkin. According to Vassiliev et al. [10], more detailed information about the biomass crops' ability to withstand metal as well as to accumulate it in the shoots is needed.

Kuboi et al. [11] divided plants into three categories according to their abilities to absorb trace elements: low accumulation (*Leguminosae*), medium accumulation (*Graminae, Liliaceae, Cucurbitaceae* and *Umbelliferae*) and high accumulation (*Chenopodiaceae, Cruciferae, Solanaceae* and *Compositae*). Tatekawa et al. [12] proved that *Compositae*, *Polygonaceae* and *Cyperaceae* accumulate high amounts of cadmium, lead, and zinc. Grodzinska et al. [13] has brought to our attention that leaf vegetables are the most effective metal accumulators in contrast to fruit and legumes. Among root vegetables, carrot contained high amounts of cadmium, red beet of lead, manganese and zinc and parsley of chromium, iron, and nickel [14, 15, 16].

The aim of the presented investigation was to determine the possibilities of using crops to remove metals from contaminated soils.

Experimental Procedures

The field experiment was conduced at the Agricultural Academy Research Station near Krakow (Poland) between 1999 and 2001, on soil classified as *Eutric Cambisols*, with loess as basement complex.

Soil Analyses

The main physical and chemical soil properties and the levels of metals were determined in samples collected from a depth of 0-20 and 20-40 cm (Table 1). The soluble metal content (Cd, Cr, Cu, Fe, Mn, Ni, Pb, Zn) was determined by atomic absorption spectrophotometry using a Varian Techtron and air/acetylene flame under standard operating conditions. The reaction was measured using a potentiometric method in 1 $mol\cdot dm^{-3}$ KCl solution. The organic carbon content was determined using Tiurin's method, based on the oxidizing of C to CO_2, using bichromate of potassium as an oxidant. Total exchangeable alkalis (S) were determined using Kappen's method; exchangeable acidity (Hh) was determined using Sokolov's method, while thesorption capacity of soil in relation to exchangeable cations (T) was calculated from the formula T = Hh+S ($me\cdot 100g$ of soil).

Plant Analyses

Nine crops were planted on experimental plots using a random block method in four replications:

- Red beet (*Beta vulgaris var. cicla* L.) – 'Wodan F_1'
- Chicory (*Cichorium intybus var. foliosum* Hegi) – 'Rubello F_1'
- Field pumpkin (*Cucurbita pepo* L. *convar. giromontiana* Greb.) – 'Astra F_1'
- Common bean (*Phaseolus vulgaris* L.) – 'Tara'
- Barley (*Hordeum vulgare* L.) - 'Stat'
- White cabbage (*Brassica oleracea var. capitata* L.) – 'Krautman F_1'
- Maize (*Zea mays* L. *convar. saccharata* Koern.) – 'Trophy F_1'
- Alfalfa (*Medicago sativa* L.) – 'Vela'
- Common parsnip (*Pastinaca sativa* L.) – 'Półdługi Biały'

Crops were harvested at the stage of harvest maturity. The fresh weight and the metal contents were determined in overground organs of chicory, field pumpkin, common bean, barley, white cabbage, maize and alfalfa, and the roots and leaves of red beet and common parsnip. Analyses of Cd, Cr, Cu, Fe, Mn, Ni, Pb, and Zn content were carried out using the ASA method.

The results were statistically evaluated using analyses of variance with the Student t test at α=0.05 and coefficients of the simple correlation between the fresh weight of plants and the amount of metals removed from the soil for the particular species.

Results and Discussion

Differences in metal contents in soil caused by growing plants depend on many factors. According to the results of the presented experiment the reduction of metal content in soil depends on the capacity of metal bioaccumulation by particular species and biomass production. Of the nine species tested, *Brassica oleracea* produced the greatest (157.1 $t\cdot ha^{-1}$) and *Cucurbita pepo* a somewhat smaller biomass (144.0 $t\cdot ha^{-1}$). The remaining species were not so effective in biomass production. Only *Hordeum vulgare* (16.6 $t\cdot ha^{-1}$) produced a biomass lower than

Table 2. Plant fresh weight and total metal removed from soil by particular plant species.

Species	Plant fresh weight (t·ha^{-1})	Cd		Cr		Cu		Fe		Mn		Ni		Pb		Zn	
		I*	II**	I	II	I	II	I	II	I	II	I	II	I	II	I	II
Beta vulgaris	71.8	1.04	145	0.7	99	7.6	1,063	252	35,111	23.5	3,279	1.9	270	3.0	425	31.2	4,340
Cucurbita pepo	144.0	2.06	143	14.8	1,028	14.1	977	468	32,528	66.5	4,617	13.2	914	12.6	875	136.3	9,465
Cichorium intybus	68.2	0.74	108	1.5	218	3.9	566	279	40,924	22.7	3,336	10.1	1,484	3.5	518	20.7	3,031
Phaseolus vulgaris	34.3	0.42	122	3.2	927	5.2	1,525	133	3,872	16.0	4,673	2.6	764	2.6	773	22.5	6,563
Hordeum vulgare	16.6	0.57	343	14.3	8,639	3.6	2,175	226	136,145	16.8	10,120	8.7	5,271	4.6	2,765	39.5	23,801
Brassica oleracea var. capitata	157.1	1.49	95	3.8	243	6.2	398	105	6,703	31.6	2,011	4.8	306	8.3	528	29.5	1,878
Zea mays	92.7	0.93	100	16.6	1,789	9.6	1,033	201	21,694	23.5	2,534	10.4	1,118	4.2	456	45.0	4,855
Medicago sativa	45.9	1.26	275	10.3	2,246	12.4	2,693	701	152,767	46.9	10,218	6.2	1,359	11.7	2,542	43.8	9,536
Pastinaca sativa	83.1	1.25	150	8.6	1,036	11.4	1,375	279	33,622	30.0	3,609	8.6	1,041	6.1	734	37.9	4,556
LSD	7.3	0.14	69	0.7	802	0.5	658	30	65,448	1.7	1,970	0.5	666	0.6	906	13.0	4,714

*I - total metal removed from soil by plant species (mg·m^{-2}·year^{-1}), **II – total metal removed in 1 t of biomass (mg·t^{-1} f.w.)

that recommended by Huang and Cunningham [9] for remediants (20 t·ha^{-1}) (Table 2). According to Ebbs et al. [8] and to Ebbs and Kochian [17], biomass production is a more significant factor in phytoextraction than the accumulating properties of particular species. Increasing plant biomass should enhance metal removal and increase the usefulness of tested species for phytoremediation.

Important differences were found in the accumulation of particular metals as a result of their chemical properties and as a consequence of differences in absorption by roots and translocation to overground plant organs. The possibility of using growing plants, i.e. vegetables, as phytoremediants depends exactly on the distribution of metals among plant organs [18].

Cadmium is readily absorbed by roots and transported to shoots and its distribution among plant organs is regular. Plants can accumulate high amounts of this element, although its concentration in the soil is low [19]. Escarre et al. [20] compared the growth, tolerance and metal hyperaccumulation of *Thlaspi caerulescens* from metal contaminated and uncontaminated soils. They found that the individuals from metal-contaminated soil accumulated twice as much cadmium but three times less zinc than those from uncontaminated soil. The results of the presented investigation show that the most effective species in cadmium bioaccumulation were *Hordeum vulgare* (343 mg·t^{-1} f.w.) and *Medicago sativa* (275 mg·t^{-1} f.w.) (Table 2). Other species showed a similar efficiency in cadmium accumulation. *Brassica oleracea* removed from the soil the least cadmium in its biomass (95 mg·t^{-1} f.w.), but due to the greatest biomass production this species was very effective in cadmium removal from surface units (1.49 mg·m^{-2}·year^{-1}). *Pastinaca sativa,* in spite of having twice as large a biomass as *Medicago sativa*, removed a similar amount of cadmium from the soil (respectively 1.25 and 1.26 mg·m^{-2}·year^{-1}). The most effective species in the phytoextraction of this element was *Cucurbita pepo* (2.06 mg·m^{-2}·year^{-1}). Because of low plant fresh weight, *Hordeum vulgare* and *Phaseolus vulgaris* were not effective in cadmium remediation. The reported results show that the efficiency of cleaning soils polluted with cadmium depends not only on biomass production but is also related to possibilities of particular species for metal accumulation in harvestable organs.

Chromium is predominantly immobilized in the roots with much less of the total Cr in the leaves [21]. The translocation of chromium from roots to shoots is extremely limited and its accumulation by roots is 100-fold higher than by shoots, regardless of the investigated species [22]. According to Chaney et al. [23] plants accumulating more than 0.1- 5.0 mg·kg^{-1} d.w. of Cr in the shoot, can be used as hyperaccumulators. Among the investigated crops, the highest amount of chromium was found in the biomass of *Hordeum vulgare* (8,639 mg·t^{-1} f.w.). Effective chromium accumulators were also *Zea mays* and *Medicago sativa*. Zayed et al. [22] found that the highest chromium concentrations were detected in members of the *Brassicaceae* family (among 18 vegetables from different families). The presented results do not support this. It was stated that the most effective species in chromium phytoextraction was *Zea mays* (16.6 mg·m^{-2}·year^{-1}), followed by *Cucurbita pepo* (14.8 mg·m^{-2}·year^{-1}) and *Hordeum vulgare* (14.3 mg·m^{-2}·year^{-1}). It is interesting that *Hordeum vulgare*, in spite of the lowest biomass production, was very effective in the remediation of chromium.

The copper content in plant tissues is proportional to its concentration in the soil solution [24, 25]. *Medicago sativa* accumulated in the biomass 2,693 mg·t^{-1} f.w. of copper; *Hordeum vulgare* 2,175 mg·t^{-1} f.w. The above-mentioned species were the most effective in copper bio-

Table 3. Simple correlation coefficients between the amount of metal removed from the soil and the fresh matter of plants (r significant at α=0.05*; α=0.01**; α=0.001***).

	Cd	Cr	Cu	Fe	Mn	Ni	Pb	Zn
Beta vulgaris	-0.9237***	-0.3603	-0.7938***	0.2092	-0.9548***	-0.8833***	-0.2429	-0.9234***
Cucurbita pepo	0.5294	0.7179**	0.7464**	0.8281***	0.7590**	0.8662***	0.5831*	0.8473***
Cichorium intybus	0.5105	0.8820***	0.7342**	-0.5246	0.6713**	0.7289**	0.5417*	-0.4480
Phaseolus vulgaris	-0.2161	0.5989*	0.3291	0.6010*	-0.2644	0.7126**	0.6313*	0.5788*
Hordeum vulgare	0.8851***	0.5606*	0.7174**	0.8689***	0.6455*	0.4393	0.8846***	0.6489*
Brassica oleracea var. capitata	-0.2225	0.6284*	-0.5924*	0.5502*	0.7187**	0.6940**	0.7035**	0.7017**
Zea mays	0.8830***	0.9027***	0.9107***	0.8002***	0.8714***	0.8844***	0.8913***	0.8891***
Medicago sativa	0.2829	-0.2617	-0.1816	0.4237	0.3979	-0.5989*	0.0016	-0.5772*
Pastinaca sativa	0.4003	0.4589	0.1838	-0.1971	0.6218*	0.0047	-0.1925	-0.5565

accumulation as opposed to *Brassica oleracea*, characterized by the lowest concentration of this element in the fresh matter (398 mg·t^{-1} f.w.). *Cucurbita pepo*, as a result of high biomass production, was the most effective species in removing copper from soil (14.1 mg·m^{-2}·year^{-1}). There were no statistical differences between the amounts of copper removed from the soil by *Cichorium intybus* (3.9 mg·m^{-2}·year^{-1}) and *Hordeum vulgare* (3.6 mg·m^{-2}·year^{-1}), although the fresh weight of *Cichorium intybus* was three times higher than that of *Hordeum vulgare*.

Plants contain great amounts of iron in their tissues, which is due to the important physiological function of this element. The most effective plants in iron removal from the soil were *Medicago sativa* (701 mg·m^{-2}·year^{-1}) and *Cucurbita pepo* (468 mg·m^{-2}·year^{-1}) despite the three-fold lower fresh weight of *Medicago sativa*. Phytoremediation efficiencies of *Beta vulgaris*, *Cichorium intybus* and *Hordeum vulgare* were comparable despite differences in biomass production. *Medicago sativa* accumulated the highest amount of iron in its biomass (152,767 mg·t^{-1} f.w.) and it is the main reason for the remediation efficiency of that species. In the case of *Cucurbita pepo*, the main factor crucial for iron remediation was the high fresh weight of this species.

Manganese was most effectively accumulated in tissues of *Medicago sativa* and *Hordeum vulgare* (respectively 10,218 and 10,120 mg·t^{-1} f.w.). The most effective species in removing manganese from the soil was *Cucurbita pepo* (66.5 mg·m^{-2}·year^{-1}), because of the high fresh matter yield. Remediation efficiency of the remaining species varied between 46.9-16.0 mg·m^{-2}·year^{-1}.

Nickel is readily transported from roots to overground plant tissues, where it is accumulated in high amounts [26]. The possibility of nickel accumulation among the investigated species oscillated within the range 270 (*Beta vulgaris*) – 5,271 (*Hordeum vulgare*) mg·t^{-1} f.w. Phytoremediation efficiency was highest in the case of *Cucurbita pepo* (13.2 mg·m^{-2}·year^{-1}), as a result of the high biomass production of the mentioned species. *Cichorium intybus* and *Zea mays* were also good remediants of this element.

Lead is accumulated particularly in plant roots and tissues rich in cellulose because of the limited mobility of this element. Brennan and Shelley [27] found that in maize lead is taken up into the root symplast, where its precipitation as Pb-phosphate occurs rapidly. Only relatively small amounts of lead are able to leak back out of the roots. This results in difficulties when using plants for phytoextraction of lead from polluted soils [28]. Among nine investigated crops, *Hordeum vulgare* and *Medicago sativa* were the best lead accumulators (respectively 2,765 and 2,542 mg·t^{-1} f.w.). *Cucurbita pepo* (12.6 mg·m^{-2}·year^{-1}) and *Medicago sativa* (11.7 mg·m^{-2}·year^{-1}) were the most effective species in lead remediation. In the case of *Cucurbita pepo* this resulted from high biomass production. *Medicago sativa* is characterized by a high probability of lead bioaccumulation.

Zinc occurs in soil mainly in the form of oxides and also in combination with organic matter [25]. Plants easily accumulate zinc in overground organs. The phenomenon of resistance of plants to high levels of zinc in tissues can be a factor favouring lead phytoextraction [29]. Schwartz et al. [30] showed that the root system of *Thlaspi caerulescens* grows better in zinc-contaminated soils. However, this species cannot be used as hyperaccumulator because of the too low zinc concentrations in its tissues (>0.1%). The effects of the presented investigations show that *Hordeum vulgare* considerably exceeds the remaining species in zinc bioaccumulation (23,801 mg·t^{-1} f.w.) but, because of low biomass, the efficiency of *H. vulgare* in the remediation of this element was not significant (39.5 mg·m^{-2}·year^{-1}). Here *Cucurbita pepo* was distinguished (136.3 mg·m^{-2}·year^{-1}). The remaining species removed from soil between 20.7-45.0 mg·m^{-2}·year^{-1} of zinc.

According to Baker et al. [6], interdependence between fresh biomass production and the effectiveness of phytoextraction is the basis for including species among indicators. Simple correlation coefficients between the amount of metal removed from soil and the fresh matter of plants, reported in Table 3, indicated i.e. that *Hordeum vulgare* and *Zea mays* could be good indicators for cadmium and lead, *Cichorium intybus* and *Zea mays* for chromium, *Zea mays* for copper, *Cucurbita pepo, Hordeum vulgare* and *Zea mays* for iron. Negative correlation was observed in the case of *Beta vulgaris* between the biomass and the level of Cd, Cu, Mn, Ni, and Zn accumulated from the soil surface. Yield enhancement is a possible method for increasing the remediation efficiency of species where positive correlation between biomass production and phytoremediation was observed.

Conclusions

1. The phytoremediation efficiency of investigated crops depended on biomass production and the possibility of metal accumulation.
2. Among the investigated species only *Hordeum vulgare* (16.6 t·ha^{-1}) produced a biomass lower than that recommended by the literature for remediants (20 t·ha^{-1}).
3. The use of the investigated species as remediants should depend on the type of contamination, because of differences in the removal of particular elements from the soil. The most effective in cadmium, manganese, copper, nickel, lead and zinc remediation was *Cucurbita pepo*; chromium - *Zea mays*; and iron - *Medicago sativa*.
4. In the case of crops that show a positive correlation between biomass production and remediation efficiency, it is advisable to use agrotechnical methods to increase yield.

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