Geophysical Research Abstracts, Vol. 7, 03285, 2005
SRef-ID: 1607-7962/gra/EGU05-A-03285

Alternatives for Phytoextraction: Biomass Plants versus Hyperaccumulators

C. Keller and D. Hammer

Ecole Polytechnique Fédérale de Lausanne, Switzerland

Introduction

Phytoextraction has been proposed as a suitable alternative to destructive techniques used so far to clean up soils contaminated with heavy metals. Indeed, the use of plants to remove metals from soils is environmental friendly and its cost is low compared to engineering-based techniques such as soil capping, soil washing, vitrification, landfilling etc.... At present, there are two main phytoextraction strategies available: the first is the use of hyperaccumulators [1, 2]. These plants are wild species that can accumulate large amounts of specific metals in their shoots, but they are often slowly growing (low biomass plants). Hyperaccumulation implies concentrations in dry matter above 0.01% for Cd and 1% for Zn [3, 4]. The second strategy is the use of fast growing plants (high biomass plants) that are usually not metal-specific and have low to average heavy metal concentrations [5, 6]. A comparison of both approaches is presented using results obtained at two experimental sites with the hyperaccumulator *Thlaspi caerulescens* and several high biomass crops including *Salix viminalis*.

Characteristics of the experimental sites in Switzerland

The two sites chosen to illustrate this comparison are presented in Table 1. They are agricultural soils moderately contaminated with metals (mostly Cu, Zn, Cd and Pb) and no significant organic contamination. The Dornach site, NW Switzerland, has been described elsewhere [7]. The source of the heavy metal contamination was a nearby brass-smelter emitting Cu, Zn and Cd in particulate form until the mid 1980's. The soil has been classified as calcaric regosol [8]. The Caslano site in southern Switzerland was contaminated with sludges from septic tanks spread on the site for 20 years until 1980. This has led to enrichment of the topsoil of the fluvisol with both organic matter and heavy metals (Cd, Cu, and Zn).

Experiments were performed with crop plants (tobacco, maize, Indian mustard, sunflower and/or bioenergy plants (*Salix viminalis*) and, hyperaccumulators (*Thlaspi caerulescens*, *Alyssum montanum*, *Iberis intermedia*) on mini-plots. Both experiments were conducted according to agronomic standards. Detailed descriptions of the experiments can be found elsewhere [7, 9].

Table 1: Site descriptions (after [7, 9, 10]). Soil parameters are average values with standard deviations given in brackets.

	Dornach	**Caslano**
Location	Jura edge	Southern Alps
Nb samples for analysis 0-0.2m	20	4
pH	7.2	4.9
% clay	$30^{(a)}$	12
% organic carbon	$2.5^{(a)}$	5.2
Total Zn in mg $kg^{-1(b)}$	645 (81)	1158 (216)
Total Cu in mg kg^{-1}	525 (62)	264 (43)
Total Cd in mg kg^{-1}	2.0 (0.4)	2.8 (0.7)
Other metals	-	As, Hg, Sn, Pb
Soluble Zn in mg $kg^{-1(c)}$	0.08 (0.03)	7.4 (5.9)
Soluble Cu in mg kg^{-1}	0.7 (0.2)	0.4 (0.1)
Soluble Cd in mg kg^{-1}	2.0 (0.6)	13 (11)

$^{(a)}$:3 samples; $^{(b)}$: Total = Extraction HNO_3 2M; $^{(c)}$ Extraction $NaNO_3$ 0.1M [11]

Hyperaccumulator plants versus high biomass plants: yield and concentrations

Hyperaccumulators are metal specific and are usually wild plants with a small biomass and a slow growth under temperate climate. Their agronomic requirements are poorly known and this may result in large variations of yield and metal concentrations variations annually and in different soils. Table 2 gives information on the variability of the results obtained with *T. caerulescens* at Dornach. It appeared that metal concentrations varied up to a factor of 30 depending on the population, the method used (planted or sown) and the time of the year. Presently, there are few species available for field application (lack of nurseries or seed producers) and within these species very few cultivars or populations so that the use of hyperaccumulators might have to be dismissed for remediation of large areas. Furthermore, methods to harvest the plants have to be adapted from crop species techniques and might not be always straightforward.

Table 2: Variations of the Cd, Cu and Zn concentrations in shoots of Thlaspi caerulescens *grown at Dornach, according to the population, the technique of propagation, the year and the time of the year or position within the rotation (after [9] and unpublished data).*

Year	**Population**	**Method**	**Concentrations in mg kg^{-1} in DM**			**Variability**
Rotation			**Cd**	**Cu**	**Zn**	
1997	Prayon	planted	7.1 (0.5)	75 (9)	2051 (315)	
1998	Prayon	planted	6.3 (2.2)	53 (4)	2011 (629)	
1999	Ganges	planted	184 (38)	53 (3)	5265 (612)	
2000/1	Ganges	planted	124 (21)	70 (17)	3419 (335)	
2000/2	Ganges	planted	67 (38)	91 (26)	2646 (1296)	
2000/3	Ganges	planted	49 (6)	43 (1)	3539 (313)	
2000/1	Ganges	sown	127 (47)	118 (17)	2551 (327)	
2000/2	Ganges	sown	77 (15)	52 (10)	3851 (558)	
2001	Ganges	sown	76 (24)	81 (2)	3836 (332)	
Factor Ganges 1999/Prayon 1998			29	1.0	2.6	*Inter-populations*
Factor Ganges 2000/1 /Ganges 2000/3			2.5	1.6	1.0	*Inter-harvests*
Factor Ganges 2000/1p /Ganges 2000/1s			1.0	0.6	1.3	*Inter-methods*

On the contrary, the crop and energy plants are well known plants with large yields and fast growth, but they are usually not metal specific and they accumulate below the hyperaccumulation thresholds as shown in Table 3, which presents results obtained for crop, biomass plants and *T. caerulescens* at Dornach. Crop and biomass plants have been selected for rather rich and fertilized agricultural soils and may thus not adapt easily to contaminated sites. Unlike for hyperaccumulators, there exists a large choice of species and cultivars that can be tested according to site specifications and metal tolerance. However, the same management as for the usual production may not be efficient for phytoextraction. For example, plants used for bioenergy, like *Salix* spp., are perennial plants that are left 20 to 30 years on site. From data obtained at Dornach, Cd and Zn concentrations measured in both leaves and stems of *S. viminalis* decreased with time [12] most probably because roots had progressively extended downwards, outside the contaminated layer [10] thus reducing the extraction efficiency with time. It may be necessary to remove the plants every 2 or 3 years in order to keep an optimal extraction.

Table 3: Heavy metal concentrations in shoots and roots of I. mustard, tobacco, wil-

lows, maize and T. caerulescens *in the Dornach field experiment.*

Harvest	**Plant**	**Age**		**Concentrations in shoots**				**Concentrations in roots**				**Yield**
year	**species**			**Cd**	**Cu**	**Zn**		**Cd**	**Cu**	**Zn**		
		year		**mg kg**$^{-1}$				**mg kg**$^{-1}$				**t ha**$^{-1}$
97	Indian mustard[a]		m	1.0	20	124		0.3	32	45		7.3
			sd	0.1	2	13		0.0	3	3		0.7
97	Tobacco[a]		m	3.5	38	146		0.6	26	36		12.6
			sd	0.8	6	21		0.2	2	2		2.1
98	Willows[a]	1+2	m	3.3	12	240		nd[b]	nd	nd		0.8
			sd	0.5	5	46		-	-	-		0.5
98	Maize[a]		m	0.6	10	129		0.7	38	41		15.6
			sd	0.2	1	30		0.3	11	10		3.8
99	Willows	2+3	m	3.4	14	294		nd	nd	nd		13.2
			sd	0.4	1	38		-	-	-		2.3
99	*Thlaspi*		m	184	53	5265		168	71	693		0.9
			sd	38	3	612		32	5	159		0.2
99	Maize		m	0.3	8	83		0.1	36	94		14.2
			sd	0.1	1	21		0.2	3	18		2.9

[a] after [7] for shoots concentrations and yield.

[b] nd=not determined

Another point is the distribution of metals inside the plants: metal concentration in the plant varies with the organ and the age of this organ for both hyperaccumulators and non-hyperaccumulators. This has a consequence on the time of the harvest and the parts to be harvested. For *Salix* it means that, while only stems are harvested for energy production, leaves will have also to be collected if it is used for phytoextraction. For the hyperaccumulator *T. caerulescens* it has also been shown that most of the Cd and Zn in shoots are soluble in water and as a consequence may increase the bioavailable metal pool in soils if leaves are left on the ground [9, 13]. Owing to the high metal concentrations in *T. caerulescens* shoots, a thorough removal of the leaves (and probably also roots) has to be performed.

Root prospecting and phytoextraction efficiency

The extent of the root systems varies with the site conditions. However, for a given soil, plants develop very different root systems as well as different root:shoot ratios. Such characteristics have been measured at Dornach for various species and the results are presented in Table 4. Maize had the largest root length density and thus was able to prospect efficiently the whole soil profile whereas *T. caerulescens* had the largest root:shoot ratio [10]. Total root length in the contaminated layer and the root length/shoot biomass ratio may have an impact on metal concentrations in the biomass (Table 4). Both types of species are different on that point: At Dornach, *T. caerulescens* (population Ganges) had a distinctly larger L_A/ shoot biomass ratio in spite of having the lowest cumulative root density. Metal concentrations in its above ground biomass were also well above concentrations measured in the other crops (Table 3).

Table 4: Cumulative root density (L_A) 0 - 0.2 m depth and L_A 0 - 0.20 m / shoot biomass ratio calculated for 5 crops grown at Dornach (after [10]). Standard deviations are in brackets.

Plants	**I. Mustard**	**Tobacco**	**Maize**	**Willows**$^{(a)}$	***Thlaspi***
Cumulative root density L_A 0-0.2 m depth in km m^{-2}	2.7 (0.7)	3.7 (0.8)	6.6 (1.8)	3.5 (0.9)	2.6 (1.1)
L_A 0-0.20 m / shoot biomass	**4**	**3**	**4**	**3**	**28**

$^{(a)}$ 2- and 3-year-old plants

As root colonisation of the soil is mostly driven by plant type and soil characteristics, it may not match properly the metal distribution. Because of the localisation of the contaminated layer and the size of their root system plants may either 1) colonise the whole contaminated layer and only it, 1) not colonise the whole layer, 2) not be able to reach the contaminated layer if it is at depth, 3) grow deeper than the contaminated layer or 4) avoid the contaminated spots. Because of their different root systems the efficiency of the hyperaccumulators and high biomass plants may also be different. In addition, *T. caerulescens* (and may be other hyperaccumulators) actively colonises specific metal hot spots [14] whereas root systems may be manipulated to a certain extent to force the root to reach the contaminated layer as experimented for high biomass crops [15]. Measurements illustrating this aspect are presented for the Dornach field experiment in Table 5.

Table 5: Matching of roots and Zn soil contamination expressed as the ratio between the maximal depth with a root length density $>$ 5000 mm dm^3 and the soil contamination depth according three scenarios: contamination as measured in the soil profile of each plot, hypothetical shallow contamination (0.2 m), and hypothetical deep contamination (0.7 m). b) and c) Values used for the "shallow" and "deep" contaminations are extreme values found in the field experiment at Dornach. Depth of contamination is calculated after removing 150 mg kg^{-1}Zn (Swiss guide value [16]) from the total soil Zn concentration. "$>$" means that the deepest root sampling gave a root length

density above 5000 mm dm^3 (after [10]). Standard deviations are in brackets.

	Depth of the contamination		
	True	**Shallow**	**Deep**
Indian mustard	0.9 (0.3)	1.9 (0.8)	> 0.5
Tobacco	0.5 (0.2)	1.3 (0.3)	0.4 (0.1)
Maize	1.4 (0.6)	> 3.3	> 0.9
Willows	1.5 (0.7)	> 3.2	0.9 (0.2)
Thlaspi (Ganges)	0.4 (0.1)	1.0 (0.0)	0.3 (0.0)

Overall phytoextraction efficiency

Models have been proposed to evaluate the time needed to decontaminate a given soil with a given plant. This time varies with the target value, the depth of contamination but also with the type of function (linear or exponential) used to describe the decrease of metal concentrations in soil. Indeed, both concentrations in the plants and yields may not be constant with time and efficiency may thus decrease because the available pools decrease but also because the roots are going deeper or because perennial plants need a certain time to establish themselves. Unfortunately there are not enough long-term data sets available to validate either of these models for neither of the two types of plants.

So far, calculations made from preliminary experiments or, at most, from a few years field experiments have led to various results (results obtained with addition of large amounts of chelating agents like EDTA are not taken into account), predicting either remediation within few years, decades or centuries [2, 6, 9, 60, 61]. For Dornach and Caslano, Hammer et al [12] and Hammer and Keller [9] have obtained better results with the hyperaccumulator *T. caerulescens* rather than with the high biomass plant *S. viminalis* (Table 6 and Figure 1). However, these results may not be transposable to other sites.

Table 6: Dry matter and metal yields of Thlaspi caerulescens obtained in 2000 at Dornach and Caslano. Natural regrowth was harvested twice and only at the Caslano site.

Figure 1: Total metal uptake by Salix viminalis grown at Dornach (left) between 1997-2001 and Caslano (right) in 2000 and 2001.

Use of the non-enriched plant parts

It is quite likely that none of the hyperaccumulator parts would be of further interest because the metal concentrations may be always higher than in other plants and also

		Dornach					**Caslano**		
	Yield DM	**Cd**	**Cu**	**Zn**		**Yield DM**	**Cd**	**Cu**	**Zn**
	t ha^{-1}	**g ha^{-1}**	**g ha^{-1}**	**kg ha^{-1}**		**t ha^{-1}**	**g ha^{-1}**	**g ha^{-1}**	**kg ha^{-1}**
Thlaspi transplanted (3 harvests)	0.9±0.3	128±19	76±15	3.7±0.3		2.1±0.2	539±127	65±15	20.0±4.2
Thlaspi sown (2 harvests)	0.6±0.3	85±50	71±37	1.7±0.8		1.0±0.7	184±138	29±13	7.8±5.5

because most of these plants are not used for any commercial purpose. On the other hand, parts of high biomass plants, which are already used for commercial purposes, may be partly recycled if their metal concentrations is low enough.

Disposal of the plant wastes

The volume of “waste” produced is obviously different between a high biomass plant and a hyperaccumulator like *T. caerulescens*. The time of the year and duration of the biomass production are also different. For both however, the accessibility of disposal facilities and the legislation will have an impact on the final disposal of the plant waste.

The contaminated parts of the plants cannot be recycled as green material, and therefore, have to be disposed off in a safe manner. Among the post treatment methods that have been proposed [17], incineration is presently viewed as the most feasible, economically acceptable and environmentally sound approach [18]. Indeed, in countries that have a high incineration standard it is assumed that co-incineration of dried plants and municipal solid waste (MSW) is the most ecological treatment, providing safe storage of the resulting residues or, even better, recovery of the heavy metals from them is guaranteed.

Incineration experiments performed on leaves of both *T. caerulescens* and *S. viminalis* have shown that volatile heavy metals such as Cd and Zn could be separated from the solid inorganic matrix of the plants quite easily [19]. Gasification (i.e. pyrolysis), which occurs under reducing conditions, was found to be a better method than incineration under oxidizing conditions to increase volatilisation and, hence subsequently recovery, of Cd and Zn from plants. It would also allow the recycling of the bottom ash as fertilizer. Thus, it confirmed that incineration (or co-incineration) was a viable option for the treatment of the heavy metal-enriched plants. There were, however, some differences between samples indicating that the technique will have to be optimized for each type of plant. In addition, because of the amount of biomass that might be produced, it is very likely that *Salix* would be incinerated alone whereas *T. caerulescens* leaves would be co-incinerated with other wastes. In both cases however energy recovery may be an additional benefit.

Conclusion

Phytoextraction has a great potential for cleaning soils contaminated with heavy metals, especially in cases where conventional technologies are not efficient, not possible or too expensive. From results obtained in the lab and in the field it is clear that phytoextraction could be applied either as the main remediation tool or more likely as a "polishing" technique combined with other conventional and "bio" techniques. Both approaches (hyperaccumulators or high biomass plants) may yield interesting results providing they are used in optimal situations. Indeed, the choice of the species (one or several) needs a thorough study of the plant's potential and its suitability for the site. The results are not easily predictable and pre-experiments in pots or even in mini-plots will be necessary before applying phytoextraction to the site. There is obviously no single phytoextraction technique and each site will need a tailor-made scheme.

Acknowledgement

This research was part of the project n°ENV4-CT97-0598/n°OFES97.0362 funded by the Swiss Federal Agency for Teaching and Research and was also financed by the Swiss Federal Institute of Technology, Zürich. I thank W. Attinger (ETHZ) for the Dornach field management, R. Schulin (ETHZ) for the scientific support and for allowing the work in Dornach. Maria Greger, University of Stockholm, Sweden, provided the *Salix viminalis* cuttings (clone 78980).

References

(1) McGrath, S. P. In *Plants that hyperaccumulate heavy metals*; Brooks, R. R., ed.; CAB International: Wallingford, Oxon, UK, **1998**, pp 261-287.

(2) Robinson, B. H.; Leblanc, M.; Petit, D.; Brooks, R. R.; Kirkman, J. H.; Gregg, P. E. H. *Plant Soil* **1998**, 203, 47-56.

(3) Baker, A. J. M.; Brooks, R. R. *Biorecovery* **1989**, 1, 81-126.

(4) Reeves, R. D.; Baker, A. J. M. In *Phytoremediation of toxic metals - Using plants to clean up the environment*; Raskin, I.; Ensley, B. D., eds.; John Wiley and Sons Inc.: New York, **2000**, pp 193-230.

(5) Huang, J. W.; Chen, J.; Cunningham, S. D. In *Phytoremediation of Soil and Water Contaminants*; Kruger, E. L., eds.; ACS Symposium Series 664, **1997**, pp 283-298.

(6) Blaylock, M. J.; Huang, J. W. In *Phytoremediation of Toxic Metals: Using Plants to Clean-up the Environment*; Raskin I; Ensley, B. D., eds.; John Wiley & Sons, Inc.: New York, **2000**, pp 53-70.

1. Kayser, A.; Wenger, K.; Keller, A.; Attinger, W.; Felix, H. R.; Gupta, S.K.; Schulin, R. *Environ. Sci. Technol.* **2000**, 34, 1778-1783.
2. Geiger, G.; Federer, P.; Sticher, H. *J. Environ. Qual.* **1993**, 22, 201-207.
3. Hammer, D.; Keller, C. *Soil Use and Manage.* **2003**, 19, 144-149.
4. Keller, C.; Hammer, D.; Kayser, A.; Richner, W.; Brodbeck, M.; Sennhauser, M. *Plant Soil* **2003**, 249, 67-81.
5. FAC *Methoden für die Bodenuntersuchungen*. Schriftenreihe der FAC 5, Bern-Liebefeld, Switzerland. **1989**, 267p.
6. Hammer, D.; Kayser, A.; Keller, C. *Soil Use Manage.* **2003**, 19, 187-192.
7. Perronnet, K.; Schwartz, C.;, Gérard, E.; Morel, J.-L. *Plant Soil* **2000,** 227, 257-263.
8. Schwartz, C.; Morel, J.-L.; Saumier, S.; Whiting, S. N.; Baker, A. J. M. *Plant Soil* **1999**, 208, 103-115.
9. Chappell, J. *Phytoremediation of TCE in Groundwater using Populus*. Washington, D.C.: Technology Innovation Office, Office of Solid Waste and Emergency Response, **1998**.
10. OIS Ordinance relating to impacts on the soil. Collection of Swiss Federal Legislation SR 814.12, **1998**.
11. Cunningham, S. D.; Berti, W. R. *In Vitro Cell. Dev. Biol.-Plant* **1993**, $29P$, 207-212.
12. Sas-Nowosielska, A.; Kucharski, R.; Malkowski, E.; Pogrzeba, M.; Kuperberg, J. M.; Krynski, K. *Environ. Pollut.* **2004**, 128, 373-379.
13. Keller, C.; Ludwig, C.; Davoli, F.; Wochele, J. *Environ. Sci. Technol.* Accepted for publication.