# Chapter 2 Protocols for Applying Phytotechnologies in Metal-Contaminated Soils

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### 2.1 Introduction

Phytoremediation is becoming well-known word in both scientific literature and more popular publications. The word itself is derived from the Greek word *phytos* (plant) and the Latin word remedium (roughly translated as restoration of balance/ equilibrium). This makes phytoremediation a very broadly applied expression: in fact, it can be defined as any use of plants to restore the quality of soil, biota, water, and air (McCutcheon and Schnoor [2003;](#page-17-0) McCutcheon and Jørgensen [2008\)](#page-17-0). Phytoremediation is considered the only solution which approaches the problem from an eco-sustainable point of view: environmentally friendly and relatively cheap. The United Nations Environment Program ([2003\)](#page-18-0) promotes its application as sustainable technology to remediate environmental pollution. Moreover, the European Union regulators proposed within the Directive [2008](#page-16-0)/1/EC a guideline to select the most suitable technique according to criteria such as environmental friendliness, preexisting scientific knowledge, or required time. Such guidelines leave stakeholders to choose the best remediation technology for their site, considering the economic, environmental, and social variables (Conesa et al. [2012\)](#page-16-0). In this chapter the use of the phenomenon phytoremediation is narrowed down to heavy metals as pollutants and soils as the environmental compartment, focusing on phytoextraction (Raskin [1995](#page-18-0); Blaylock et al. [1997\)](#page-16-0) and phytostabilization (Berti and Cunningham [2000;](#page-16-0) Bolan et al. [2011](#page-16-0)). Phytoextraction aims to remove the heavy metal using specific plants, often in combination with specific soil additives,

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while phytostabilization aims to reduce the mobility/bioavailability of heavy metals in the soil and the re-vegetation of the site, often in combination with adding adsorbents and other chemicals to the soil (Kucharski et al. [2005](#page-17-0); Mench et al. [2003\)](#page-17-0). Normally technologies should be defined in detail regarding their application protocol, efficiency, and cost–benefit calculations. In the case of phytoextraction and phytostabilization, however, it is not possible to establish fixed schemes and procedures based on exact data from technology evaluations. This is limited by the nature of the technology itself which has to deal with soil complexity in relation to heavy metal biogeochemistry, plant behavior in relation to agronomic practice and climate conditions, variations in plant varieties within one species regarding uptake, phytotoxicity of heavy metals, etc. The authors of this chapter gained experience on this issue during the past 15 years, developing a realistic and balanced view on the applicability of phytoextraction and phytostabilization of heavy metals in soils. This includes awareness of the intrinsic methodic limitations and site-specificity, thus contributing to avoiding phytoremediation to become a "hype" which after unavoidable failures would possible have backfired to the approach itself. Many studies have been conducted in this field in the last two decades. Numerous plant species have been identified and tested for their traits regarding the uptake and accumulation of different heavy metals. Mechanisms of metal uptake at the whole plant level and at cellular levels have been investigated (Clemens [2006](#page-16-0)). Progress has been made in the mechanistic and practical application aspects of phytoremediation. They are briefly reviewed and reported in this chapter.

### 2.1.1 The Importance of a Feasibility Test

As the technology is based on site-specific variables (soil characteristics, contaminant levels, vegetation type, etc.), many variables during the implementation of a phytoremediation process make fulfilling the objectives not always easy to attain. In order to avoid that this could happen or, better, in order to minimize the likelihood that the process proves to be not corresponding with our goals at the end, it is imperative, before starting any real-life phytoremediation project, to perform checks, which together are defined as a "feasibility test" (Nowolsieska-Sas et al. [2005\)](#page-17-0). In practice, a feasibility test simulates in a controlled environment the chemical, physical, and biological processes at stake and the conditions which are assumed to prevail in the field during phytoextraction or phytostabilization implementation.

A feasibility study or test is therefore an essential step to imitate as closely as possible the real situation. The test is basically carried out by sampling the soil matrix to be treated in a way as representative as possible for the whole site; the test will therefore be carried out on real samples taken from the site. The test includes all the analyses to characterize the soil and the contaminant behavior. After that, the test proceeds with the selection of the most appropriate plant, based on the soil analyses and on available literature experiences and references. This selection can include specific lysimeter or pot experiments. The results obtained from the feasibility test can be used subsequently to decide whether it is possible or not to apply phytotechnology in the real field context, and if so, which approach gives the lowest risk of failure in attaining remediation goals (Koopmans et al. [2008a](#page-17-0), [b](#page-17-0)).

## 2.1.2 The Concept of Heavy Metal Bioavailability and Its Importance in Phytotechnologies

It is scientifically accepted that the risky fraction of metals are the mobile/ bioavailable fractions, despite the fact that this terminology (especially regarding bioavailability) is vague and various definitions are given in the last few decades. It is well-known that during workshops attended by both soil chemists and soil biologists normally additional definitions are invented. Despite the lack of widely accepted definitions, the message is clear: the total heavy metal content in a soil gives no accurate indication regarding risks which are related to the heavy metal contamination, including phytotoxicity, leaching risks, and uptake by plants (i.e. food-chain propagation) (Barbafieri et al. [1996;](#page-15-0) Barbafieri [2000](#page-15-0)). It can be boldly stated that elimination/reduction/stabilization of the risky fractions is the most necessary and valuable action to solve the problems caused by contaminated soil. The main problem of this statement is the fact that policy makers have to convince; this might be difficult as many soil quality standards are still based on total concentrations in the soil. In this chapter, authors will focus on the description of applicability protocols for phytoremediation in heavy metal-contaminated soils focusing on the importance of "mobile/bioavailable" fractions of heavy metals in the soil. Despite the numerous articles appearing in scientific journals, very few field applications of phytoextraction have been successfully realized until now. To overcome the imbalance between the technology's potential and its drawbacks, there is growing interest in the use of plants to reduce only the fraction that is the most hazardous to the environment and human health, which is to target the bioavailable fractions of metals in soil.

At a first glance phytoextraction and phytostabilization seem to have a different goal and, regarding many practical aspects, they indeed do. But despite this, it can be stated that both approaches aim at reducing the amount of mobile/bioavailable heavy metal fractions in the soil. In phytoextraction this is done by removing such fractions and in phytostabilization this is done by reducing heavy metal mobility and bioavailability without removing heavy metals. In the case of phytoextraction, the action of plants only targets the mobile/bioavailable fraction unless other "stronger actions" are taken, e.g., the use of additives to increase the heavy metal mobility, making them more available for plant uptake. Plants can, using their absorbing roots, deal only with the "plant-available" fractions, which can themselves be manipulated by chemical additives or biological action. Moreover, such fractions can strongly vary among different plant species and even varieties. Some plants used in phytoextraction, so-called hyperaccumulators, apparently have the

capacity to modify the mobility/bioavailability of heavy metals in the rhizosphere and seem to have access to basically non-plant-available heavy metal pools in the soil as well. "Bioavailable Contaminant Stripping" (BCS) firstly discussed by Hamon and McLaughlin ([2003\)](#page-17-0) can be further developed as a remediation approach which is focusing at the removal of all actually and potentially bioavailable heavy metal fractions (see Chap. [13](http://dx.doi.org/10.1007/978-3-642-35564-6_13)).

Monitoring the mobility and bioavailability of inorganic pollutants (including heavy metals) in contaminated soil provides important information regarding the fate of these contaminants in the environment, time-dependent changes in heavy metal speciation, mobility towards the water table, and ecotoxicological risks (Environmental Agency [2004;](#page-16-0) Mulligan and Yong [2004](#page-17-0)). Some authors tend to promote that risk assessment of soils should consider both mobile and bioavailable fractions of heavy metals, which of course depends on the definition of bioavailability (Wahle and Kordel [1997](#page-18-0)). Despite such considerations, it remains clear that total concentrations of heavy metals in soils are poor indicators of heavy metal toxicity since heavy metals exist in different solid-phase forms that vary considerably in terms of (potential) bioavailability (Nolan et al. [2003\)](#page-17-0). Phytoextraction has proved to be effective, relatively straightforward, and inexpensive compared to other procedures for extracting bioavailable metal fractions from soils. Bioavailable heavy metal fractions, removed by plants, probably correspond to fractions of soil heavy metals that are most prone to affect the soil ecosystem. However, there are surprisingly few reports which show that bioavailable fractions of heavy metals in soils are indeed reduced after concluding a phytoextraction project in the field (Ban˜uelos et al. [2011;](#page-15-0) Willschera et al. [2012\)](#page-18-0). As other bioavailable heavy metal fractions can be slowly released by nonmobile heavy metal fractions in the soil (aging), a longer term decrease of the bioavailable fraction might be difficult to observe experimentally. Moreover, this is an argument for considering both mobile and immobile (bioavailable and potentially bioavailable) heavy metal fractions in the soil, when estimating risks.

More data are available regarding phytostabilization; Phytostabilization often uses chemical additives to immobilize heavy metal mobile fractions, especially at heavily polluted sites, which are initially without vegetation due to heavy metal phytotoxicity. Such immobilization is a prerequisite for plant growth. Immobilization therefore has to be measured and monitored.

### 2.2 How Can We Use Phytoextraction?

### 2.2.1 Technology Description

Phytoextraction refers to the translocation of metal contaminants from soil up to the above-ground tissues by the root system. After plants have grown for a certain period, they are harvested and may be incinerated to recycle the metals. This procedure, repeated several times, brings soil contaminant levels down to below legally acceptable limits (Chaney et al. [1997](#page-16-0)). The time required for remediation depends on the type and extent of heavy contamination, the duration of the growing season, the amount and characteristics of the produced biomass, and the plants natural capability for heavy metal accumulation. Two different strategies can be used (Lombi et al. [2001;](#page-17-0) Robinson et al. [2003a\)](#page-18-0): continuous phytoextraction using natural metal hyperaccumulator plants which absorb, translocate, and accumulate an enormous amount of metals during their entire life period without visible toxicity symptoms (Baker and Brooks [1989](#page-15-0); Brooks [1998](#page-16-0)); assisted phytoextraction—the accumulation process is induced in tolerant plants by the increased contaminant bioavailability in soil (Blaylock et al. [1997\)](#page-16-0). Synthetic amendments such as chelates (e.g., EDTA, EDDS, NTA—Cooper et al. [1999;](#page-16-0) Evangelou et al. [2007\)](#page-16-0), organic acids (e.g., citric acid), or ion competitors (e.g., phosphate—Tassi et al. [2004](#page-18-0)) added to the soil enhance metal bioavailability, although the soil microbial community is usually neglected and there is a potential risk of leaching of metals to groundwater (Dickinson et al. [2009](#page-16-0); Evangelou et al. [2007\)](#page-16-0).

Generally, phytoextraction is only applicable to sites containing low-to-moderate levels of metal contamination. Effective phytoextraction requires both plant genetic ability and optimal soil and crop management practices (Di Gregorio et al. [2006](#page-16-0); Tassi et al. [2008;](#page-18-0) Pedron et al. [2009](#page-18-0)). Thlaspi caerulescens (Cd and Zn hyperaccumulator) and *Brassica juncea* (heavy metal accumulator) are examples of species that well represent the two phytoextraction strategies described above. Metals such as Ni, Zn, Cu, and As are the best candidates for removal by phytoextraction, although Cd, Pb, etc., have been extensively studied as well. Genetic engineering studies have been performed to manipulate plant accumulation with the overexpression or knockdown of membrane transporter proteins (Rogers et al. [2000](#page-18-0)).

The accumulation of hazardous plant biomass must be disposed of, in order to minimize environmental risk. The waste volume can be reduced by thermal, microbial, physical, or chemical means such as composting, compaction, or thermo-chemical conversion processes (combustion, gasification and pyrolysis). Recycling the biomass from phytoextraction for fuel and other uses cuts down on the need for landfills and provides the contaminated site with an economical value. Added value to the phytoextraction process could be obtained by combining the biomass produced as an energy source, resulting in an ore after incinerating the residual biomass. This would be possible in the case of phytomining, a particular example of phytoextraction. Phytomining involves the exploitation of subeconomic ore bodies using hyperaccumulating plants. For instance, the species Alyssum bertolonii, Berkheya coddii have a high potential in extracting Ni because of their high biomass and a Ni concentration of 1 % in the dry matter (Robinson et al. [2003b\)](#page-18-0). Other metals such as gold, thallium, and cobalt have been exploited from tailings or other residues of low commercial value (LaCoste et al. [2001;](#page-17-0) Keeling et al. [2003](#page-17-0)). Heavy metal phytoextraction refers to the use of plants that can remove contaminants from soil and accumulate them in a harvestable part in a process alongside water and nutrient absorption by roots. Therefore plant biomass

production and the metal concentration in the biomass are fundamental success factors for the practical efficiency of phytoextraction (McGrath and Zhao [2003;](#page-17-0) Robinson et al. [2003b\)](#page-18-0).

### 2.2.2 Protocols for Enhancing Metal Phytoextraction

Several strategies for achieving more efficient heavy metal removal have been recently developed such as the enhancing concentration of soluble heavy metals in the soil with the application of synthetic chelate agents (e.g., EDTA). This then leads to an increase in the metal uptake of high biomass crop plants (e.g., Brassica juncea, Helianthus annuus, Zea mays, and Nicotiana tabacum) (Meers et al. [2005;](#page-17-0) Di Gregorio et al. [2006](#page-16-0); Pedron et al. [2009](#page-18-0)).

An alternative strategy, to increase the efficiency of the assisted phytoextraction, is to use plant growth regulators (PGRs) to counteract the negative effects of heavy metal stress in growing plants and boost the shoot biomass (Ouzounidou and Ilias [2005;](#page-18-0) Lopez et al. [2007](#page-17-0); Barbafieri and Tassi [2010](#page-15-0); Zhao et al. [2011;](#page-18-0) Barbafieri et al. [2012\)](#page-16-0). PGRs play a major role in cell division and cell differentiation. They can stimulate shoot initiation, bud formation, the growth of lateral buds, leaf expansion, and chlorophyll synthesis. They can also delay leaf senescence, enhance resistance to salinity, low temperature and drought, and induce stomatal opening in some species (Letham et al. [1978](#page-17-0); Barciszewski et al. [2000](#page-16-0); Pospisilova et al. [2000\)](#page-18-0). The combined effects of EDTA and cytokine resulted in an increase in the Pb and Zn phytoextraction efficiency (up to 890 % and 330 %, respectively, compared to untreated plants) and up to a 50 % increase in foliar transpiration (Tassi et al. [2008\)](#page-18-0). Cytokinins have also showed potential use for the increasing of Ni phytoextraction capability in Alyssum murale, a well-known Ni hyperaccumulator (Cassina et al. [2011\)](#page-16-0). Application of exogenous PGRs was examined as a viable technique to increase the efficiency of plant metal extraction from contaminated soils. However, further experiments are needed to increase the knowledge of the dynamics of the transport mechanism involving metal uptake, since this mechanism is dependent on plant characteristics and environmental parameters. In order to increase the efficiency of phytoextraction, fertilizers can be used to enhance the productivity of selected plants; positive results have been reported recently in the case of the boron-contaminated soils (Giansoldati et al. [2012\)](#page-17-0).

# 2.2.3 Experimental Protocols for Phytoextraction: Applicability Test at Different Scales

In practice there are always many variables that render each situation "site-specific," so cases in which it is possible to skip feasibility test and proceed to large scale field projects are very rare. In general, the following sequential test steps are applied:

Sequential period	Type of investigation
Ante operam phase	Site characterization
	Plant and treatment selection
	Organization and preparation of site intervention
	Sowing
	Control of plant growth
In itinere phase	Agronomic care and administration of any fertilizer
	Administration of the chelating agent if necessary
	System monitoring
	Plants harvesting
Post operam phase	Safety of the site
	Waste management
	System monitoring

Table 2.1 Micro steps characterizing each phase in a phytotechnology

- Ante operam phase (preoperational)
- *In itinere* phase (during the process)
- *Post operam* phase (post-operational)

Each of these phases is characterized by micro-steps aimed at providing the necessary basic information for site characterization. Table 2.1 shows the microsteps characterizing each of the three main sequential steps, above. In Fig. [2.1](#page-7-0), is shown the flow chart of the procedure for the evaluation of the applicability of in situ phytoextraction. The efficiency of phytoextraction is difficult to assess and depends on the nature of contaminants, additive specifications (if used), plant characteristics, and the environmental and soil conditions. To better enhance phytoextraction efficiency, preliminary tests at a laboratory scale and at a greenhouse scale are fundamental, but treatment, biomass, and plant performance are also severely influenced by local environmental conditions. For these reasons, field tests for phytoremediation applicability should be planned for a more realistic estimation of its effectiveness at a specific contaminated site. As for other technologies, treatability could require time and money, but results are fundamental and can be responsible for the success or failure of the project, and can at the end reduce costs. A scheme that could be adopted is subdivided in three steps, which is shown in Fig. [2.2](#page-7-0) and briefly indicated below:

First step: characterization of chemical and physical characteristics of the soil matrix

Second step: selection of plant species and/or treatments to be used in phytoextraction Third step: evaluation through a field-scale pilot test

The first step should be conducted directly on the specific contaminated site in order to evaluate the level of contamination, the agronomic characteristics, and a screening of the indigenous vegetation. The following analyses have to be carried out:

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Fig. 2.1 Diagram of applicability of the phytoextraction procedure in situ



Fig. 2.2 Diagram of the "feasibility study" of phytoremediation technique for soils/sediments contaminated by metals

- Determination of soil biogeochemical parameters together with the agronomic characteristics to verify the status of the soil matrix and to evaluate the potential for plant growth.
- Evaluation of the mobility/bioavailability of contaminants in relation to plant action.
- Determination of contaminants contents in the indigenous plants.

After the first and preliminary evaluation, the treatability test needs to pass additional tests (see Fig.  $2.3$ ) for the selection of the best protocols to adopt.

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Fig. 2.3 Site-specific feasibility test: (a) microcosm, (b) mesocosm, (c) field test

- Microscale/Lab test (microcosm, Fig. 2.3a): at first the screening test to select the most suitable plants and treatments and to verify eventually heavy toxic effects of the contaminated matrices.
- Mesoscale/Greenhouse (mesocosm, Fig. 2.3b): the most effective protocols (plant plus treatment) tested at the microscale are further investigated at a more "realistic scale" as plants can grow to the end of their vegetative cycle in bigger pots under controlled conditions (in a greenhouse). It allows for the verification of the efficiency of a complete plant and moreover (as pots are provided with leachate collectors) it is possible to check the mobility of contaminants in soil core profile.
- Macroscale/pilot trials (lysimeter, field test, Fig. 2.3c): have to be carried out to verify the performance of the protocols (plants plus treatments) selected from the best performances observed during the mesoscale tests. This last stage allows for the monitoring of plant growth biomass production and contaminants uptake verifying how the local and specific site conditions can influence the phytoremediation process. Moreover appropriate measures can be selected for biomass treatment protection of the area. Uncertainty in the process should be taken into account due to the uncontrolled weather conditions that cause diverse plant response to stress (Tassi et al. [2011;](#page-18-0) Barbafieri et al. [2010;](#page-16-0) Barbafieri and Raffaelli [2010\)](#page-15-0).

During all test phases it is very important to monitor reduction of contaminants from the soil as this is main critical success factor of the whole process. This determination if often "forgotten" in scientific articles albeit that it reflects the real effectiveness of the applied phytoextraction protocol. Few show the metal

reduction in soil after a phytoremediation treatment. Pot experiments by Ye et al. [2011](#page-18-0) showed a reduction of about  $11-38$  % after 9-month period of *Pteris vittata* growing for arsenic potentially available (phosphate extractable) and 18–77 % in soil pore water As. Tassi et al. [2011](#page-18-0) reported a reduction of 45 % of bioavailable boron after two consecutive growing cycles in microcosm test. Cassina et al. [2012](#page-16-0) reported a reduction of 33-45 % of mobile mercury after one growing of  $H$ . annuus and B. juncea respectively in microcosm pot simultaneously treated by cytokinin and thiosulphate. In field experiments this approach is often not considered. The main cause is the high heterogeneity of metal distribution in contaminated soil. Blaylock and Elless [2009](#page-16-0) reported a 5-year field study on arsenic removal. But after different sampling grid conducted after each growing season to verify the arsenic removal from soil, they do not observe a significant arsenic removal due to the high soil heterogeneity in arsenic content. The sampling variability challenges the phytoremediation evaluation when approaching a study of mass balance in field experiments (Brus et al. [2009](#page-16-0); Van Nevel et al. [2007](#page-18-0)).

### 2.2.4 Decision Support Systems

For phytoextraction, a very important critical success factor is the duration of a phytoextraction, i.e., the period between starting the process and the moment when the total concentration or the bioavailable concentration of heavy metal(s) has reached regulatory target levels for soils (Koopmas et al. [2007\)](#page-17-0). To use the total or the bioavailable concentration as target value depends on the legislator's demands; total or bioavailable fractions are determined by standard extraction procedures, e.g., a diluted calcium chloride extraction to mimic plant-availability (Römkens et al. [2009\)](#page-18-0). Many authors simply use a linear phytoextraction model in which the amount of phytoextracted heavy metal is assumed to be independent of the actual heavy metal concentration in soil or soil solution at a certain stage during phytoextraction. Such an approach is definitely a gross simplification which in most cases will underestimate the real phytoextraction duration. It is more probable that the phytoextraction rate in the case of non-hyperaccumulators depends on the actual supply of plant-available heavy metals in the soil, which steadily decreases during the phytoextraction duration. In the case of hyperaccumulators the story might be different; as uptake by such plant species is assumed to be (not only) supply-driven, as "active" processes in the plant root zone may play a role as well. Anyway it is not very likely that a simple model can easily predict phytoextraction duration for both types of plants. Instead of this an experimental protocol can be used, based on mixing the polluted soil with different amounts of clean soil with the same general composition and determine after a period of aging both the plant-available heavy metal concentration (by chemical extraction) and the actual uptake by the chosen phytoextraction plant species. Albeit time-consuming (several months), it results in a better prediction of phytoextraction duration than just using a linear model. Results of such tests also confirm the hypothesis that a nonlinear model is more likely to predict phytoextraction duration and, more important that thus predicted durations are 20–50 % longer than when the linear model is used. It should be noted that slower processes releasing "new" plant-available fractions from the soil matrix cannot be predicted by this procedure. It may be obvious that phytoextraction duration is an important indicator and decision instrument for phytoextraction, but it is just as obvious that costs play an important role as well (Koopmas et al. [2007;](#page-17-0) Koopmans et al. [2008a\)](#page-17-0).

### 2.3 How Can We Use Phytostabilization?

### 2.3.1 Technology Description

Phytostabilization aims at the use of plants to reduce the impact of soil pollutants on adjacent environmental compartments, including water bodies, agricultural land, etc. Phytostabilization is most effective on land which is highly contaminated by heavy metals, other (in)organic pollutants, and also crude oil residues. Such land is characterized by marginal or nonexistent vegetation and by degenerated soil and surface ecosystems; such land therefore is highly prone to serve as a secondary pollution source due to high wind and water erosion rates and high levels of surface run-off and leaching to the groundwater (Berti and Cunningham [2000](#page-16-0); Barbafieri et al. [2011](#page-16-0)). Phytostabilization of such land areas can be defined as a set of measures which permit re-establishment of vegetation and which at least include the use of chemical/biological soil additives and introduction of productive plants or natural vegetation. In its simplest form, it consists of the addition of adsorbing materials and/or other chemicals which reduce the plant-available fraction of heavy metals and therefore reduce phytotoxicity; the natural vegetation can then return with or without human assistance. An example is the re-establishment of a natural perennial vegetation cover on extremely polluted soil in Poland (up to 4 % of heavy metals) after just adding substantial amounts of rock phosphate and lignite to the soil (Kucharski et al. [2005](#page-17-0)); see Fig. [2.4.](#page-11-0) The benefits of such a vegetation cover are obvious. Wind erosion rates are decreased and heavy metals are no longer transported to residential areas and gardens nearby the site.

Leaching is decreased by reducing vertical water transport in the soil as a result of phytoevaporation in combination with a lower mobility of heavy metals after addition of adsorbents. The main risk of the re-establishment of such natural vegetation covers on extremely polluted soil is high uptake of heavy metals by the (hyperaccumulating) plants which can survive on the site and subsequent foodchain contamination. At this specific site in Poland, the non-hyperaccumulating perennial grass gradually won the competition with a hyperaccumulating nonperennial weed, so that food-chain contamination was not a problem anymore after some time. The main disadvantage of phytostabilization from a legislator's point-of-view is the fact that the pollutant is not removed from the soil, but only

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Fig. 2.4 Heavily polluted site in Poland  $(4\%$  heavy metals) before *(left)* and 1 year after (*right*) application of lignite and phosphate rock. Perennial grass and flowering hyperaccumulating species start growing spontaneously

turned less harmful. The main problem legislators have with this is the fact that in the future, heavy metals may become mobile again and once again can cause environmental problems. Another disadvantage is the fact that the land will remain unproductive on the longer term which gives a longer term management burden to authorities or problem-owners. The reason why phytostabilization remains a good polluted land management option despite the above-mentioned disadvantages is the fact that other options are absolutely not possible due to high costs.

A method to reduce or to completely mitigate the longer term polluted land management costs is to grow non-food crops on the polluted land; this includes energy crops and especially energy crops which provide a perennial vegetation cover (grasses, woody species) and do not cause food-chain contamination problems. Recent research in China and Vietnam has shown that growing energy crops on polluted land can be made profitable (considering the low economic value of the land) even if crop yields are lower than on good agricultural soil. Figure [2.5](#page-12-0) shows an energy crop test site in China, nearby a copper/zinc smelter. An interesting example of the interrelation of productive crops and natural vegetation is the effort by Chinese researchers to grow energy crops on extremely polluted (copper, arsenic) mine tailings in Tongling (Anhui, China). After adding rock phosphate and liming the tailings, different tested potential energy crops grew but provided only very low yields which made the whole process economically nonviable. However, after dismantling the energy crop test area, abundant natural vegetation recovered on the site, which has been bare during decades. So no economic profits could be obtained, but the natural vegetation cover which started to reappear did not require high management costs and at the same time reduced the transport of pollutants to neighboring paddy field by decreasing erosion rates and controlling leaching.

### 2.3.2 Protocols for Phytostabilization

The principal critical success factors for the phytostabilization process are:

1. The effectiveness of the soil additives regarding their effect on reducing the mobility/bioavailability of heavy metals in the soil at the polluted site.

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Fig. 2.5 Energy crop demonstration site in the vicinity of make-shift copper/zinc smelters in Fuyang valley (Zhejiang, China)

- 2. The capacity of the proposed crops or local natural vegetation species to grow on the polluted soil after application of the additives, mainly concerning phytotoxicity.
- 3. The price of the used additives in combination with the duration of their effectiveness; generally unpolluted waste materials like compost, fly ash, etc., are considered the best option.
- 4. The longer term effectiveness of the proposed additives and the need to be effective for a longer period (it is possible that the system on the longer term does not need the additives any more).
- 5. The risk of food-chain contamination induced by the selected plant species.
- 6. The capacity of the selected plant species regarding their erosion mitigating potential, with special emphasis on all-year effectiveness (perennial vs. nonperennial).
- 7. The need of fertilizers and pesticides to sustain healthy growth of the selected plant species.

The last five issues  $(3-7)$  are general characteristics of additives/plant species and therefore can normally be assessed adequately on the basis of a literature check and/or a very simple decision support system containing literature dataor simply based on an expert opinion, which offers the advantage of integrating the different issues.

Factors 1 and 2, however, are highly site specific and do need preliminary laboratory tests. Such laboratory tests can be a simple series of solvent extractions of the soil/additive mixture (with and/or without aging of the mixtures) especially to chemically assess heavy metal mobility and plant-availability. A simple test to assess potential phytotoxicity is the standard barley root elongation test (see



Fig. 2.6 Barley root elongation test. Phytotoxicity increases from left to right dependent on the used additive mixture

Fig. 2.6) (Kapustka [1997](#page-17-0)). The root development of barley seeds is highly sensitive to stress caused by pollution and the root length is a good indicator of such stress. The picture shows such a standard test. Using this cheap, fast, and technically easy test many soil/additive combinations can be assessed in a relatively short time and the most suitable combinations can be selected, also taking into account the other success factors, especially the price and local commercial availability of the additives. After this, the best performing additives with the optimum application rates can be tested in pot experiments or small lysimeter studies using the proposed vegetation types (natural species or production crops) to assess crop performance. Accumulation of heavy metals in the crops (issue v) can then be assessed easily as well. When performing these preliminary tests, a check of site heterogeneity has to be carried out as well. If the site is very heterogeneous regarding soil biogeochemical characteristics and pollution levels, it can be decided whether it is (economically) most viable to investigate and apply different phytostabilization schemes to account for the spatial differences in site characteristics or to physically homogenize the upper soil layer, possibly in combination with additive application.

### 2.4 Conclusions and Recommendations

• In most cases, phytoextraction still requires a long time to attain target pollutant levels in the soil which satisfy the legislators. Therefore commercial applications are being hindered not only by a lack of legal acceptance of the technology as a soil remediation option but also because of the often unpredictable financial burden over a long period of time. These constraints can only be overcome if it can be shown to policy makers that the risk to the environment at the end can be effectively eliminated. To add a standard ecotoxicology test as a monitoring tool as an integrated part of a phytoextraction project may help to lead to technology acceptance. Research reports and reports on feasibility studies should not only focus on plant accumulation and translocation data but also on an effective reduction of different heavy metal fractions in the soil; they should also provide sound heavy metal mass balances to show that no leaching and other losses occurred.

- Decision Support Tools are not commonly used to help decision-making on which approach is the most appropriate for a specific polluted site. Some tools mainly focus on "hard technology" (e.g., DARTS developed by ICS-UNIDO) and do not specifically deal with phytotechnologies. To improve the use of such a specific Decision Support Tool to decide upon the best approach when phytotechnologies already have been selected for remediation, has to be further developed, to include a database for calibration and validation based on real experimental phytoremediation field trials.
- An agreement on a regulatory base for the use of remediation techniques which only reduce the concentration of heavy metal fraction which pose the major human health and ecosystem risks still has to be developed in many countries. The scientific community already agrees upon the need to do so. Such a regulatory basis will greatly facilitate the introduction of phytotechnologies as an accepted method to reduce risks caused by heavy metals in soils. It will also avoid that phytotechnologies are used where and when they are not appropriate and, on the contrary, avoid situations where more invasive and expensive technologies are used where phytotechnologies represent a better option. Major hurdles for the successful use of remediation approaches based on reduction of bioavailable heavy metal fractions in the soil, which include phytotechnologies, continue to be mainly political and regulatory rather than scientific.
- Regarding phytostabilization, the need of a regulatory framework is even more pressing than in the case of phytoextraction. The reason is that in phytoextraction the bioavailable heavy metal fraction in the soil is effectively removed, which satisfies regulators and public opinion. This is not the case with phytostabilization. Introducing phytostabilization on a broader scale should focus on the following issues:
	- Stressing the need of doing something to stop/reduce the transport of heavy metals from extending extremely polluted sites to cleaner adjacent environmental compartments. Emphasizing that hard technological clean-up is no option, due to extreme costs and emphasizing that dig and dump is not a sustainable solution.
	- Putting emphasis on the fact that there are no other options (except capping in combination with clean-up of groundwater) than phytostabilization and revegetation to improve the situation of extremely polluted extended sites.
	- Promoting the possibility of making phytostabilization economically sustainable on the longer run by using perennial non-food crops like deep-rooting

<span id="page-15-0"></span>high biomass production grasses (Miscanthus, Vetiver) and tree species to be used for energy production. Stress the added value of the combination of economic sustainability and erosion control.

- The development and application of phytotechnologies as an environmentally sound approach involves a number of additional challenges. These include the development of local capacity to understand and apply phytoremediation technologies and make them suitable for local economic and environmental conditions and the establishment of an effective regulatory framework. In some countries, there is a lack of experience in the use of phytoremediation. This is often coupled with a lack of data, performance standards, and cost–benefit analyses regarding phytotechnologies. In summary, there is a need for:
	- Appropriate phytoremediation technologies and techniques applicable to different geographic regions with varying weather conditions
	- Site characterization, clean-up, and technology selection criteria, including decision support tools
	- Assessment and evaluation methods that can be applied to determine the applicability and appropriateness of various phytoremediation techniques
	- Local training for environmental remediation practitioners on the planning and implementation of phytoremediation schemes.
- Extended complex polluted sites, including mining sites and smelter areas, often are characterized by a high spatial variation in pollutant levels and soil parameters, relevant for determining mobility, and bioavailability of heavy metals. Developing such sites gives good chances for phytotechnologies to be among a mix of invasive and noninvasive techniques and approaches to be used for site development, especially when creating parks and recreational areas.

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