LAND REVITALIZATION

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Contents

Summary

The use of green plants to remove, contain, inactivate or degrade harmful environmental contaminants (generally termed phytoremediation) and to revitalize contaminated sites is gaining more and more attention.

In this chapter an overview is given of existing information concerning the use of plants and their associated microorganisms whether or not combined with soil amendments for the revitalization of (mainly trace element-) contaminated soils. We will concentrate on field experiments using various amendments to immobilize toxic trace elements.

It is clear that, in spite of a growing public and commercial interest and the success of several pilot studies and field scale applications, more fundamental research still is needed to better exploit the metabolic diversity of the plants themselves, but also to better understand the complex interactions between contaminants, soil, plant roots and micro-organisms (bacteria and mycorrhiza) in the rhizosphere. Further, more data are still needed to quantify the underlying economics, as a support for public acceptance and last but not least to convince policy makers.

1. Introduction: Phytostabilization (Revitalization) of Trace Element-Contaminated Soils: Technological Aspects

Plant-based *in situ* stabilization, termed "phytostabilization", reduces the risk posed by a contaminated soil by reducing the bioavailability of the trace elements making use of a combination of plants and soil amendments (Vangronsveld et al. 1995a, 1996, Vangronsveld and Cunningham, 1998). This technique is based on the practice of revegetation for the reclamation of (old) mine sites and areas around smelters, in which soil amendments are often essential for the establishment of a plant cover. Application of these soil amendments strongly reduces the availability of trace elements to be taken up by plants and limits eventual phytotoxicity, allowing revegetation of contaminated sites. Establishment of a vegetative cover markedly reduces trace element leaching to the groundwater and prevents the dispersal of polluted dusts through wind and water erosion from formerly bare sites (Vangronsveld et al. 1995, a,b, 1996)

Application of trace element-immobilizing soil amendments can also be an interesting alternative for slightly contaminated soils. Due to the application of suitable amendments, trace element uptake by (crop) plants, for instance, can be strongly decreased resulting in a reduction of trace element transfer to higher trophic levels.

Summarized, the application of the soil amendments should lead to: (a) change the trace element speciation in the soil aiming to reduce the easily soluble and exchangeable fraction of these elements; (b) stabilize the vegetation cover and limit trace element uptake by crops; (c) reduce the direct exposure of soil-heterotrophic living organisms and (d) enhance biodiversity. The integration of the trace element immobilization and subsequent phytostabilization not only results in the installation of a normal functioning ecosystem but at the same time in an inhibition of lateral wind erosion, and reduction of trace element transfer to surface- and groundwater.

The amendments (for reviews see Mench et al., 1998, 2007; Vangronsveld et al., 2000b; Adriano et al. 2004; Kumpiene et al. 2008) commonly include liming agents, phosphates (H_3PO_4, triple calcium phosphate, hydroxyapatite, phosphate rock), trace element (Fe/Mn) oxyhydroxides, and organic materials (e.g., biosolids, sludge or composts). More recent research has investigated other materials that may have value in phytostabilization, including synthetic zeolites, cyclonic and fly ashes, and iron grit (zerovalent iron grit).

In phytorestoration (land revitalization) plants perform two principal functions by protecting the contaminated soil from wind and water erosion, and reducing water percolation through the soil to prevent leaching of contaminants (Vangronsveld et al., 1995b). Plants may also help to stabilize contaminants by accumulating and precipitating trace elements in the roots (or root zone), or by adsorption on root surfaces. Plants may contribute by altering the chemical form of the contaminants by changing the soil environment (e.g., pH, redox potential) around plant roots. The microorganisms (bacteria and mycorrhiza) residing in the rhizosphere of these plants also perform an important role in these processes: they can not only actively assist to change the speciation of the trace elements, but they can also help the plant in overcoming phytotoxicity, thus assisting in the revegetation process (van der Lelie, 1998).

Ideally, contaminants should not be accumulated in aerial plant tissues which could be consumed by humans or animals and cause harm to these organisms. Phytostabilization of trace element contaminated soils requires plants tolerant to the trace element concentrations and other growing conditions for a given site. Often, the plants chosen for phytostabilization include pioneer dicotyledonous and grass species that are rather fast growing to provide a quick and complete surface coverage; by preference, these species should possess many shallow roots to stabilize soil and take up soil water, and should be easy to care for once established.

It is important to mention that phytostabilization (land revitalization) is not a technology for real clean-up of contaminated soils, but a management strategy for stabilizing (inactivating) trace elements with a labile pool in excess leading to biological effects. This revitalization should lead to an attenuation of the impact on site and to adjacent ecosystems. Contamination is ‘inactivated’ in place preventing further spreading and transfer into the food chain. Therefore, long term monitoring of the contaminants will be part of any successful management scheme using phytostabilization as a remediation tool.

The basis used for evaluating and ranking the effectiveness of a soil treatment is not standardized, and has to be evaluated on a case to case basis. For screening the most suitable amendments different approaches have been used in different batch and pot experiments. The effectiveness of the amendments has been assessed in different ways including chemical methods (e.g., selective or sequential chemical extractions, isotopic dilution techniques, adsorption-desorption isotherms, long-term leaching and weathering simulations) and biological (e.g., plant growth and dry-matter yield, plant metabolism, ecotoxicological assays on soil invertebrates and bacteria and microbial populations). One of the lessons learned was the evaluation of the amendments with unpolluted control soils, as some amendments may show undesirable matrix or other side effects (f.i. zeolites with high sodium content destroying soil structure; cyclonic ashes causing Mn deficiency, etc.)

Through the selection of plants and soil amendments, the phytostabilization based revitalization may be adapted to different trace element contaminants and soil types, including heavier textured soils, which are sometimes problematic to remediate.

In situ inactivation of trace elements by strong immobilizing agents combined with subsequent revegetation may be an economically realistic and cost-effective remediation alternative not only for vast industrial sites, but also for agricultural soils and kitchen gardens, and even for dredged sediment dumps and other dumping grounds where due to the huge volumes of material to be treated, excavation plus landfilling or cement stabilization are impractical and especially cost-inefficient.

Land revitalization may not be appropriate at certain contaminated sites. Many contaminated sites have less than ideal cultural conditions due to pH, soil structure, salinity, or the presence of other toxic substances. At contaminated sites where soils cannot be made suitable for plant growth without extensive efforts, time, and money, other remediation alternatives should be considered. At sites contaminated with several heavy trace elements, or combinations of trace elements and organics, the revitalization process may require an innovative approach. Many heavy trace element tolerant plants are usually tolerant of only one or two trace elements at high levels, and or not always jointly suited for the remediation of organic compounds. On the other hand, in many cases the degradation of many organic contaminants is strongly stimulated in the plant rhizosphere. In the case of mixed pollution the selection of the most appropriate vegetation cover should address both trace element tolerance and phytodegradation properties. Alternatively, at sites with multiple contaminants, revitalization may be conducted in stages with varying crops or treatments, and may possibly be combined with other remediation techniques to provide complete remediation.

2. Indicators for Remediation Efficacy

Three main routes of exposure to trace elements are existing. Soluble contaminants migrate with soil water, can be taken up by plants and aquatic organisms. The other pathways concern direct ingestion, and inhalation of contaminated particulates blown up by wind erosion. In view of this, any thorough evaluation of the overall effect of immobilization and the sustainability of trace element inactivation should combine physico-chemical and biological methods.

As already mentioned, there exist no specific criteria for monitoring revitalized sites where *in situ* immobilization was applied. Physico-chemical evaluation of the trace element solubility or availability of the soil contaminants (see below) is obvious.

However, a more thorough evaluation of the overall effect of additives and the sustainability (durability) of trace element immobilization in contaminated soils should combine physico-chemical and biological methods.

Several chemical test protocols are frequently used. Leaching potential can be estimated under landfill conditions by TCLP (toxicity characteristic leaching procedure, US-EPA (1990)) and under acid rain conditions by SPLP (simulated precipitation leaching procedure, US-EPA (1995)). Selective (single) and sequential chemical extractions estimate the extractable fraction of one element at a given moment with a well-defined substrate/solution ratio. Even though it is difficult to predict the mobile pool of trace elements in a natural situation on this basis alone, it can be used as a rapid tool for evaluating changes in extractable fractions after addition of amendments. One advantage of neutral salt solutions such as $Ca(NO_3)_2$ is that these have a limited effect on both the operative pH at the exchange sites and on complex formation (Lebourg et al, 1996). Sequential extractions (*e.g.* Tessier et al. 1979) are intended to dissolve various chemically defined pools, usually defined as the following: soluble, exchangeable, carbonate bound, oxide bound, organic matter bound, and residual (Geebelen, 2002; Geebelen et al. 2002). A mild extractant, such as pure water or a dilute salt, is generally the first step. Extraction continues with progressively harsher extractants until the total digestion of solid phases is complete. These methods can more or less quantify changes in exposure, but do not necessarily measure the risk attenuation because organism response is not taken into account. Soil pore water can be directly sampled using the Rhizon sampling system, and diffusive thin gel (DTG) is a promising method to kinetically estimate the root exposure. *In vivo* animal feeding studies are used to determine to what degree ingested soil is solubilized in the gastro-intestinal (GI) tract and taken in the blood. The PBET-test (physiologically based extraction test, Ruby et al (1993)) was developed to predict trace element availability in humans following ingestion. It incorporates gastro-intestinal tract parameters representative of a human (including stomach and small intestine pH and chemistry, soil-to-solution ratio, stomach mixing and stomach emptying rates). Swine and rat dosing studies correlate well with PBET data for Pb, but the correlation for As is less good (Berti and Cunningham, 2000).

Chemical forms of soil trace elements can be studied using X-ray diffraction (XRD), X-ray absorption spectroscopy (XAS), scanning electron microscopy with energy dispersive X rays (SEM/EDX) and extended X-ray absorption fine structure spectroscopy (EXAFS) (Manceau et al, 2002, 2008). These techniques deliver valuable information on both chemical forms and oxidation states. Spectroscopic techniques are unsuitable to determine small changes in soluble soil trace element pool fractions.

Biological methods complement physico-chemical evaluation methods, which do not directly address biological availability or toxicity. Several case studies showed that amendments such as lime and hydrous iron oxides decrease the soluble and exchangeable trace element fractions, but that changes in trace element uptake by plants were not really significant (Sappin-Didier 1995; Müller and Pluquet 1997, Chlopecka and Adriano, 1996).

In function of land revitalization, plant tests are useful to determine both the need for and the effect of amendments. These tests may also allow us to detect other limitations to plant growth, such as nutrient deficiency or high salt levels. Other bioassays are used which target specific organisms such as earthworm, swine and rat (used to estimate bioavailability to humans), and bacteria (Berti and Cunningham, 2000; Van der Lelie et al, 2001; Geebelen, 2002).

For ecotoxicological evaluation, it is important to use several endpoints, *e.g.* biodiversity, bioaccumulation in living organisms, metabolomics and proteomics as well as genotoxicity, at different trophic levels, with a 'gradient' from a well-defined battery of tests to more complex conditions representative of real ecosystems. The combined use of chemical extraction, microbial biosensors, phytotoxicity and zootoxicity tests was used as a test system for evaluation and monitoring of efficacy and durability of *in situ* inactivation of trace element contaminated soils (Vangronsveld et al 2000a). A good conformity was found between the different evaluation criteria.

Evaluation of the durability of soil trace element immobilization asks for additional observation *in situ*. The evolution of biodiversity (bacteria, plants, mycorrhiza, soil invertebrates) should be examined to allow an evaluation of the revitalization process (Renella et al. 2008). The establishment of for instance a well-developed mycorrhizal network in revegetated areas is considered to be essential for the development of a sustainable ecosystem, while highly mycotrophic plants are characteristic for stable, sustainable ecosystems (Jeffries and Barea 1994; Vangronsveld et al. 1996). *In situ* plant sampling for chemical analysis should further be considered. Results from this analysis indicate to what extent the treatment continues to prevent food chain transfer of trace elements to animals and humans by consumption of plants grown on contaminated sites after reclamation. Along with contaminant monitoring, soil sampling for fertility purposes should be conducted on a regular basis (every 3 to 5 years) to indicate fertilizer and lime requirements.

3. Land Revitalization in the Field

3.1. Liming.

Application of chalk or limestone ($CaCO_3$), quicklime (CaO) or hydrated lime ($Ca(OH)_2$) to increase soil pH has been commonly used for centuries (Goulding and Blake, 1998). Amendments containing Mg such as dolomitic limestone are often applied to obtain an adequate Mg-nutrition to crops. Rothamsted Experimental Station (UK) possesses a set of long-term experiments (e.g. Park Grass Experiment) already established in the mid 19^{th} century that are particularly useful in understanding the relationship between land use, acidification, lime use and trace element mobility (Goulding and Blake, 1998). The effect of liming in agricultural soils with low Cd and Zn contents was illustrated by data from two long-term liming experiments established in 1963 (Sun et al, 2000). The fact that immobilization of low Cd contents by liming is not always effective was illustrated by increased Cd concentrations in potato tubers at 3 sites in South Australia (McLaughlin et al, 2000). Dolomite combined with organic compost can successfully restore plant growth in Cu-contaminated soils (Bes and Mench, 2008). This was confirmed at a wood treatment site with tree plantings, especially with mycorrhizal *Populus nigra* and *Salix viminalis* (Bes et al., 2008)

Due to the pH dependence of As sorption reactions on oxide minerals and layer silicates, the practice of liming for treatment of contaminated soils and mine tailings has the potential to mobilize arsenic (Jones et al, 1997). It may also be of concern for other trace elements such as Mo, U, V, and Se.

3.2. Biosolids and Liming.

The use of biosolids and similar organic wastes such as paper mill sludge, alone and in combination with other materials also is a long-standing practice, already used for restoration of many sites (Sopper, 1993). First of all, these amendments provide organic matter to improve soil physical properties, water infiltration and water holding capacity. They further contain essential micro- and macronutrients for plant growth, and also decrease bulk density of the soil. Biosolids may be combined with other materials that have a high calcium carbonate equivalent to restore trace element affected ecosystems, despite trace element concentrations in these biosolids (Brown et al, 2000). Biosolids can be combined with different alkaline materials such as limestone, and cyclonic ashes. This combined application of biosolids and lime should increase pH of the soil and reduce trace element availability. Decrease of direct exposure *via* soil ingestion is not evident since a remobilization of trace elements can be expected in the acidic conditions of the stomach.

Experiments at Palmerton (PA, USA), Leadville (CO, USA), Bunker Hill (ID, USA) Baltimore (MD, USA) and Pronto Mine (Ontario, Canada) investigated the efficacy of biosolids and high calcium carbonate to revitalize and/or to decrease human exposure at trace element contaminated sites.

3.2.1. Palmerton Experiment (PA, USA)

The activities of a zinc smelter that operated from 1890 until 1980 resulted in a high contamination of the site. In the surrounding area, zinc contamination is leading to serious problems with growing lawns and crops. On highly zinc contaminated soils at Blue Mountain, Rufus Chaney and co-workers installed test plots that compare the growth of various turf grasses in combination with different soil additives (http://www.soils.wisc.edu/~barak/soilscience326/agres.htm). Mixing high-iron and high-lime sewage sludge compost into soil resulted in a reduced level of zinc toxicity in grasses because soil zinc binds to iron in the compost. This reduced the soluble zinc in the soil and by consequence zinc uptake by plants. The fact that grasses obtained adequate iron nutrition resulted in a further reduction of zinc uptake.

3.2.2. Leadville Experiment (CO, USA).

High pyrite containing wastes from historic Pb and Zn mine tailings piles entered the Arkansas River and contaminated areas along an 18 km stretch. Oxidation of the pyrite resulted in strong reductions of soil pH (1.5 – 4.5) (Compton et al, 2001). A mixture of 224 tons ha^{-1} municipal biosolids and 224 tons ha^{-1} agricultural limestone was applied at several contaminated areas and subsequently seeded with a mixture of native grasses.

Further, a field experiment was established using 90 – 180 tons ha^{-1} of biosolids, alone or in combination with 224 tons ha^{-1} lime, and cultivated with annual rye grass. In year 1, treatments increased pH from 3.9 up to 6.4 (biosolids + lime). Calcium nitrate-extractable Cd, Pb, and Zn were strongly decreased in the surface horizon. Trace element concentrations in annual rye grass were also decreased: Cd (–54%), Zn (-40%), and Pb (-51%). The first results suggested that biosolids, in combination with lime, were effective for the restoration of a plant cover on the treated area.

However, trace element contents in plants still were too high to prevent animal exposure and spreading in food chains. Soil organisms, *i.e.* flagellates, ciliates, amoebae, and nematodes were found in higher amounts in the treated soils than in the uncontaminated control soil collected upstream of the contaminated area. Earthworm assays showed similar survival and biomass in the uncontaminated control soil and in the majority of the amended soils. Lime dust combined with biosolids showed the highest pH neutralization capacity and the lowest Zn concentration in cereal rye (Svendsen et al, 2001).

3.2.3. Bunker Hill Experiment (ID, USA)

At Bunker Hill, extensive trace element contamination of the surrounding hillsides and waterways and more than 500 ha barren of vegetation originated from the mining and smelting of Zn and Pb ores. The mining waste material contained 5500-14700 mg Zn kg^{-1}, 1500-4900 mg Pb kg^{-1}, and 7-28 mg Cd kg^{-1}. Soil pH ranged from 4.6 to 7.0 and organic matter content was extremely low. In 1997, biosolids (112 Mt ha^{-1}) were applied in combination with wood ash (220 Mt ha^{-1}) and log yard debris (20% by volume).

This resulted in the restoration of a vegetation cover on the trace element contaminated materials (Brown et al, 2000, 2001). Application of high N (4.4-5.3%) and low N (2.8%) biosolids was also investigated at 55 and 110 Mg DW ha^{-1} plus 140 Mg wood ash ha^{-1}. Ryegrass and vetch mixture were sown on the plots. Application of high N biosolids was leading to higher biomass than the low N amendment.

An increase of the soil pH and a decrease of the $Ca(NO_3)_2$ extractable trace elements (with a factor 15 compared to the untreated plots) may explain that plant roots could enter the untreated subsoil below the biosolids treated upper layer of the treated plots. Trace element concentrations in aerial parts of plants were within background concentrations for all treatments during the 3 years investigation period.

In the wetland site, surface application of a biosolid compost (60% DW) and wood ash (40% DW) to a depth of 15 cm was shown to enable a spontaneous recolonization. Trace element concentrations of reeds (*Typha latifolia*) were within the normal range. Nutrient concentrations in water from the outflow of the site indicated that application of the amendment did not affect the water quality.

In pot experiments, a mixture of biosolids and alum showed to be the most effective of five treatments in reducing soluble Zn species and increasing plant yield due to improvements of soil structure, nutrient status and organic matter content (Christensen and Brown, 2001).

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Biographical Sketches

Jaco Vangronsveld is full professor Biology and director of the interdisciplinary Centre for Environmental Sciences of Hasselt University. He studied biology at Hasselt University and the University of Antwerp (PhD in 1990, Antwerp) with emphasis on plant physiology. His research group has a longstanding experience in the field of heavy metal uptake by plants and the effects of toxic metal concentrations on plants and mycorrhiza. The fundamental research program of the group is concentrated on the (eco-)physiological effects and the molecular and biochemical sequence of events after application of contaminants. Studies of defense and tolerance mechanisms against heavy metals from the cellular to the population level are also part of the research program. Special attention is paid to subcellular localization of both contaminants and defense systems. Based on this fundamental research, biological tests for the evaluation of soil toxicity were developed.

The group is involved in several projects concerning the zinc, cadmium and lead contamination in the surroundings of the zinc smelters in the north-east of Belgium. Laboratory and *in situ* studies on phytoremediation (phytostabilization and phytoextraction) of heavy metal contaminated soils were started in 1985. Phytoremediation of organics also belongs to the research area of the group. Special attention is paid to the interaction between plants and their associated micro-organisms. The use of poplar and willow plantations as bioscreens for contamination plumes in groundwater is studied on laboratory and field scale.

Nele Weyens obtained her Master degree (Bio-engineer) in 2005 at the Catholic University of Leuven Belgium and actually is preparing a PhD concentrating on phytoremediation at Hasselt University.

Ann Ruttens (PhD in 2006 at Hasselt University) was research leader at Hasselt University. She started with research on phytoremediation and risk assessment of contaminated soils in 1993. From mid-June 2008, she is project leader at the CODA (Centrum voor Onderzoek in Diergeneeskunde en Agrochemie) in Tervuren (Belgium)

Jana Boulet obtained her Master degree (Biology) in 2005 at the Free University of Brussels and actually is preparing a PhD concentrating on phytoremediation at Hasselt University.

Andon Vassilev is an associate professor in Plant Physiology in the Agricultural University of Plovdiv, Bulgaria. He studied agronomy at Timiryazev Agricultural Academy in Moscow and plant physiology at the Agricultural University of Plovdiv (PhD, 1997). The interests of his research group are focused on plant – heavy metal interactions and sustainable use and management of metal-contaminated land. The group is involved in several projects, aimed to: (1) characterize phytotoxicity of different heavy metals, (2) optimize plant test system for evaluation of soil metal toxicity, (3) study physiological bases for observed cultivar differences in grain Cd accumulation in durum wheat as well as (4) improve Cd phytoextraction.

Michel Mench is senior scientist (PhD, HdR) at the UMR BIOGECO INRA 1202, University of Bordeaux 1. He studied Environmental Sciences and Agronomy at the National Polytechnic Institute of Lorraine, Nancy, France (PhD in 1985) working on trace element behavior in the rhizosphere. He was qualified as Professor at the Pau and Pays de l,Adour University, Pau, France in 1999. He works on the phytoremediation of trace element contaminated soils (TECS), and especially *in situ* stabilization and phytostabilization, since 1991, from individual plant level (oxidative stress, changes in soluble proteins) to plant community level. He has contributed to European projects (e.g. Phytorehab, 5th PCRD, and currently SUMATECS in the 6th PCRD ERA-NET Snowman) and French projects aiming to restore either a vegetation cover or crops on TECS and to break exposure pathways in contaminant linkages resulting in risks for the living organisms and their environment. He has developed the aided phytostabilization of metals and arsenic through the use of zerovalent iron grit in amendment combinations, a technology implemented at sites as La Combe de Sault, France (collaboration with Pr. J. Vangronsveld, Hasselt University, Belgium). He is leading researches on the sustainable management of TECS at wood treatment facilities (Cu, As, Cr, PAHs derived from creosote) using various phytoremediation options. He has gained experiences (>15 years) on risk assessment and sustainable management strategies for TECS through his contribution to field scale demonstration projects in France, Belgium, and Portugal. He has developed with the Warsaw University (Pr Gawronski et al) and J. Guinberteau (INRA MYCSA) some plant-microorganism associations for improving tree plantings at Cu-contaminated sites. He is developing new strategies based on selection of Cu-tolerant plant ecotypes and the valorization of the plant biomass through thermal oxidation (collaboration with ICMCB, Bordeaux 1 University).