
Review: Phytoremediation of Potentially Toxic Elements in Swiss Soils

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Abstract

Phytoremediation is a subprocess of bioremediation that aims to remediate contaminated soils in situ. Early research on phytoextraction of potentially toxic elements (PTE) concluded that remediation of heavily contaminated sites could take decades to centuries. Nevertheless, the field of research has grown over the last 30 years. This review examines the current state of research and commercialization of phytoextraction for PTE-polluted soils in Switzerland, Europe and North America.

Field trials at sites contaminated with lead, copper or mercury did not show any reasonable short to medium-term results due to the low extraction efficiency or - in the case of Switzerland - due to unsuitable plants. On the other hand, for cadmium and zinc an extraction efficiency of up to 30% of the original soil concentration was achieved within one growth period. These two PTEs thus appear to be promising candidates for in-situ remediation through phytoextraction. In case of multiple contamination (sole contamination of Cadmium or Zinc can occur), a combination of different bioremediation strategies may be applicable. Nevertheless, the mitigation of a single contaminant can facilitate soil reuse. Some studies have investigated the potential for enhancing the efficiency of extraction through the introduction of chemical additives. While this approach may facilitate a higher uptake of PTE by the plants, the more effective chemicals also tend to exhibit a higher negative environmental impact. Consequently, their field application is controversial, and cannot be supported by the authors.

Despite ongoing research efforts since the late 1980s/early 1990s, the number of private companies conducting commercial projects in the field of phytoextraction is still marginal. A search of the Swiss market revealed two companies with a focus on in-situ remediation of organic contaminants rather than on PTEs.

Based on our literature study, we identified potential for the phytoextraction of cadmium and zinc. Especially from soils with contamination levels around the trigger value, where restrictions have been issued, remediation (below the guide value) within five years seems plausible. To enhance the extraction efficiency, methods to increase the bioavailability of PTEs in soils, such as lowering the pH, could be further investigated.

Zusammenfassung

Die Phytosanierung ist ein Teilverfahren der Bioremediation, mit dem Ziel kontaminierte Böden in situ zu sanieren. Frühe Forschungsarbeiten zur Phytoextraktion potenziell toxischer Elemente (PTE) kamen zum Schluss, dass die Sanierung stark kontaminierter Standorte Jahrzehnte bis Jahrhunderte dauern könnte. Dennoch ist das Forschungsgebiet in den letzten 30 Jahren gewachsen. Dieser Bericht untersucht den aktuellen Stand der Forschung und der Kommerzialisierung der Phytoextraktion für PTE-belastete Böden in der Schweiz, in Europa und in Nordamerika.

Feldversuche an Standorten, die mit Blei, Kupfer oder Quecksilber belastet sind, zeigten aufgrund der geringen Extraktionseffizienz, oder – im Falle der Schweiz – aufgrund ungeeigneter Pflanzen keine vernünftigen kurz- bis mittelfristigen Ergebnisse. Hingegen konnte für Cadmium und Zink innerhalb einer Wachstumsperiode eine Extraktionsleistung von bis zu 30 % der ursprünglichen Bodenkonzentration erreicht werden, was sehr vielversprechend ist. Dies macht diese beiden PTEs zu vielversprechenden Kandidaten für die In-situ-Sanierung durch Phytoextraktion. Im Falle einer Mehrfachkontamination (eine Kontamination mit nur Cadmium oder Zink ist möglich), könnte eine Kombination verschiedener Bioremediationsstrategien angewandt werden. Dennoch kann bereits die Entfernung eines einzelnen Schadstoffs die Wiederverwendung des Bodens erleichtern. In einigen Studien wurde untersucht, inwiefern sich die Effizienz der Extraktion durch die Einführung chemischer Zusätze steigern lässt. Dieser Ansatz kann zwar die Aufnahme von PTE durch die Pflanzen erleichtern, allerdings haben die wirksameren Chemikalien in der Regel auch grössere negative Umweltauswirkungen. Folglich ist ihre Anwendung in der Praxis umstritten und kann von den Autoren nicht empfohlen werden.

Trotz der seit Ende der 1980er/Anfang der 1990er Jahre unternommenen Forschungsanstrengungen ist die Zahl der privaten Unternehmen, die kommerzielle Projekte im Bereich der Phytoextraktion durchführen, immer noch gering. Eine Recherche auf dem Schweizer Markt ergab zwei Unternehmen, die sich auf die In-situ-Sanierung von Belastungen mit organischen Schadstoffen und nicht auf PTEs konzentrieren.

Basierend auf unserer Literaturstudie haben wir ein Potenzial für die Phytoextraktion von Cadmium und Zink identifiziert. Insbesondere bei Böden mit Schadstoffgehalten um den Prüfwert, für welche Beschränkungen erlassen wurden, scheint eine Sanierung (bis unterhalb des Richtwerts) innerhalb von fünf Jahren plausibel zu sein. Zur Optimierung der Extraktionseffizienz könnten Methoden zur Erhöhung der Bioverfügbarkeit von PTEs in Böden, wie etwa die Senkung des pH-Werts, einer weiteren Untersuchung unterzogen werden.

Résumé

La phytoremédiation est un sous-processus de la bioremediation qui vise à assainir les sols contaminés *in situ*. Les premières recherches sur la phytoextraction d'éléments traces métalliques (ETM) permettent de conclure que l'assainissement de sites fortement contaminés pourrait prendre des décennies, voire des siècles. Néanmoins, le champ de recherche s'est développé au cours des 30 dernières années. Cette étude examine l'état actuel de la recherche et de la commercialisation de la phytoextraction pour les sols pollués par les ETM en Suisse et à l'étranger.

Les essais sur le terrain dans des sites pollués par le plomb, le cuivre ou le mercure n'ont pas donné de résultats raisonnables à court ou moyen terme en raison de la faible efficacité d'extraction ou, dans le cas de la Suisse, de plantes inadaptées. En revanche, pour le cadmium et le zinc, une efficacité d'extraction allant jusqu'à 30 % de la concentration initiale du sol a pu être atteinte en l'espace d'une période de croissance, ce qui est très prometteur. Cela fait de ces deux ETM des candidats prometteurs pour la dépollution *in situ*. En cas de contamination multiple (une contamination unique par le cadmium ou le zinc est possible), l'application combinée de différentes stratégies de bioremediation peut être pertinente. Néanmoins, l'atténuation d'un seul contaminant peut faciliter la réutilisation du sol. Certaines études ont examiné dans quelle mesure l'efficacité de l'extraction pouvait être améliorée par l'ajout d'additifs chimiques. Si cette approche peut faciliter l'absorption des PTE par les plantes, les produits chimiques plus efficaces ont généralement un impact plus négatif sur l'environnement. Par conséquent, leur utilisation dans la pratique est controversée et ne peut pas être recommandée par les auteurs.

Malgré les efforts de recherche déployés depuis la fin des années 1980/début des années 1990, le nombre d'entreprises privées menant des projets commerciaux dans le domaine de la phytoextraction reste encore marginal. Une étude de marché suisse a révélé l'existence de deux entreprises axées sur la dépollution *in situ* des contaminants organiques plutôt que sur les ETM.

Sur la base de notre étude bibliographique, nous avons identifié un potentiel pour la phytoextraction du cadmium et du zinc. En particulier pour les sols dont les niveaux de contamination se situent autour du seuil d'investigation, où des restrictions d'utilisation ont pu être émises, la dépollution (en dessous de la valeur indicative) dans les cinq ans semble plausible. Pour améliorer l'efficacité de l'extraction, des méthodes visant à augmenter la biodisponibilité des ETM dans les sols, telles que l'abaissement du pH, pourraient être étudiées.

1. Introduction

In Switzerland, land, and especially arable land, is limited and a diminution caused by multiple factors will continue to increase their scarcity. Alone between 1997 and 2009, a loss of 2.2% of agricultural areas was taking place, due to growing settlements and urban areas and natural reforestation in mountain regions (Federal Statistical Office, 2013). Besides irreversible losses caused by construction sites, also successive contamination due to anthropogenic emission is an important factor in the loss of farming land. In the last decades, the awareness of environmental pollution grew and new legislative and regulatory measures were enacted. For example, in the late 70s, it was common to produce compost from municipal solid waste and solid waste mixed with sewage sludge to produce soil conditioner for farmland, private gardens and vineyards (Gubler et al., 2015; Gysi & Koblet, 1975; Keller et al., 1980). An accumulation of Potentially Toxic Elements (PTEs) was measured on vineyards in different places in Switzerland, caused by this ‘fertilizer’ application (Keller et al., 1980). While the application of municipal solid waste compost (MSWC) and MSWC mixed with sewage sludge (MSWCSS) was stopped after a few years, the application of sewage sludge (SS) was still permitted until 2006. The application of MSWC, MSWCSS and SS arable soil can lead to a the long term contamination with plastic and metal packaging, organic pollutants, PTEs and pathogens (Keller et al., 1980; Reilly, 2001). According to Kupper and Fuchs (2007), compost can still contain organic pollutants like PAH, PCB, PFAS and many others. Soil contaminants like PTEs and radioactive substances can also enter agricultural land through mineral fertilizer and animal manure (Gross et al., 2021; Hermann, 2009). Even in organically managed farms, copper inputs to soils continue due to the application of animal manure or cupriferous fungicides (Speiser et al., 2015; Trewavas, 2001; Yakuba et al., 2021).

Soil is a non-renewable natural resource, hence an inexpensive and non-destructive method to remediate contaminated soil would be of great interest. For gradual decontamination of slightly to heavily polluted soils, a possible solution could be the use of bioremediation. It consists in a biological treatment to remove or immobilize pollutants from soil and is based on the action of one or several of the following organisms: i) plants; ii) prokaryotes; and iii) fungi. Between 1995 and 2010 several research projects on bioremediation were conducted in Switzerland (*e.g.*, Hammer & Keller, 2003; Herzig et al., 2014; Kayser et al., 2000), but have since then not been continued due to modest results, despite the still increasing worldwide research output. The aim of this literature review is to explore the state of knowledge on bioremediation of PTE-contaminated soils and examine approaches to accelerate the process in view of identifying the potential for such remediation of contaminated soils in Switzerland. To assess this potential, we focus on research results from field trials. These studies are the most realistic with respect to the applicability on contaminated sites. However, the number of studies is very limited, as they are, in comparison with greenhouse trials, more resource intensive (time and money) and less controllable (susceptible to the weather and herbivores).

2. Government Regulation for Soil Protection

The Swiss Ordinance relating to Impacts on the Soil (OIS; German: [VBBo](#); French: [OSol](#)) restricts the level of most common soil pollutants, such as polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), dioxins (PCDD), furans (PCDF) and PTEs (Cr, Ni, Cu, Zn, Mo, Cd, Hg, Pb, F). The soil protection strategy in Switzerland (Figure 1) distinguishes between three levels of contamination: i) guide value; ii) trigger value; and iii) clean-up value. Guide, trigger and clean-up values for PTEs are given in Table 1. In between guide and trigger value (with exceptions) Federal regulations allow the relocation of soils to locations with equivalent contamination patterns (BAFU, 2021). Nevertheless, every year tons of fertile soils are disposed of in landfills, incinerated, or irreversibly treated by soil-washing. Some of these soils are only slightly above the guide value and could be remediated (Umwelt-Zentralschweiz, 2022).

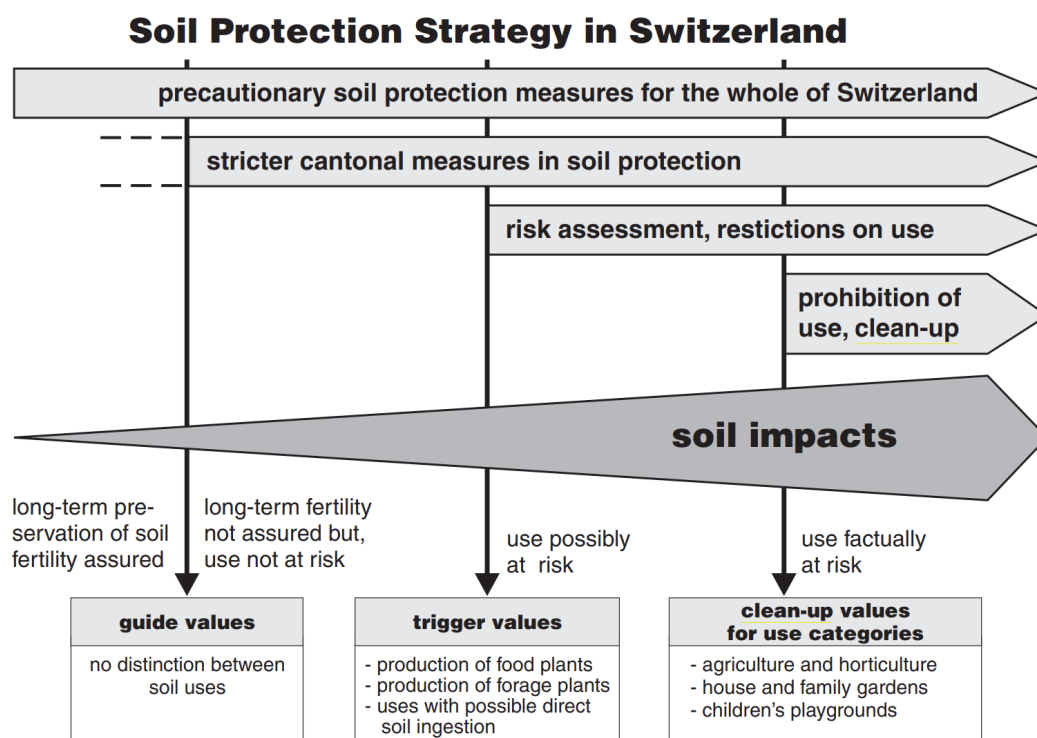


Figure 1: Soil protection strategy in Switzerland (figure adopted from FOEN, 2001)

Table 1: Guide, trigger and clean-up values according to OIS (Federal Council, 1998) (table adapted from BAFU, 2021) and RECOSOL (Reiser & Hutter, 2019; Reiser & Meuli, 2013)¹; (DM = Dry matter content)

Contaminants	Maximum content according to OIS guide values		
	Soil with ≤15% humus content = mg/kg _{soil} DM Soil with >15% humus content = mg/dm ³		
	Guide value mg/kg _{soil}	Trigger value mg/kg _{soil} (food / for-age plants)	Clean-up value mg/kg _{soil} (agriculture/residential)
Cadmium (Cd)	0.8	2/2	30/20
Chromium (Cr)	50	-	-
Copper (Cu)	40	-/150	1000/1000
Lead (Pb)	50	200/200	2000/1000
Mercury (Hg)	0.5	0.5/0.5 ¹⁾	20 ¹⁾
Molybdenum (Mo)	5	-	-
Nickel (Ni)	50	-	-
Zinc (Zn)	150	-	2000/2000

3. State, Sources and Trends of Potential Toxic Element Concentrations in Swiss Soils

In Switzerland, the majority of soil contamination can be attributed to anthropogenic activities or sources. These sources can be distinguished between point and diffuse sources. Examples for point sources of PTEs are industries, shooting ranges (Pb, Sb) or galvanized structures (Gubler et al., 2015). More relevant in the context of the OIS, however, are diffuse or ubiquitous sources (Table 2) such as sewage sludge, tire wear (Zn), leaded gasoline (Pb) or the application of pesticides or mineral fertilizers (As, Cd, Hg, Pb, U) (Gubler et al., 2015; Jänsch & Römbke, 2009; Samartin, 2021). According to a recent report from Samartin (2021), where they investigated mineral fertilizers for their PTE content, 26% of examined fertilizers had a Cd content exceeding the threshold of the Chemical Risk Reduction Ordinance ([ORRChem](#)) (for fertilizers: 50 g/t P, according to Annex 2.6) and 34% were above the recommendation of the German Federal Environmental Agency threshold for U (50 mg/kg P₂O₅, Kommission Bodenschutz beim Umweltbundesamt, 2012). Hg and Pb were also found in the fertilizer, but all were below the EU thresholds for harmful substances. Switzerland has not (yet) regulated As, Hg, Pb and U in mineral fertilizer.

Table 2: PTEs and their possible anthropogenic sources.

Pollutant	Sources	References
Cadmium (Cd)	Mineral fertilizer, oil/coal combustion, iron and steel production, sewage sludge, waste incineration	FitzGerald & Roth, 2015; Wegelin & Gsponer, 1997
Chromium (Cr)	Metal industry and sewage sludge	Gonnelli & Renella, 2013
Copper (Cu)	Animal manure, feed additives and pesticide in organic farming, metal industry	Gubler et al., 2015; Speiser et al., 2015
Lead (Pb)	Pb in gasoline (until 2000), shooting range, waste deposal, compost	Gubler et al., 2015; BAFU, 2020; Wegelin & Gsponer, 1997
Mercury (Hg)	Atmospheric deposition, sewage sludge, incineration plants, mineral fertilizer	Samartin, 2021; Suess et al., 2020
Molybdenum (Mo)	Mine waste, fertilizer, metal industry	Harkness et al., 2017; Neunhäuserer et al., 2001
Nickel (Ni)	Industry (metal, cement, chemical, batteries), smelting operations, mining, pesticides, fertilizer, sewage sludge	El-Naggar et al., 2021; Gonnelli & Renella, 2013; Iyaka, 2011
Zinc (Zn)	Galvanic industry, alloys, feed additive, tire wear, livestock manure, sewage sludge, inorganic fertilizers	Gubler et al., 2015; BAFU, 2012; Wegelin & Gsponer, 1997

According to the Swiss Soil Monitoring Network (NABO, Gubler et al., 2015) PTE concentrations are mainly stable or declining. Hence, most of the contamination is inherited from the past such as Pb and Hg and inputs into soil have decreased in the last decades (*e.g.*, leaded fuel has been prohibited and Hg-containing products (thermometers, light bulbs, dental amalgam fillings etc.) are lessened). The concentration of Cd in soil has remained stable over the past decade, despite a decrease in atmospheric deposition. This may be attributed to an increase in fertilizer-derived emissions, which could have offset the effects of reduced deposition. The main current contaminations in agricultural soil are Cu and Zn, which increased in the last 20 years in intensively managed grasslands and agriculture.

Naturally occurring geogenic soil contamination in Switzerland are mostly containing As, Cd, Ni, V or Tl, however, levels higher than anthropogenic contamination are only found in certain regions (Desaules & Studer, 1993; Knecht et al., 1999; Reusser et al., 2023; Schmutz & Uttinger, 2015). It is estimated, that around 4% – 11% of the monitoring sites showed PTE contaminations above the guide values regarding Cd, Cu, Pb, Ni or Cr (Gubler et al., 2015).

4. Phytoremediation

Phytoremediation is the main term for the remediation of contaminated soil or water using plants (Shmaefsky, 2020a). As part of the bioremediation process, phytoremediation includes plant-based treatments and is further divided into sub-segments depending on their output, for example, extraction, degradation, stabilization and others (Figure 2).

Phytoremediation started to get popular in the 1990s for the restoration of contaminated sites and wastewater. Phytoremediation is a plant-based method to mitigate harmful substances such as PTEs in the environment. Diverse plants have different abilities to uptake toxic chemicals such as PTEs (*e.g.*, As, Cd, Cu, Pb, Hg and others), radionuclides and organic compounds from the environment. While most plants exposed to elevated concentrations of pollutants wither and/or die (Morkunas et al., 2018), some plants have shown high tolerance to PTEs. These plants can be divided into two categories: Excluding and sequestering plants. Plants belonging to the first category manage to prevent the uptake of PTEs with selective membrane channels (the uptake of PTEs is mainly driven by the water sink of the shoot). The second category of plants also have selective membrane channels but with a high affinity for PTEs, which will then be sequestered in cell organelles like the vacuole and/or detoxified with phytochelatins/enzymes. Plants suitable for phytoremediation have a high tolerance for PTEs, a high root-to-shoot transfer, a fine root network and either have a very high root heavy metal accumulation and/or a high biomass production within one season. For successful practical application, the plants should also show some resistance to environmental impacts (*e.g.*, weather, pathogens, herbivores) and low cultivation costs (Manorama Thampatti et al., 2020).

The process of phytoremediation can be divided into three main categories regarding removal, degradation and stabilization of soil contaminants (Figure 2).

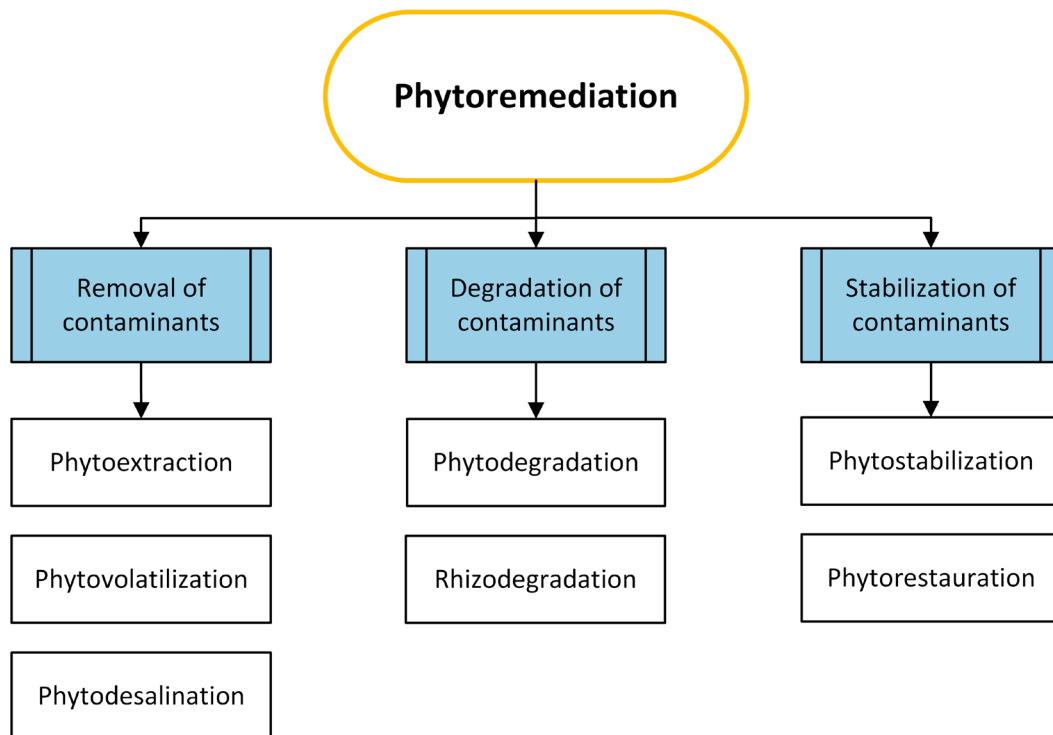


Figure 2: Diagram of different phytoremediation treatments.

For each group, different techniques are used to treat the contaminated site. General treatment methods are briefly explained in Table 3.

Table 3: Different techniques of phytoremediation (Etim, 2012; Manorama Thampatti et al., 2020)

Techniques	Description
Phytoextraction	Uptake of chemical pollutants from the soil into the above-ground plant biomass
Rhizofiltration / Phytosequestration	Sequestration of contaminants into or on the plant root, or surrounding solutions. While rhizofiltration is referred to as water treatment, phytosequestration is used for soil remediation.
Phytovolatilization	Uptake of contaminants and conversion into gaseous state with subsequent release into the atmosphere
Phytostabilization	Immobilization and reduction of bioavailability of contaminants
Phytodegradation / Phytotransformation	Degradation or incorporation of contaminants by the plant
Hydraulic control	Controlling the water table and the soil field capacity by transpiration to reduce the leaching of pollutants to groundwater or infiltration from the vadose zones
Rhizodegradation / Phytostimulation	Degradation of organic pollutants by plant roots. Can be a supportive mechanism for bioremediation.
Rhizoremediation	Degradation of contaminants by rhizospheric microbes
Phytodesalination	Specialist plants to remove excess salts from saline soils

There are some remediation methods that are not suitable for the remediation of PTE-contaminated soils. Degradation methods like phyto- and rhizodegradation are not applicable, as PTEs cannot be degraded. Phytovolatilization of PTEs has only been observed with Selen (Se to $\text{Se}(\text{CH}_3)_2$) and Hg, which has been made possible with genetic engineering (methyl-Hg to Hg^0) (Greipsson, 2011). The two major remaining methods are stabilization and extraction. Phytostabilization does not remove the contaminants and requires constant monitoring to detect potential decreases in stabilization and potential treatment corrections and is thus not an interesting candidate for long-term remediation. However, for phytoextraction, such monitoring is not necessary as the contaminants are transferred to the above-ground biomass, which is subsequently harvested. Additionally, with phytoextraction, contaminants are removed from the soil, leaving the soil intact, which makes this remediation strategy very attractive from a soil conservation perspective.

Due to the aforementioned considerations, it can be concluded that phytoextraction represents the most appropriate phytoremediation strategy for PTEs. Consequently, the present report focuses primarily on this approach.

5. Phytoextraction of Potentially Toxic Elements

In the last half-century, plants with special abilities to tolerate above average PTE concentrations in their plant tissue (even > 1% of their dry mass (DM)) have been investigated. Research has shown, that extraction capabilities and favorable plant species depend on the kind of PTE. Baker & Brooks (1989) defined high sequestering plants as PTE hyper-accumulators when they accumulate more than the following thresholds: i) 10 mg/kg plant DM for Hg; ii) 100 mg/kg plant DM for Cd; iii) 1'000 mg/kg plant DM for Ni, Co, Cr, Cu, Pb; and iv) 10'000 mg/kg plant DM for Zn and Mn (Baker et al., 2000; Baker & Brooks, 1989; Nedjimi, 2021; Yan et al., 2020). Even though this classification is rather arbitrary and other factors such as above-ground biomass production are important for a successful phytoremediation, these values give some indication on the potential of bioaccumulation in plants.

As the primary goal was to evaluate the feasibility of phytoremediation in Switzerland, we further only listed plants that have a bioaccumulation factor above 1 (higher concentration in plant than in the soil), which can be cultivated in the Swiss climate, and we further focused on field trials. There exists further research focusing on pot or hydroponic experiments, however, the transferability to the field is challenging to assess. Moreover, it is difficult to make comparisons between the results of different field trials due to the use of different acid mixtures for PTE extractions from soil, which consequently result in different pseudo-total concentrations¹. In Switzerland the extraction method to measure total concentrations of heavy metals in soils is rather mild (2N HNO₃ according to OIS) compared to some of the extraction methods used for the field trials described in the following subchapters (see also the summary of the field-study results in Table 4). Thus, the relative extraction efficiencies shown in Table 4 could be higher than when the same samples were extracted according to the OIS. Only PTEs with clean-up values were investigated (Cd, Cu, Pb, Hg and Zn), as remediation is mandatory only above this value. In the following sub-chapters, the study results are grouped according to the extracted PTE and plants utilized.

5.1 Cadmium

Cd is a toxic, non-essential element, which can already influence soil fertility in small quantities (Niño-Savala et al., 2019). Its guide and clean-up values are 0.8 respectively 30 for agriculture or 20 mg/kg for residential (if not otherwise noted, values are given in mg/kg_{soil} DM, for readability we write mg/kg; plant concentrations are noted as mg/kg DW).

Sedum alfredii and *Brassica napus*:

A field trial with *Sedum alfredii* and *Brassica napus* on lightly Cd-contaminated paddy soil was conducted in Shaoxing, China with 9 plots of 192 m² each. The initial Cd concentration was 0.372 mg/kg (allowable concentration is 0.3 mg according to Chinese Soil Environmental Quality Standard, using a 5:1:1 HNO₃, HClO₄ and HF mix as soil extractant) and soil pH was 5.4. Each plant was tested separately and in an intercropping system. Results show that *S. alfredii* extracted 147.7 g/ha after the first year and Cd concentration decreased to 0.327 mg/kg. The intercropping system extracted 78.9 g/ha and Cd concentration was reduced to 0.345 mg/kg. *Brassica napus* had a significantly lower Cd extraction of 5.7 g/ha which resulted in a decrease to 0.361 mg/kg. The Cd concentration after the second year was further decreased

¹ The extraction of PTEs from silica minerals is only possible with the use of HF. The use of acid mixtures without HF results pseudo-total concentrations.

to 0.285 mg/kg with *S. alfredii* (and thus below the threshold value), to 0.316 mg/kg with the intercropping system and to 0.348 mg/kg with *Brassica napus* (Zhang et al., 2021).

Noccaea caerulescens:

Field trials in two locations, Gare Royal (GR) and Masui (MAS), were conducted with *Noccaea caerulescens* in an urban wasteland in Brussels, Belgium. GR had a Cd concentration of 1.7 mg/kg and a pH of 7.2, MAS had a Cd concentration of 2.1 mg/kg and pH of 8.2. A tri-acid mix (HCl 37%, HNO₃ 65%, HF 40%) was used as soil extractant for total Cd concentration. Two *N.caerulescens* variations, “Ganges” (GAN, from the south of France) and “Wilwerwiltz” (WIL, from Luxembourg) were used in both locations. The experiment duration was 6 months.

GAN extracted 200 g Cd/ha, which resulted in a Cd reduction from 1.7 to 1.42 mg/kg at GR. At MAS, GAN extracted 100 g Cd/ha, which resulted in a Cd reduction from 2.1 to 1.98. WIL extracted 140 g Cd/ha, which resulted in a Cd reduction from 1.7 to 1.49 mg/kg at GR. At MAS, WIL extracted 30 g Cd/ha, which resulted in a Cd reduction from 2.1 to 2.06 (Jacobs et al., 2017).

Another study was also conducted with *N. caerulescens* in field trials in nine plots of the Woburn Garden Market Experiment in Bedfordshire, England. Cd concentrations ranged from 2.6 mg/kg soil to 12.5 mg/kg soil. A mixture of HNO₃ and HClO₄ was used as extractant. Soil pH was not reported. EDTA, NTA and citric acid were used for mobilizing PTEs. Deionized water was used as a control. The *N. caerulescens* variation was “Ganges” (GAN).

The addition of citric acid and NTA didn’t affect biomass production significantly, however, the addition of EDTA resulted in significantly reduced biomass production. Interestingly, the Cd concentration in plants treated with EDTA was lower than in control plants (or NTA and citric acid treated plants). Except for 2 plots, *N. caerulescens* shoots had concentrations of more than 100 mg/kg and exceeded even 1000 mg/kg in one case. The calculated proportion of soil Cd extracted ranged from 1.3% to 21.7%. The much higher extraction could only be achieved with a 14-month growth period, which was significantly larger than the combined extraction of two consecutive growth seasons (4-5 months in each). Amount of Cd extracted correlated significantly with Cd concentration in the soil (McGrath et al., 2006).

In a third study, *N. caerulescens* was used in field trials in Dornach (DOR) and Calsano (CAL), Switzerland. Cd concentrations were 2.5 and 2.8 mg/kg (using 2 N HNO₃ as soil extractant) and the pH were 7.3 and 5.2 in DOR respectively CAL. Maximum Cd extraction for DOR was 130 and 540 g/ha for CAL, this was achieved by transplanting and sowing the field three times within the 14 months of the experiment time frame. Cd soil concentration after treatment was not measured/stated, however, they mention that remediation within 10 years should be possible (Hammer & Keller, 2003).

Nicotina tabacum:

Two field trials in Chaling and Guanxi, China, were conducted with *Nicotiana tabacum*. Cd concentration was 0.59 mg/kg in Chaling with a pH of 4.8 and 1.35 mg/kg in Guanxi with a pH of 5.4. A tri-acid mix (HCl-HNO₃-HClO₄) was used as soil extractant. The overall experiment duration was 5 months; however, the plants were cut at 2/3 of the stalk after 2 months to allow for regeneration. This increased Cd accumulation due to the new plant tissues that developed.

N. tabacum extracted a combined amount of 132 g Cd/ha in Chaling and 204 g Cd/ha in Guanxi over the duration of the experiment. There were no significant Cd extraction differences between cuts. This led to a Cd reduction from 0.59 mg/kg to 0.53 mg/kg in Chaling and from 1.35 mg/kg to 1.27 mg/kg (Yang et al., 2017).

Solanum nigrum:

A field trial with *Solanum nigrum* was conducted in Shenyang, China on contaminated agricultural soil. Cd concentration in the soil was 1.91 mg/kg and pH 6.1. A mix of HNO₃-HClO₄ (7:1) was used as soil extractant. The experiment had a duration of 5 months; however, due to the fast growth and maturation of *S. nigrum* two full harvests were possible.

S. nigrum extracted a combined 402 g Cd/ha over the whole experiment (two harvests). The total Cd extraction was significantly higher in the first batch. This resulted in an overall Cd reduction from 1.91 mg/kg to 1.73 mg/kg (Ji et al., 2011).

***Salix smithiana* and *Populus nigra*:**

A field trial on contaminated agricultural soil was conducted in Podlesí, Czech Republic with two clones of each *Salix* and *Populus* were tested. The location had a concentration of 7.3 mg Cd/kg, using an HNO₃-HCl mix as a soil extractant. Soil pH was 5.7 and the experiment duration was 6 years.

The best clone *Salix smithiana* extracted 268 g Cd/ha within 2 years, which resulted in a Zn reduction over 6 years from 7.3 to 7.2 mg/kg (0.94% reduction). The best clone of *P. nigra* extracted 158 g Cd/ha within 2 years (Kubátová et al., 2016).

Conclusion:

A wide variety of plants can accumulate Cd at high foliar concentrations. Furthermore, the bioavailability of Cd significantly increases below pH 6.5. Remediation achievements of approximately 10% reduction in soil concentration (initial concentration around trigger value) per growth season have been reached. Under the assumption that such extraction efficiencies could be maintained a 50% reduction of the soil concentration could be achieved in seven years. We, thus, conclude that Cd is good candidate for phytoremediation.

5.2 Copper

Cu is an essential nutrient for plants and is also required by humans and animals in limited amounts. Its guide and clean-up values are 40 and 1'000 mg/kg respectively.

Bryophyllum pinnatum:

A trial with *Bryophyllum pinnatum* was conducted in Gazipur, Bangladesh on contaminated soil close to textile industries. Cu concentration in the soil was 28.57 mg/kg and pH 5.7. A mix of HNO₃-HCl was used as soil extractant. The experiment had a duration of 4.5 months with measurement intervals of 45 days. *B. pinnatum* lowered soil Cu content from 28.57 mg/kg to 20.27 mg/kg after 135 days. During the last 45 days interval, the bioaccumulation factor was significantly reduced (from 2-3.5 to 0.8-1) but the translocation factor significantly increased (from 0.4-0.6 to 1.9-2.6) (Riza & Hoque, 2021).

***Zea mays*, *Helianthus annuus* and *Nicotiana tabacum*:**

A large-scale field trial was conducted in Dornach Switzerland on soil contaminated with Cu by industrial metal smelters. *Zea mays*, *Helianthus annuus* and *Nicotiana tabacum* were used. Cu concentration was 542 mg/kg (using 2 N HNO₃ as soil extractant) and pH 7.3. The experiment lasted 2 years, during the second year NTA (chelating agent) was added to the soil (see Chapter 6).

Z. mays extracted a combined 190 g Cu/ha during the first year and 280 g Cu/ha during the second year. *H. annuus* extracted a combined 460 g Cu/ha during the first year and 820 g Cu/ha during the second year. *N. tabacum* extracted a combined 270 g Cu/ha during the first year and 410 g Cu/ha during the second year (Kayser et al., 2000). Cu soil concentration after treatment was not measured/stated.

***Sedum plumbizincicola* and *Medicago sativa*:**

A field trial was conducted in Zhejiang, China on Cu-contaminated agricultural soil. Cu concentration was 468 mg/kg, using an HNO₃-HCl mix as soil extractant. Soil pH was 5.7 after liming (pH before liming was 4.6). *Sedum plumbizincicola* and *Medicago sativa* were chosen in an intercropping system as well as *M. sativa* alone. The experiment duration was 6 months.

S. plumbizincicola and *M. sativa* reduced soil Cu concentration from 468 mg/kg to 446 mg/kg. *M. sativa* reduced soil Cu concentration from 468 mg/kg to 451 mg/kg. Extracted grams of Cu/ha were not measured/stated (Wu et al., 2012).

Conclusion:

Remediation achievements of close to 30% reduction in soil concentration (initial concentration below guide value) per growth season have been reached. However, such achievements are only possible with tropical plants (e.g., *Bryophyllum pinnatum*) which mostly origin from the Katanga Copper Belt and are not suited for the temperate climate in Switzerland (Lange et al., 2017). Further limitations are the increases of bioavailability of Cu below 4.5-5, which is more difficult to achieve if not impairing plant growth, and most plants start accumulating only at high Cu concentrations (around clean-up value). We, thus, conclude that Cu is a potential candidate for phytoremediation.

5.3 Lead

Pb is toxic and neither essential for plants nor humans and animals. Its guide and clean-up values are 50 and 2'000 for agriculture or 1'000 mg/kg for residential areas.

***Cannabis sativa*:**

A field trial with *Cannabis sativa* was conducted in Sardinia, Italy on Pb-contaminated agricultural soil. Pb concentration before the experiments in the soil was 752 mg/kg. An HNO₃-HCl mix was used as soil extractant. Three clones of *Cannabis sativa* were chosen as test plants. Soil pH was 6.4 and the experiment duration was 6 months.

The best *C. sativa* clone extracted 34.1 mg/kg DW Pb, of which 17.8 mg were in the roots (Canu et al., 2022). The decrease in soil Pb concentration was not measured/stated.

***Sonchus arvensis*:**

A field trial was conducted on three sites in Bo Ngam, Thailand on soil contaminated by an abandoned Pb mine with *Sonchus arvensis*. The Pb concentration before the experiments in the soil was 230 mg/kg on site 1, 5'998 mg/kg on site 2 and 96'423 mg/kg on site 3. HNO₃ was used as soil extractant and the pH was 6.9, 6.8 respectively 7.7. The experiment lasted for 6 months.

S. arvensis extracted 126 mg/kg (59.9 in the shoot, 66.7 in the roots) on site 1, 441.5 mg/kg (138.9 in the shoot, 302.6 in the roots) on site 2 and 5'340 mg/kg (3'664.1 in the shoot, 1'675.9 in the roots) on site 3 (Surat et al., 2008). The decrease in soil Pb concentration was not measured/stated.

***Salix smithiana* and *Populus nigra*:**

A field trial on contaminated agricultural soil was conducted in Podlesí, Czech Republic with two clones of each *Salix* and *Populus* were tested. The location had a concentration of 1368 mg Pb/kg before the experiments, using an HNO₃-HCl mix as a soil extractant. Soil pH was 5.7 and the experiment duration was 6 years.

The best clone *Salix smithiana* extracted 163 g Pb/ha within 2 years. The best clone of *P. nigra* extracted 429 g Pb/ha within 2 years (Kubátová et al., 2016). The decrease in soil Pb concentration over 6 years was not measured/stated.

Conclusion:

Field studies measuring the decrease of Pb concentrations in soil over the experiment (before and after) are missing. An evaluation of the suitability of Pb for phytoremediation is therefore difficult. However, based on the low bioavailability (a significant increase below pH 4) and the lack of suitable plants for a temperate climate, we can conclude that Pb is a poor candidate for phytoremediation. *Sonchus arvensis* accumulated high Pb concentrations, but the accumulation factor was less than one and hence below soil concentration. However, it is remarkable that a plant can survive in an environment with Pb soil concentrations of 10%.

5.4 Mercury

Hg is toxic, especially methyl-Hg and neither essential for plants nor humans and animals. Its guide and clean-up values are 0.5 respectively 20 mg/kg.

Barley, wheat and yellow lupin:

A field trial in Spain was conducted on Hg-contaminated agricultural soil with barley, wheat and yellow lupin over three consecutive years. Hg concentration in the soil was 29.17 mg/kg (extractant: HCl, HNO₃, HF, HClO₄) and a pH ranging from 7.3 to 8.1. Wheat extracted 0.48, barley 0.4 and lupin 0.2 mg Hg/kg. With barely having the highest biomass an extraction of 719 mg Hg/ha was achieved (Rodriguez et al., 2005).

Conclusion:

Among the here discussed elements, Hg is probably the least suited for phytoremediation. A significant increase in mobility occurs only below pH 4. Above, less than 2% is bioavailable (Rodriguez et al., 2005). Such a low soil pH is not feasible for almost all plants to grow. The low mobility makes an efficient extraction impossible; this is also reflected in the above-mentioned trial. According to the literature, this trial was also the only field trial that has been conducted. Other data on phytoextraction of Hg are mostly from measured concentrations in wild plants and some experiments in hydroponic systems or spiked soil experiments.

5.5 Zinc

Zn is essential for plants, animals and humans, however, exceeding concentrations lead to adverse effects. Its guide and clean-up values are 150 respectively 2'000 mg/kg for both agricultural and residential areas.

Noccaea caerulescens:

In the aforementioned study on Cd (Chapter 5.1) in Brussels, Belgium also Zn was investigated. GR had a Zn concentration of 480 mg/kg and a pH of 7.2. MAS had a Zn concentration of 710 mg/kg and pH of 8.2. A tri-acid mix (HCl, HNO₃, HF) was used as soil extractant. Two *N.caerulescens* variations, "Ganges" (GAN, from the south of France) and "Wilwerwiltz" (WIL, from Luxembourg) were used in both locations. The experiment duration was 6 months.

GAN extracted 18'000 g Zn/ha, which resulted in a Zn reduction from 480 to 434 mg/kg at GR. At MAS, GAN extracted 5'900 g Zn/ha, which resulted in a Zn reduction from 710 to 690. WIL extracted 47'000 g Zn/ha, which resulted in a Zn reduction from 480 to 350 mg/kg at GR. At MAS, WIL extracted 7'900 g Zn/ha, which resulted in a Zn reduction from 710 to 677 mg/kg (Jacobs et al., 2017).

The study on Cd (Chapter 5.1) in England, also investigated Zn. Zn concentrations ranged from 107.6 mg/kg soil to 365.7 mg/kg soil. A mixture of HNO₃ and HClO₄ were used as extractant. Soil pH was not reported. EDTA, NTA and citric acid were used for mobilizing PTEs. Deionized water was used as a control. The *N. caerulescens* variation was "Ganges" (GAN).

The addition of citric acid and NTA didn't affect biomass production significantly, however, the addition of EDTA resulted in significantly reduced biomass production. Interestingly, the Zn concentration in plants treated with EDTA was lower than in control plants (or NTA and citric acid treated plants). Although, this relationship was weaker than in the case of Cd. The plant Zn concentrations ranged from 1200 mg/kg to 6400 mg/kg. The calculated proportion of soil Zn extracted ranged from 0.3% to 4.4%. The much higher extraction could only be achieved with a 14-month growth period, which was significantly larger than the combined extraction of two consecutive growth seasons (4-5 months in each). In contrast to Cd, the amount of Zn extracted did not correlate at all with Zn concentration in the soil (McGrath et al., 2006).

The study on Cd (Chapter 5.1) in Switzerland, also investigated Zn. Zn concentrations were 673 and 1158 mg/kg (using 2 N HNO₃ as soil extractant) and the pH were 7.3 and 5.2 in DOR respectively CAL. Maximum Zn extraction for DOR was 3'700 and 20'000 g/ha for CAL, this was achieved by transplanting and sowing the field three times within the 14 months of the experiment time frame. Zn soil concentration after treatment was not measured/stated, however, they mention that remediation in a realistic time frame would not be possible (Hammer & Keller, 2003).

Salix smithiana and *Populus nigra*:

A field trial on contaminated agricultural soil was conducted in Podlesí, Czech Republic with two clones of each *Salix* and *Populus* were tested. The location had a concentration of 218 mg Zn/kg, using an HNO₃-HCl mix as a soil extractant. Soil pH was 5.7 and the experiment duration was 6 years.

The best clone *Salix smithiana* extracted 2'160 g Zn/ha within 2 years, which resulted in a Zn reduction over 6 years from 218 to 217 mg/kg (0.34% reduction). The best clone of *P. nigra* extracted 1'720 g Zn/ha within 2 years (Kubátová et al., 2016).

***Helianthus annuus* and *Nicotiana tabacum*:**

A field trial on contaminated industrial soil in Bettwiesen, Switzerland with *Helianthus annuus* and *Nicotiana tabacum*. The experiment duration was five years, however, there were also seasonal trials of 6 months. The location had an average concentration of 1'608 mg Zn/kg, using an HNO₃-HCl mix as a soil extractant and the soil pH was 7.1. Several clones of each *Nicotiana tabacum* and *Helianthus annuus* were tested.

During the seasonal trial, the best clone of *N. tabacum* extracted 20'100 g Zn/ha (or 617 mg/kg plant DW). The best clone of *H. annuus* extracted 9'300 g Zn/ha (or 346 mg/kg plant DW) (Herzig et al., 2014). Total Zn reduction in soil was not measured/stated.

***Zea mays*, *Helianthus annuus* and *Nicotiana tabacum*:**

In the aforementioned study on Cu (Chapter 5.2) in Dornach, Switzerland also Zn was investigated. *Zea mays*, *Helianthus annuus* and *Nicotiana tabacum* were used. Zn concentration was 542 mg/kg (using 2N HNO₃ as soil extractant) and pH 7.3. The experiment lasted 2 years, during the second year NTA (chelating agent) was added to the soil (see Chapter 0).

Z. mays extracted a combined 2'000 g Zn/ha during the first year and 3'100 g Zn/ha during the second year. *H. annuus* extracted a combined 1'900 g Zn/ha during the first year and 3'600 g Zn/ha during the second year. *N. tabacum* extracted a combined 1'100 g Zn/ha during the first year and 1'900 g Zn/ha during the second year (Kayser et al., 2000). Zn soil concentration after treatment was not measured/stated.

Conclusion:

For Zn several plants with high accumulation potential (e.g., various *Noccaea* species) which are suitability for temperate climates exist. Furthermore, the bioavailability of Zn significantly increases below pH 6-6.5. Remediation achievements of >10% reduction in soil concentration (initial concentration above guide value) per growth season have been reached. Under the assumption that such extraction efficiencies could be maintained, a 50% reduction of the soil concentration could be achieved in less than seven years. We, thus, conclude that Zn is a good candidate for phytoremediation.

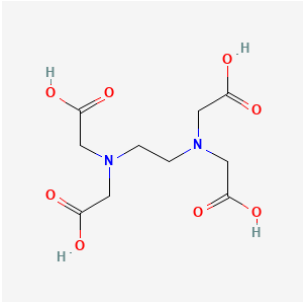
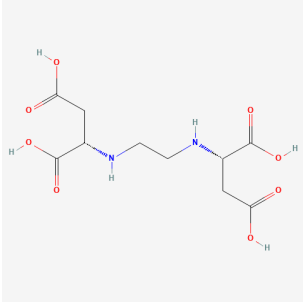
Table 4: Summary of aforementioned field-trials with data on soil concentration before and after treatment. The comparison of different study results is often difficult and can be misleading, due to the use of different mixtures of acids during the extraction of PTEs from soil (see annotations). Hg and Pb are not shown, as there is no data for before and after treatment available.

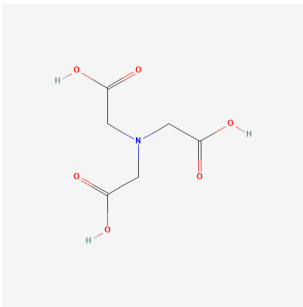
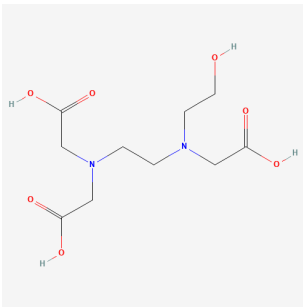
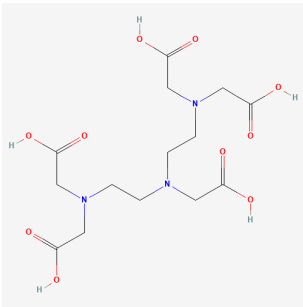
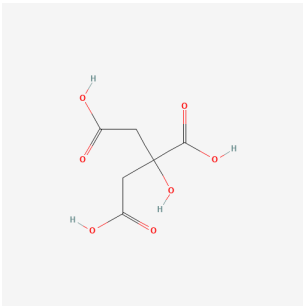
PTE	Plant	Experimental Duration [months]	Before [mg/kg]	After [mg/kg]	Soil pH	Reduction in Soil Concentration per Season [%]	Source
Cd	<i>Sedum alfredii</i>	12	0.372 ^a	0.327 ^a	5.4	12	Zhang et al., 2021
		24		0.285 ^a		12	
Cd	<i>Brassica napus</i>	12	0.372 ^a	0.361 ^a	5.4	3	Zhang et al., 2021
		24		0.348 ^a		3	
Cd	<i>Sedum alfredii</i> and <i>Brassica napus</i> intercropping	12	0.372 ^a	0.345 ^a	5.4	7	Zhang et al., 2021
		24		0.316 ^a		8	
Cd	<i>Noccaea caerulea</i>	6	1.7 ^b	1.42 ^b	7.2	16	Jacobs et al., 2017
Cd	<i>Noccaea caerulea</i>	6	2.1 ^b	1.98 ^b	8.2	6	Jacobs et al., 2017
Cd	<i>Noccaea caerulea</i>	6	1.7 ^b	1.49 ^b	7.2	12	Jacobs et al., 2017
Cd	<i>Noccaea caerulea</i>	6	2.1 ^b	2.06 ^b	8.2	2	Jacobs et al., 2017
Cd	<i>Nicotina tabacum</i>	5	0.59 ^c	0.53 ^c	4.8	10	Yang et al., 2017
Cd	<i>Nicotina tabacum</i>	5	1.35 ^c	1.27 ^c	5.4	6	Yang et al., 2017
Cd	<i>Solanum nigrum</i>	5	1.91 ^d	1.73 ^d	6.1	9	Ji et al., 2011
Cd	<i>Salix smithiana</i>	72	7.3 ^e	7.2 ^e	5.7	1	Kubátová et al., 2016
Cd	<i>Populus nigra</i>	72	7.3 ^e	7.2 ^e	5.7	1	Kubátová et al., 2016
Cu	<i>Bryophyllum pinnatum</i>	4.5	28.57 ^e	20.27 ^e	5.7	29	Riza & Hoque, 2021
Cu	<i>Medicago sativa</i>	6	468 ^e	451 ^e	5.7	4	Wu et al., 2012
Cu	<i>Sedum plumbizincicola</i> and <i>Medicago sativa</i> intercropping	6	468 ^e	446 ^e	5.7	5	Wu et al., 2012
Zn	<i>Noccaea caerulea</i>	6	480 ^b	434 ^b	7.2	10	Jacobs et al., 2017
Zn	<i>Noccaea caerulea</i>	6	710 ^b	690 ^b	8.2	3	Jacobs et al., 2017
Zn	<i>Noccaea caerulea</i>	6	480 ^b	350 ^b	7.2	27	Jacobs et al., 2017
Zn	<i>Noccaea caerulea</i>	6	710 ^b	677 ^b	8.2	5	Jacobs et al., 2017
Zn	<i>Salix smithiana</i>	72	218 ^e	217 ^e	5.7	0	Kubátová et al., 2016
Zn	<i>Populus nigra</i>	72	218 ^e	217 ^e	5.7	0	Kubátová et al., 2016
a) 5:1:1 HNO ₃ , HClO ₄ , HF b) HNO ₃ , HCl, HF c) HCl, HNO ₃ , HClO ₄ d) 7:1 HNO ₃ , HClO ₄ e) HNO ₃ , HCl							

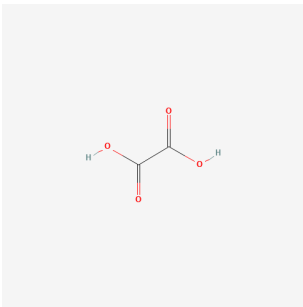
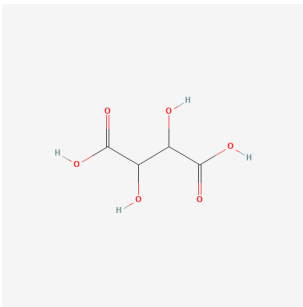
6. Chemical-Assisted Phytoremediation

To improve the efficiency of phytoremediation, the application of chemical additives can have a positive, synergetic effect by mobilizing the PTEs and, thus, increasing the bioaccessible fraction. Aminopolycarboxylic acids (APCA), a group of chemicals, are often used as chelating agents to mobilize PTEs (Chen & Cutright, 2001; Kaur et al., 2020) (Table 5). They increase the mobility of PTEs and therefore the availability for the plant. Ethylenediaminetetraacetic acid (EDTA) is one of the most commonly used chelators for PTEs (Kaur et al., 2020). As EDTA is difficult to degrade, the use of more biodegradable substitutes such as nitrilotriacetic acid (NTA), ethylenediamine-N,N'-disuccinic acid (EDDS), citric acid and others are often investigated (Table 5). The negative effects of chelating agents are the leaching of PTEs to lower soil levels and the potential contamination of groundwaters with PTEs. According to Chen & Cutright (2001) EDTA and N-(2-Hydroxyethyl)ethylenediaminetriacetic acid (HEDTA) increased the PTE content in plant tissues, while at the same time decreasing the plant biomass, resulting in a lower total removal of PTEs. In addition, most chelators are not specific for PTEs, which can lead to interference with other cations in the soil and reduce the efficiency of the treatment (Evangelou et al., 2007). For these reasons, the use of chelating agents in phytoremediation trials has decreased in the last decade. Additionally, the financial costs for the application of chelating agents on larger areas over possibly several years should be considered. Hence, the use of chelating agents is not recommended.

Table 5: List of APCAs (Chen & Cutright, 2001; Kaur et al., 2020); Chemical structures were downloaded from PubChem (<https://pubchem.ncbi.nlm.nih.gov/>).

Chelating agent (CAS No)	Chemical structure	Advantages	Disadvantages
EDTA (60-00-4)		Increase in PTE uptake in plant tissue	Decrease in biomass; Toxic to groundwater cause changes in soil composition, affects microbial activities, low biodegradability, can cause eutrophication, affect soil nutrients
EDDS (20846-91-7)		Biodegradable, better chelator than EDTA and NTA	Leaching to groundwater

Chelating agent (CAS No)	Chemical structure	Advantages	Disadvantages
NTA (139-13-9)		highly biodegradable,	Leaching to groundwater, less effective than EDTA
HEDTA (150-39-0)			Decrease in biomass; Toxicity unclear
DTPA (67-43-6)			Less effective than EDTA, costly
Citric acid (77-92-9)		biodegradable, non-toxic	Low efficiency

Chelating agent (CAS No)	Chemical structure	Advantages	Disadvantages
Oxalic acid (144-62-7)			Low efficiency
Tartaric acid (133-37-9)			Less effective than citric acid

7. External Effect of Soil Conditions

Environmental conditions, biological activity and soil properties can impact the ability and efficiency of PTE uptake by plants (Figure 3). A list of important soil parameters and the interactions regarding PTE mobility are described in Table 6.

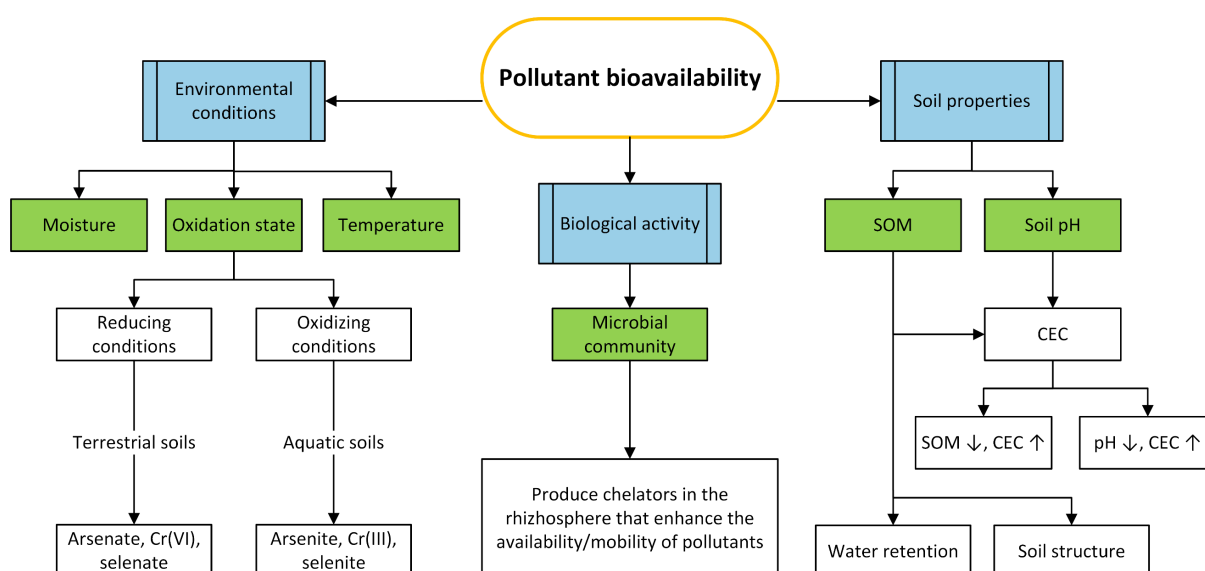


Figure 3: Important parameters for pollutant uptake (SOM = soil organic matter, CEC = cation exchange capacity). (Adapted from Pinto et al., 2014)

Table 6: Important soil parameters affecting phytoextraction. (Adopted from Pinto et al., 2014)

Parameter	Effect on PTE
pH	A lower pH will increase the bioavailability of PTEs and increase plant uptake
Redox potential (Eh)	An increasing Eh decreases heavy PTE mobility and decreases plant uptake
Soil Organic Matter (SOM) / Clay fraction	Differs from element to element, e.g., Cd and Zn are predominantly bound to SOM below pH 6.5, while clay only matters as an adsorbent at very high concentrations
Cation Exchange Capacity (CEC)	Higher CEC can lead to better adsorption of PTEs in soil
Other PTEs	Al, Mn and Fe as oxides or hydroxides decrease PTE mobility and subsequently decrease plant uptake

Depending on the physical and chemical properties of the soil, PTEs are differently bound to the soil matter and therefore unequally mobile and bioavailable (Brümmer & Herms, 1983). A soil pH < 6.5 can already cause the mobilization of Cd (Table 7) while at a pH of 4 most PTEs become mobile and therefore available to plants and soil organisms. However, at acidic soils (pH < 5-5.5) phytotoxicity due to solubilization of aluminum becomes an issue. Values in Table 7 must be treated qualitatively as there is no exact threshold to define when mobilization increases. Furthermore, soil biological activity and environmental conditions play an important role in the mobilization and uptake of pollutants by phytoextraction.

Table 7: Approximate pH-threshold values for PTEs mobilization according to Neuendorff (2010; Cu, Cd, Pb and Zn values are based on the study of Brümmer et al., 1986)

Contaminants	Increase in mobilization (Soil pH-threshold)
Cadmium (Cd)	<6.5
Chromium (Cr) ¹	<4.5
Copper (Cu)	<4.5
Lead (Pb)	<4.0
Mercury (Hg)	<4.0
Molybdenum (Mo)	-
Nickel (Ni)	<5.5
Zinc (Zn)	<6.5-7.0

¹speciation is not given, but most likely in the form of Cr(III)

8. Phytoextraction market

These days there are a few companies in Europe and USA, which are offering guidance and performing phytoremediation of PTE contaminated soils. However, most projects are still led by research institutes, which are partnering with private companies. In the USA more applied projects can be found at universities and US companies. A lot of companies listed by Eapen et al. (2007) and Schwitzguébel et al. (2002), which offered phytoremediation in the late 90s or early 2000, no longer exist (based on Google search and company webpage availability). A further search via Google enabled to establish a list of companies located in North America and Europe that are currently offering phytoremediation treatments (see Table 8). As a positive example of commercial phytoremediation, Edenspace Systems Corporation (Virginia, USA) remediated an arsenic-contaminated residential site with brake fern (genus *Pteris*) (Beans, 2017). Concentrations were not given, but according to them, lower-level contaminated sites could be remediated during only one growing season of around five months. Higher level contaminations required several growing seasons and were at a safe level after five years.

A short survey conducted among European bioremediation companies reveals that the use of phytoextraction of PTEs only accounts for a small part of their projects and they are mostly focused on research. Most bioremediation projects deal with the stabilization, degradation or removal of organic pollutants (no information was given with respect to type of pollutant) from contaminated soils. One example is the French company Microhumus, which offers, among others, phytoremediation solutions. So far, they conducted a single-digit number of phytoextraction projects and only for research purposes. According to a personal communication, this is due to the uncertain duration of phytoextraction projects which could last from several years to over 100 years. In Switzerland, no company was found which provides phytoextraction as a treatment method for PTE contaminated soils.

Table 8: Companies using bioremediation (plants and/or microorganisms) (OP = organic pollutants)

Company, country	Service	Website
MADEP SA, Switzerland	• Mycoremediation • Use of bacteria and fungi • Treatment of OP only	www.madep-sa.com
EDAPHOS SA, Switzerland	• Mycoremediation of OP	www.edaphos-engineering.ch
Microhumus, France	• Phytoremediation and -management of PTEs and OP sites	www.microhumus.eu www.microhumus.fr
SAS Biomédé, France	• Phytoremediation • Phytoextraction • Phytomining	www.biomede.fr
Waterloo Environmental Biotechnology Inc., Canada	• Phytoremediation of OP and salts from soils	www.web-i.ca
Whiterock Resources LLC, USA	• Phytoremediation	http://www.whiterockresourcesllc.net
Biovala, Lithuania	• Phytoremediation • Biodegradation of OP with microorganisms	www.biovala.lt
Intrinsyx Environmental, USA	• Endophyte-assisted Phytoremediation	www.intrinsyxenvironmental.com
Applied Natural Science, USA	• Phytoremediation • Endophyte treatment	https://treemediation.com
Ecolotree, USA	• Phytoremediation	www.ecolotree.com/
Thomas Consultants, USA	• Phytoremediation	http://thomas-consultants.com/
Viridian Resources, USA	• Phytomining	www.viridianresources.com/

9. Discussion and Recommendations

Among all phytoremediation trials, field trials are rare. This has two reasons: 1. They are more time and cost-intensive than pot or hydroponic trials in a greenhouse. 2. Environmental factors (precipitation, temperature, pathogens, herbivores, etc.) cannot be controlled, which could result in a failed experiment in the worst case. Additionally, these environmental factors, which might influence the phytoremediation efficacy, make comparison and replication of these studies challenging. Furthermore, comparison of study results found for this review is challenging due to the use of different soil extraction methods (e.g., digestion with HF will yield a higher total PTE content than using HNO₃ and HCl) aimed at measuring bioaccessible respectively total PTE concentrations in the soil. Hence, study results from field trials mostly describe the phytoextraction potential under given conditions and transferability or generalization is challenging.

Nevertheless, the field studies give an idea of the feasibility of phytoremediation of PTE-contaminated soils and certain trends can be observed. The total amount of extracted PTEs depends on the accumulation rate and biomass production. While most study results suggest that hyperaccumulating species extract more total PTEs than high biomass-producing species and are, therefore, better suited for phytoremediation. This can be illustrated with the example of Zn, where the Wilwerwitz variation of *N. caerulescens* extracted 2.5 to 5 times more Zn/ha (47 kg Zn/ha) than *H. annuus* and *N. tabacum* (9.3 and 20.1 kg Zn/ha) despite 3 times lower soil concentrations (similar pH and same experimental duration). Other field studies with different conditions (e.g., pH or total PTE concentration) suggest that high biomass producing species could perform equally or better, as can be seen by the experiments with *S. alfredii* and *N. tabacum* for Cd at lower soil pH values. Similar in the field trial in Dornach, the biomass-producing species (*N. tabacum*, *H. annuus*, *Z. mays*) performed better than the hyperaccumulating species (*N. caerulescens*). However, we see two possible reasons for these observations. First, during the second season the soil with *Z. mays*, *H. annuus* and *N. tabacum* was treated with the chemical additive NTA to enhance the uptake while the soil with *N. caerulescens* was not. Second, while optimal plant density of *N. tabacum*, *Z. mays* and *H. annuus* was already known 25 years ago, it is only recently known that up to 100 *N. caerulescens* plants per m² can be successfully sustained and will improve remediation performance (Jacobs et al., 2018). Hence, it is likely, that biomass production was better optimized for the high biomass production plants than for the hyperaccumulating specie. Furthermore, large biomass-producing plants usually have deeper roots, which could lead to increased PTE extractions from sub-soil (i.e., a portion of extracted PTEs were accumulated from sub-soil below 20 or even 50 cm deep, which is not relevant if the remediation aim is only topsoil).

Beside choosing the best suitable plant species (highest total PTE extraction per area) for a specific site, the field trials with *N. caerulescens* also showed the potential of choosing the best plant variation (e.g., different clones or variations of different geographical origin). Differences of close to three times higher extraction could be observed among different *Noccaea* variations (with a maximum of 27% Zn extracted from the soil within 6 months, Jacobs et al., 2017). Furthermore, these trials indicate higher phytoextraction at a lower soil pH, as expected according to Table 7.

Overall, the main limitations and challenges for the application of phytoextraction as a remediation measure are:

- the duration of the measures to reach the remediation goal since it takes time to grow and harvest plants
- the distribution of contaminants within the soil can be inhomogeneous and extraction is only around the root system (Shmaefsky, 2020b)
- high PTE (pseudo) total concentrations and low PTE solubility or bioavailability in soil increase the duration of phytoremediation measures (Shmaefsky, 2020b)
- the soil composition, pH and chemistry which can influence the removal efficiency and are crucial for conducting successful phytoremediation due to their influences on PTE mobility and bioavailability (Pinto et al., 2014, Król et al., 2020).

Recommendations:

Based on inherent PTE mobility and listed field trials, we divided the PTEs into three recommendation groups for phytoextraction feasibility of contaminated soils:

1. good candidates for phytoremediation due to high mobility and an abundance of suitable plant species in the concentration range of trigger values: Cd and Zn
2. potential candidates for phytoremediation due to less pronounced mobility and few suitable species in the concentration range of trigger values: Cu
3. poor candidates for phytoremediation due to very limited mobility and few suitable species: Pb and Hg

Highly contaminated soils (above clean-up value) may lead to phytotoxic effects and, hence, lowering the biomass production lessening the overall phytoextraction performance (Schulin et al., 2014). Lightly to moderately contaminated soils (around or below trigger value) are, thus, more promising soils for phytoremediation. Especially for Cd, where the guide and trigger values are relatively close together and a decrease from *e.g.*, 1.0-2.0 mg/kg Cd to *e.g.*, 0.5-0.7 mg/kg Cd within 5 years seems achievable. Similarly, a reduction of Zn concentrations from around 300 to < 150 mg/kg within 5 years seems feasible. To preserve long-term soil fertility in agricultural land, the range between guide and trigger value is also the most effective target since further PTE accumulation above trigger value will result in restrictions on soil usage.

Phytoextraction of soils above clean-up value to (ideally below) guide value is likely to require one to several decades, resulting in high financial and opportunity costs (*i.e.*, the location cannot be used for other purposes during the phytoremediation process). However, for areas where remediation is not needed within ten years, pilot studies to test the potential of phytoextraction of soils contaminated above the clean-up value could be conducted. For soils around trigger value, phytoextraction of PTEs below guide value concentrations might be achievable within less than ten years. Even though there are currently only limited scientific results from field studies, as shown in Table 7, lowering the soil pH (*e.g.*, through the addition of pyrite, sulfur, compost) could increase the phytoextraction (Ali et al., 2013; Shaheen et al., 2017) (independent of initial PTE concentration). However, these methods, including possible negative effects, such as leaching of the PTE, loss of nutrients and increase of Al toxicity, should be investigated, and managed accordingly (*e.g.*, liming after successful remediation).

The use of chelating agents to increase the PTE uptake into plants is considered controversial due to potential groundwater contamination through increased PTE leaching. Additionally, some chelating agents like EDTA are non-biodegradable and remain in the soil, negatively affecting plant health, due

to increasing the bioavailability of phytotoxic PTEs, even after successful phytoremediation. Furthermore, the application of chelating agents is financially expensive. We, therefore, cannot recommend the use of chelating agents.

We reviewed the phytoremediation potential of PTEs for which a clean-up value exists in the Ordinance relating to Impacts on the Soil (VBBo; OSol). However, also other PTEs could potentially be extracted from the soil via phytoremediation. For organic contaminants, other in-situ remediation methods are possible (*e.g.*, bioremediation through degradation by bacteria and/or fungi seems promising) rather than phytoextraction.

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