

Sarah Neilson and Nishanta Rajakaruna

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## 11.1 Introduction

Industrial pursuits such as mining and manufacturing produce large amounts of heavy metal pollution worldwide (Anderson et al. 2005; Sánchez 2008; Wuana and Okieimen 2011). Heavy metals such as cadmium (Cd), chromium (Cr), copper (Cu), lead (Pb), mercury (Hg), nickel (Ni), and zinc (Zn) and metalloids such as arsenic (As) and selenium (Se) not only pollute soils in the immediate vicinity within which they are produced but can be easily dispersed via air and water, leading to contamination of soils far from the source of the pollutants (Neilson and Rajakaruna 2012). Heavy metal contamination poses a significant threat to arable land around the world (Efremova and Izosimova 2012a, b; Liu 2006; Lin et al. 2012; Lone et al. 2008; Mico et al. 2006), reducing the availability of land suitable for producing the global food supply. Unsound agricultural practices that intensify contamination of soils by heavy metals further exacerbate this problem, making it challenging to produce food safe for human or animal consumption. As the amount of land available for agriculture decreases (Lone et al. 2008), the need for more land, or at least better use of currently available arable land, increases. According to Tang et al. (2012), one fifth of agricultural land in China is already contaminated despite such land being exploited for food production. Therefore, it is critical to consider what measures can be taken to grow food safe for consumption, even on arable land that may have varying levels of heavy metal contamination (Adefemi et al. 2012; Nicholson et al. 2003).

In this chapter, we explore methods for utilizing heavy metal-contaminated soils for agricultural production. Such methods include phytoextraction, or remediating contaminated soils using plants that hyperaccumulate heavy metals (van der Ent et al. 2012; Gall and Rajakaruna 2013); phytomining (Chaney et al. 2007), where metal-hyperaccumulating plants are harvested for disposal or extraction of the metal from processed tissues; phytostabilization (Mendez and Maier 2008), in which plant roots immobilize or take up metals to reduce or eliminate the threat of leaching; sound agricultural practices including the use of soil amendments such as lime to increase pH levels to make heavy metals less bioavailable; and non-remediation options such as growing fuel or fiber crops rather than food crops on metal-contaminated land, growing food plants which translocate little or no contaminants to edible tissues, or using raised beds so that the plant roots are not in immediate contact with contaminated soil. First, we consider the potential dangers posed to plants, humans, livestock, and ecosystems by heavy metal contamination. We then explore some of the sources of heavy metals commonly found in arable lands and methods for assessing heavy metal concentrations and bioavailability in soils and the potential for uptake of heavy metals into the tissues of crop plants. We also discuss potential methods for utilizing heavy metal-contaminated soils for agricultural production, including both remediation- and non-remediation-based approaches. We finish with a brief consideration of the potential for biotechnology to offer solutions to the problem of growing crops on arable lands contaminated by heavy metals.

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## 11.2 Dangers of Heavy Metal Contamination

The presence and bioavailability of heavy metals may vary from site to site, depending upon the chemical form of the individual metal and the chemical and physical attributes of the soil (Rajakaruna and Boyd 2008). High concentrations of heavy metals in soil can negatively affect plant growth, as these

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S. Neilson, M.Sc.  
Faculty of Natural and Biological Sciences, Copenhagen  
University, Bülowsvej 17, Copenhagen, Denmark

N. Rajakaruna, Ph.D. (✉)  
College of the Atlantic, 105 Eden Street, Bar Harbor, ME 04609, USA

Unit for Environmental Sciences and Management, North-West  
University, Private Bag X6001, Potchefstroom 2520, South Africa  
e-mail: [nrajakaruna@gmail.com](mailto:nrajakaruna@gmail.com)

metals interfere with physiological and biochemical processes, including photosynthesis and respiration, contributing to the degeneration of organelles and cells, and even plant death (Nagajyoti et al. 2010; Gupta and Sandallo 2011; Shaw 1990). Heavy metal contamination in soils may also cause changes in the composition of the soil microbial community, potentially adversely affecting soil characteristics (Giller et al. 1998; Kozdrój and van Elsas 2001) and thereby also potentially impacting plant growth and crop productivity. Consumption of plants with high heavy metal concentrations may lead to toxicity in humans and other animals and can cause acute or chronic illnesses and even death (Appenroth 2010; Bánfalvi 2011).

The specific dangers of heavy metal contamination in plants, animals, humans, and ecosystems can take many forms (Boyd and Rajakaruna 2013). Cadmium, for example, is one of the most toxic heavy metals that can enter the food chain when accumulated in edible plant tissue (Singh et al. 2011). Cadmium is also the most mobile heavy metal, with significantly increased mobility at even slightly acidic pH levels (<6.5) (Felix-Henningsen et al. 2010). Cadmium, along with Zn, can lead to acute gastrointestinal and respiratory problems and can contribute to acute heart, brain, and kidney damage (Anderson et al. 2005). People who have nutritional deficiencies—especially people with low levels of calcium (Ca), iron (Fe), and Zn—are more prone to Cd-related disorders such as kidney failure or bone demineralization and fracturing (Singh et al. 2011).

Heavy metals can be transferred through soil-plant-animal food chains and accumulate in plant and animal tissues, a process called bioaccumulation (Gall and Rajakaruna 2013). For example, Nica et al. (2012) found that Cd, Cu, Pb, and Zn transferred from contaminated soil to *Urtica dioica* (nettle; Urticaceae) leaves to *Helix pomatia* (Roman snail; Helicidae), affecting shell height and whorl number, while also accumulating in the muscular foot. Miranda et al. (2009) found that cattle raised on Ni-enriched serpentine soils in Spain accumulated toxic levels of Ni in their kidneys and of Cu in their livers. The authors found a direct correlation between concentrations of Ni in the kidneys of cattle and both total and extractable levels of Ni found in the soil and forage. There is much evidence that toxic amounts of heavy metals can enter the food chain through contaminated soils (Gall and Rajakaruna 2013), necessitating research into ways in which heavy metal-contaminated soils can be safely used for agricultural production.

### 11.3 Sources of Contamination and Common Contaminants

Contamination of agricultural soils by both natural and anthropogenic sources of heavy metals is a global problem (Arao et al. 2010; Efremova and Izosimova 2012a; Kien et al. 2010; Li et al. 2008; Lone et al. 2008; Rahman et al.

2012). Agricultural soils can become contaminated via atmospheric deposition of heavy metals from factories, vehicular exhaust, and other sources; application of chemical and organic fertilizers (pig slurries, manures, sewage sludge) and pesticides; and weathering of rocks containing high levels of heavy metals (Singh et al. 2011; Qishlaqi and Moore 2007; Rajakaruna and Boyd 2008). France, Belgium, and the Netherlands all suffer from heavy metal contamination of agricultural soils due to smelter emissions. In China, 13,330 ha of farmland are contaminated by Cd (Singh et al. 2011). In Western Europe, approximately 1,400,000 sites have been contaminated with heavy metals (Wei et al. 2005). In the country of Georgia, irrigation water has been contaminated with heavy metal-laden mining waste for several decades (Felix-Henningsen et al. 2010). In the United States, there are 600,000 brownfield sites contaminated with heavy metals and need reclamation (McKeehan 2000).

The dangers posed by each heavy metal are variable. For example, Cu, Molybdenum (Mo), and Zn are essential, in small quantities, for humans, animals, and plants. However, As, Cd, Hg, and Pb are not essential and can cause toxicity even at very low concentrations (Singh et al. 2011). Cadmium, Cr, Cu, Ni, Pb, and Zn are all known to be harmful to human and ecosystem health when they enter the food chain (Singh et al. 2011; Felix-Henningsen et al. 2010; Qishlaqi and Moore 2007). Lead, for instance, can remain in the soil for thousands of years (Kumar et al. 1995) and is known to cause cognitive dysfunction, neurobehavioral disorders, neurological damage, hypertension, and renal impairment in humans (Flora et al. 2012; Patrick 2006).

### 11.4 Assessing Soil Conditions and Potential for Crop Contamination

The risks of heavy metals being transferred into the food chain are dependent on the mobility of the heavy metal species in question and its bioavailability in soil (Richards et al. 2000; Rajakaruna and Boyd 2008). The processes of uptake and accumulation of heavy metals by plants are influenced by several soil factors, including pH, redox potential, clay content, soil organic matter (SOM) content, cation exchange capacity (CEC), nutrient balance, concentrations of other trace elements in soil, soil moisture (and aeration), and soil temperature (Neilson and Rajakaruna 2012; Gall and Rajakaruna 2013; Qishlaqi and Moore 2007; Singh et al. 2011; Tang et al. 2012). Two of the most important factors affecting the bioavailability of heavy metals are pH and SOM (Felix-Henningsen et al. 2010; Guo et al. 2011; Puschenreiter et al. 2005). Soil pH is important because most heavy metals, including Cd, Cr, Cu, Ni, Pb, and Zn, become more bioavailable under acidic (low pH) soil conditions (McLaughlin 2002; Qishlaqi and Moore 2007; Rajakaruna and Boyd 2008).

Acidic soils have a higher amount of hydrogen ions ( $H^+$ ) compared to alkaline soils, and cationic metals become more bioavailable under acidic conditions because they are displaced from negatively charged binding sites of soil particles such as clay and SOM by the abundant  $H^+$  in the soil solution. In some cases, however, a decrease in soil pH may not necessarily result in an increase in metal bioavailability. Molybdenum in soil, which is in the form  $MoO_4^{2-}$ , is less soluble under low pH levels (Kabata-Pendias and Pendias 2001); similarly, anionic forms of some heavy metals may become more bioavailable under increased pH levels.

Soil organic matter, including humic compounds, bears negatively charged sites on carboxyl and phenol groups, allowing for metal complexation (Brady and Weil 2007). Thus, the presence of high amounts of SOM is often negatively correlated with plant metal uptake. Cation exchange capacity, a function of clay and organic matter content in soil, also controls the bioavailability of heavy metals. In general, an increase in CEC causes a decrease in the uptake of heavy metals by plants. Bioavailability of heavy metals in soil is also directly correlated with the redox potential; under similar pH values, heavy metal bioavailability generally increases as redox potential decreases (Yaron et al. 1996). Heavy metals are also more available in sandy soils than in clayey soils, as sand particles have a much lower surface area and contain fewer cation exchange sites relative to clay particles. Soil drainage is another critical factor affecting the bioavailability of heavy metals. Drainage improves soil aeration and allows for metal oxidation, often causing heavy metals to be less soluble and therefore less bioavailable. However, some heavy metals, such as Cr, can be more available in oxidized forms (Chattopadhyay et al. 2010). Finally, absorption of heavy metals by roots is controlled by the concentration of other elements in the soil solution (Taiz and Zeiger 2010). Such relationships may be positively or inversely correlated, with the uptake of a heavy metal being enhanced or suppressed by the concentration of other elements in the soil.

Heavy metals frequently interact strongly with the soil matrix, and soil conditions can greatly influence heavy metal availability. Assessments of the suitability of soils for agricultural production should take into account any potentially available heavy metals (i.e., heavy metals that are strongly bound to free Fe- or Mn-oxides or to organic substances or carbonates) as this fraction of the heavy metal pool is most likely to be mobilized with changes in soil factors that influence adsorption of heavy metals onto soil particles (i.e., pH, SOM, CEC, redox potential, aeration, clay content, etc.; Felix-Henningsen et al. 2010). Adding alkaline materials such as lime, tillage and rotation practices, and fertilizer management all contribute to changing physicochemical factors that could directly impact the bioavailability of heavy metals in agricultural soils (Lasat 2000; Singh et al. 2011).

The chemical behavior of heavy metals in agricultural soils is not only influenced by factors such as pH, SOM, CEC, redox potential, clay, and other elemental interactions but also by biotic factors such as morphological and physiological characteristics of crop species and the microbial community within the crop rhizosphere (Singh et al. 2011). Hence, when assessing the potential for agricultural production in heavy metal-contaminated soils, it is important to make decisions based on both the abiotic and biotic factors affecting heavy metal bioavailability. For example, one could plant a heavy metal hyperaccumulator to remove contaminants, choose crops which exclude heavy metals or do not translocate them in toxic amounts to edible parts, grow crops for fiber and fuel instead of food, or pursue a combination of such options. These approaches will be further explored in the following section.

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## 11.5 Remediation Options

The use of metal-hyperaccumulating plants should be explored as a viable option to remediate agricultural soils moderately contaminated with heavy metals. Of the approximately 582 species of known metal hyperaccumulators from more than 50 families of vascular plants worldwide, approximately 25 % belong to the Brassicaceae (Gall and Rajakaruna 2013), a family containing many food crop species. There are well over 400 hyperaccumulators of Ni globally, as well as two dozen or so for Cu; at least a dozen each for Co, manganese (Mn), and Zn; and a few for As, Cd, Cr, Pb, Se, thallium (Tl), and uranium (U) (Cutright et al. 2010; Islam et al. 2007; Li et al. 2011; van der Ent et al. 2012). Although metal hyperaccumulators have the ability to detoxify and accumulate metals in their leaf tissues, they do have limits to this extraordinary capacity to deal with metals, and the threshold for hyperaccumulation depends on the metal under consideration. The threshold concentration for hyperaccumulation is generally two or three orders of magnitude greater than that of most species growing on “normal” soils and at least one order of magnitude greater than the usual range found in other plants from metal-enriched soils. Hyperaccumulators of Cd, Se, and Tl accumulate  $>100 \mu\text{g g}^{-1}$  in their dry leaf tissue; hyperaccumulators of cobalt (Co), Cr, and Cu accumulate  $>300 \mu\text{g g}^{-1}$  in their dry leaf tissue; and hyperaccumulators of As, antimony (At), Ni, and Pb accumulate  $>1,000 \mu\text{g g}^{-1}$  in their dry leaf tissue. Hyperaccumulators of Zn accumulate  $>3,000 \mu\text{g g}^{-1}$ , whereas those of Mn accumulate  $>10,000 \mu\text{g g}^{-1}$  in their dry leaf tissue (Reeves and Baker 2000; van der Ent et al. 2012). For recent reviews of metal hyperaccumulation, see Krämer (2010) and van der Ent et al. (2012).

Metal-hyperaccumulating species such as *Noccaea caerulea* and *N. rotundifolia* (Brassicaceae), *Haumaniastrum robertii* (Lamiaceae), *Ipomoea alpina* (Convolvulaceae),

*Vitotia* (formerly, *Macadamia*) *neurophylla* (Proteaceae), and *Psychotria douarrei* (Rubiaceae) are good candidates for removing metals from agricultural soils (Islam et al. 2007). A common condiment crop in North America and Europe, *Brassica juncea* (Indian mustard; Brassicaceae), is also a popular choice for phytoremediation (Lim et al. 2004; Neilson and Rajakaruna 2012). Although not a hyperaccumulator, with the ability to accumulate Cd, Pb, Se, and Zn and a biomass at least tenfold greater than that of *N. caerule-scens*, *B. juncea* has been used with success in several phytoremediation studies and field trials (Bhargava et al. 2012; Szczyglowska et al. 2011; Warwick 2011). Although Pb hyperaccumulation is rare, several species, including *Apocynum cannabinum* (hemp dogbane; Apocynaceae), *Ambrosia artemisiifolia* (common ragweed; Asteraceae), *Carduus nutans* (nodding thistle; Asteraceae), and *Commelina communis* (Asiatic dayflower; Commelinaceae), appear to accumulate high levels of Pb in their leaf tissues (Lasat 2000) and could be used for phytoremediation in agricultural settings. Recent experiments have shown that some populations of *N. caerule-scens* from southern France can accumulate Pb at  $>1,000 \mu\text{g g}^{-1}$  in leaf dry matter in the field and under hydroponic conditions (Mohtadi et al. 2011). Similarly, Pb accumulation was documented in 26 taxa collected from a Pb mine in Thailand (Rotkittikhun et al. 2006). High foliar concentrations of Pb can be achieved with the use of Pb-complexing and mobilizing agents such as EDTA and EDDS (“induced phytoextraction” sensu Salt et al. 1998), as documented for *Brassica carinata* and *B. juncea* grown in hydroponic solution or in EDTA-treated soil (Kumar et al. 1995; Vassil et al. 1998).

Hyperaccumulators can selectively accumulate heavy metals in their aerial parts at 10 to 500 times the level of heavy metals found in edible crops (Islam et al. 2007), making them model species for remediation of contaminated agricultural soils (but see Vamerali et al. 2010). However, not all regions of the world have native species that hyperaccumulate the various heavy metals of concern, making it unsafe or unsuitable to utilize non-native hyperaccumulators for agricultural purposes (see Neilson and Rajakaruna 2012). Hyperaccumulators are not edible and must be considered toxic waste unless the metals are to be extracted via phytomining (Wilson-Corral et al. 2012) or tissue can be used as fertilizer to treat micronutrient deficiencies in crop plants (Wood et al. 2006). Thus, other remediation options, such as those that can be combined with agricultural production, may be more appealing in agricultural settings.

Many options are available for crop production on soils contaminated with heavy metals. Appropriate techniques for growing crops on heavy metal-contaminated soils depend primarily on the concentration of metals in the soil. The approach to remediation of heavy metal contamination should be risk-based in the sense that if metals are tightly

bound to soil particles and are not bioavailable, as determined with bioassays and other toxicity assays, it may not be necessary to remove heavy metals from the soil entirely. Singh et al. (2011) describe “gentle” and “harsh” remediation techniques which are further categorized into soil-specific and plant-specific approaches. Gentle techniques are mainly geared toward stabilizing heavy metals, and “harsh” techniques are mainly geared toward removal of heavy metals from the soil. One of the most common gentle soil-specific approaches is the addition of alkaline soil amendments such as lime (i.e., liming). In situ stabilization using lime, organic matter, phosphates, and mineral oxides is aimed at reducing the bioavailability of heavy metals and thereby reducing transfer of these metals into food crops. However, such approaches are dependent on the crop species or cultivar used, soil conditions, and agricultural practices (Singh et al. 2011). Liming can reduce mobility and the soluble fraction of Cd, Ni, Zn, and other heavy metals, but results are variable and over-liming can reduce the availability of essential nutrients such as Fe and Zn (Singh et al. 2011). Liming can also influence microbial activity in the soil leading to increases or decreases in metal availability (Weyman-Kaczmarkowa and Pedziwilk 2000). Adsorption agents with high CEC, such as clay, can also increase the metal-binding capacity of soil (Singh et al. 2011). Other soil amendments that can decrease solubility or precipitate metals include SOM and phosphate- or silicon-based amendments (Tang et al. 2012). Silicon has been shown to decrease toxic effects of heavy metals on plants and can be applied as a foliar spray. Phosphate can immobilize Pb by binding or precipitation due to its negative charge, although care should be taken when using phosphate fertilizers as they can contain up to  $300 \text{ mg Cd kg}^{-1}$  dry product and can cause Cd to accumulate in soils if applications are too frequent or their rates are too high (Grant 2011). Organic materials such as manure can have dual effects of increasing yield and decreasing metal uptake (Tang et al. 2012). Rhizospheric interactions and root activity can also reduce the solubility and transport of heavy metals. For a detailed review of rhizospheric interactions, see Neilson and Rajakaruna (2012). See Tang et al. (2012) for a review of agricultural practices that can reduce metal contamination.

A novel approach to removing heavy metals from soil described by Guo et al. (2011) consists of “washing” contaminated soil with a mixture of acidic chelators, including EDTA, citric acid, and KCl, followed by the application of lime. In this study, *Zea mays* (corn; Poaceae) was planted following initial soil washing to assess the bioavailability of heavy metals after the treatment with chelators, and after the corn was harvested, *Sedum alfredii* (Crassulaceae) was used for phytoextraction to further reduce heavy metals in the soil. This method turned out to be somewhat ineffective, as levels of Cd, Pb, and Zn still exceeded Chinese food

safety limits, and liming the washed soil significantly increased heavy metal leaching and failed to reduce Pb and Cd concentrations in the corn. However, levels of Cd, Cu, Pb, and Zn were all increased in the phytoextractor *S. alfredii* after soil washing (Cd and Zn concentrations increased by almost 50 % compared to unwashed soils). Therefore, phytoextraction by *S. alfredii* after soil washing may be effective at removing the mobile Cd activated by the soil washing (Guo et al. 2011). Interestingly, they found that although the liming treatment and phytoextraction by itself successfully reduced exchangeable fractions of heavy metals in the soil, this was not the case when the two approaches were combined. Liming is most effective at decreasing metal concentrations in crops when the soil is already acidic and is only moderately contaminated (Guo et al. 2011; Islam et al. 2007); when soils are not already acidic or are heavily contaminated by heavy metals, liming may be less effective. Phytoremediation using soil amendments such as solubilizing ligands or chelators can be a time-consuming process; therefore, creating the right balance between metal bioavailability and metal uptake potential of the hyperaccumulator species is needed. Application of chelators to the rhizosphere should also be restricted to avoid leaching to groundwater (Singh et al. 2011).

Both greenhouse and field studies have reported success in reducing metal bioavailability with liming (Puschenreiter et al. 2005). When applying lime as a soil remediation technique, it is important to take into account that lime works best with acidic soils with low levels of heavy metal contamination restricted to the upper layers of the soil profile and that liming may need to be repeatedly applied over time (Guo et al. 2011; Islam et al. 2007; Puschenreiter et al. 2005). In addition, the effectiveness of liming treatments varies with the form of the metal and the crop species being grown. Liming seems to be more effective in reducing uptake of Ni and Zn than Cd, and lime-induced reductions in Cd accumulation are more pronounced, for example, in carrots (Apiaceae) and lettuce (Asteraceae) than potatoes (Solanaceae) and peanuts (Fabaceae; Puschenreiter et al. 2005). The application of Zn to soil has been shown to reduce uptake of Cd in flax (Linaceae) and durum wheat (Poaceae) by 40 and 60 %, respectively, and to reduce translocation to seed and grain, respectively, by more than 30 % (Singh et al. 2011). However, Zn amendments are only effective in soils that are already low in Zn and high in Cd so as to avoid potential Zn contamination and toxicity.

Another technique for reducing heavy metal transfer to crops is to grow plants that are heavy metal-tolerant but that are also heavy metal-excluding. Some heavy metal-tolerant crops may still accumulate relatively high levels of metals in their aerial parts, increasing the potential for re-deposition of heavy metals with leaf senescence (Wei et al. 2005). One way to avoid the accumulation of heavy metals is through phyto-

stabilization, or the use of soil amendments to immobilize contaminants and then grow a metal-tolerant (but metal-excluding) crop. As discussed above, lime, SOM, silicon, and carbonates could serve as such amendments. An experiment carried out by Krzyzak et al. (2013) found that As-, Cd-, Pb-, and Zn-contaminated soil amended with lignite and lime reduced metal accumulation in *Festuca arundinacea* (tall fescue; Poaceae) threefold for As, Pb, and Zn and twofold for Cd.

A lesser-studied but important area in agricultural phytoremediation is the role of bacteria, arbuscular mycorrhizal (AM) fungi, and other microorganisms in the rhizosphere. Studies have shown that populations of soil microorganisms are many orders of magnitude larger in the rhizosphere than elsewhere in the soil and that these organisms release organic compounds which may facilitate root uptake of essential as well as non-essential nutrients, including heavy metals (Lasat 2000). Arbuscular mycorrhizal fungi have been implicated in the survival of plants on contaminated soils by enhancing nutrient acquisition and phytostabilization while absorbing and detoxifying metals (Leung et al. 2013). For example, a strain of the bacterium *Stenotrophomonas* (formerly, *Pseudomonas*) *maltophilia* (Xanthomonadaceae) was found to reduce the toxic and mobile Cr<sup>6+</sup> to the immobile and nontoxic Cr<sup>3+</sup>, in addition to reducing the mobility of other toxins like Cd<sup>2+</sup>, Hg<sup>2+</sup>, and Pb<sup>2+</sup> (Lasat 2000). While it is widely accepted that relations between plants and microorganisms in the rhizosphere are important for plant health and crop production, more research is needed on the prevalence and importance of such relationships in heavy metal-contaminated agricultural soils.

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## 11.6 Non-remediation Options

If the level of heavy metal contamination of soil is not excessively high, one of the easiest and simplest ways to use the land for agricultural production is to choose crops which do not translocate high amounts of heavy metals to their edible tissues and crops that are less likely to become contaminated on the surface due to soil splashing or dry/wet deposition. Levels of uptake and translocation of heavy metals can vary drastically among plant species as well as among crop cultivars (Puschenreiter et al. 2005; Tang et al. 2012; Table 11.1).

For example, leafy vegetables accumulate higher amounts of heavy metals in edible parts than in fruits or roots due to high levels of transpiration, translocation, and aerial deposition; spinach (Amaranthaceae) and lettuce have a particularly high capacity to uptake heavy metals (Puschenreiter et al. 2005; Tang et al. 2012). Tobacco (Solanaceae) and celery (Apiaceae) have also been found to accumulate relatively high Cd concentrations when grown on Cd-contaminated soil (Puschenreiter et al. 2005). Other crops that have been

**Table 11.1** Crop plants known to accumulate metals above 'normal' concentrations in shoot and roots. Latin names for crops provided if mentioned in the source

Crop	Metal accumulation in shoot	Metal accumulation in root	Source
<i>Amaranthaceae</i>			
Spinach	Pb, Zn	–	Islam et al. (2007); Puschenreiter et al. (2005); Singh et al. (2011)
<i>Apiaceae</i>			
Carrots	Cd, Zn	Zn	Islam et al. (2007); Singh et al. (2011)
Celery ( <i>Apium graveolens</i> var. <i>dulce</i> )	Cd, Cu, Zn	Cd, Cu, Zn	Islam et al. (2007); Puschenreiter et al. (2005)
Parsley	Cd, Cu, Pb, Zn	–	Islam et al. (2007); Maleki and Zarasvand (2008)
<i>Amaryllidaceae</i>			
Leek ( <i>Allium ampeloprasum</i> )	Cr, Cu, Pb	–	Maleki and Zarasvand (2008)
<i>Asteraceae</i>			
Lettuce	Pb, Zn	–	Islam et al. (2007); Puschenreiter et al. (2005); Singh et al. (2011)
Tarragon ( <i>Artemisia dracunculus</i> )	Cd, Cr, Cu, Pb	–	Maleki and Zarasvand (2008)
Sunflower	–	Cd, Cr, Cu, Zn	Tang et al. (2012)
<i>Brassicaceae</i>			
Chinese cabbage ( <i>Brassica chinensis</i> L. cv. Zao-Shu 5)	Cu	Zn	Islam et al. (2007)
Garden cress ( <i>Lepidium sativum</i> )	Cd, Cr, Cu, Pb	–	Maleki and Zarasvand (2008)
Pakchoi ( <i>Brassica chinensis</i> )	Cd, Cu, Zn	–	Islam et al. (2007)
Radish root	Zn	–	Puschenreiter et al. (2005)
Winter greens ( <i>Brassica rosularis</i> var. Tsen et Lee)	Cd	–	Islam et al. (2007)
<i>Cucurbitaceae</i>			
Cucumber	Cd, Cu, Pb, Zn	–	Islam et al. (2007)
<i>Fabaceae</i>			
Beans	–	Cd	Puschenreiter et al. (2005)
Pea	–	Cd, Zn	Puschenreiter et al. (2005)
<i>Lamiaceae</i>			
Mint ( <i>Mentha piperita</i> and <i>M. arvensis</i> )	–	Cd, Cu, Mn, Pb, Zn	Zheljzakov and Nielsen (1996)
Sweet basil ( <i>Ocimum basilicum</i> )	Cd, Cr, Cu, Pb	–	Maleki and Zarasvand (2008)
<i>Poaceae</i>			
Durum wheat	Cd	–	Singh et al. (2011)
Maize ( <i>Zea mays</i> )	Cd, Pb	Zn	Lasat (2000); Puschenreiter et al. (2005)
Oats ( <i>Avena</i> spp.)	–	Cd	Puschenreiter et al. (2005)
Rice ( <i>Oryza sativa</i> )	Cd	–	Singh et al. (2011)
Wheat ( <i>Triticum</i> spp.)	–	Cd	Puschenreiter et al. (2005)
<i>Salicaceae</i>			
Poplar ( <i>Populus</i> spp.)	–	Cd, Cr, Cu, Zn	Tang et al. (2012)
Willow ( <i>Salix</i> spp.)	–	Cd, Cr, Cu, Zn	Tang et al. (2012)
<i>Solanaceae</i>			
Potatoes	Cd, Cu, Pb, Zn	–	Islam et al. (2007)
Tobacco ( <i>Nicotiana tabacum</i> )	Cd	–	Puschenreiter et al. (2005); Singh et al. (2011)
Tomatoes	Cd, Cu, Pb, Zn	–	Islam et al. (2007)

found to accumulate Cd include leafy greens, carrots, durum wheat, and rice (Poaceae; Singh et al. 2011). On the other hand, legumes (Fabaceae) and cereals (Poaceae) have low transfer factors (i.e., total metal concentration in plant relative to the total metal concentration in soil; Puschenreiter et al. 2005). Lavender and mint (Lamiaceae) can also be grown in heavy metal-contaminated soils without affecting essential oils. Although a yield reduction may occur when growing these species on heavy metal-contaminated soils, a profit can still be made on such crops (Puschenreiter et al. 2005; Zheljzkov and Nielsen 1996).

Bioenergy-producing plants like *Populus* spp. (poplar; Salicaceae), *Salix* spp. (willow; Salicaceae), and *Helianthus* (sunflower; Asteraceae) have high tolerance to Cd, Cr, Cu, and Zn and may be good alternatives to the more metal contamination-prone crops (Tang et al. 2012). Another alternative bioenergy crop is *Jatropha curcas* (Euphorbiaceae), an oil-yielding perennial in tropical/subtropical regions that can tolerate extreme growing conditions, including heavy metal toxicity, and could be used for phytostabilization (i.e., binding contaminants to roots to reduce mobility and leaching; Tang et al. 2012). Another option for a bioenergy crop includes *Eucalyptus* species (Myrtaceae), all of which are non-hyperaccumulating but can contribute toward phytoremediation while also providing agroforestry products such as fuel and timber (Rockwood et al. 2004).

Phytomining, or using hyperaccumulator plants to reclaim heavy metals from contaminated soils, has proved promising in greenhouse experiments, but field conditions, including fertilization practices, pest control methods, plant phenology, cropping calendar, temperature, and rainfall, have myriad influences on the actual success of such operations (Neilson and Rajakaruna 2012; Tang et al. 2012). For such undertakings, it can also be difficult to determine the best stage for harvesting (i.e., when metal concentrations are highest in shoots; Tang et al. 2012). Important fiber crops that are tolerant to heavy metals include *Cannabis sativa* (hemp; Cannabaceae) and *Boehmeria nivea* (ramie; Urticaceae), although these crops require the addition of soil amendments which reduce the bioavailability of heavy metals, even on moderately contaminated soils (Tang et al. 2012).

Co-cropping of hyperaccumulators with non-accumulators could have synergistic or antagonistic effects, such as accumulating more than one heavy metal or preferentially accumulating one heavy metal and leaving another for increased accumulation by the crop (Tang et al. 2012). Co-cropping of two non-accumulator crops could also alter metal availability (Tang et al. 2012), especially if one crop tends to acidify the soil. The soil matrix is a complicated system, and there are many factors influencing effective agricultural use of contaminated soils that are not yet well understood or documented. Antagonistic and synergistic effects between crop species, as well as soil microorganisms, must be taken into account when

selecting potential crops or soil amendments for use in heavy metal-contaminated soils (Puschenreiter et al. 2005).

Healthy agricultural management practices can also contribute to the safety of food crops grown on contaminated soils. Heavy metal levels in edible parts of plants are influenced by agricultural practices and the genotype of the crop used (Singh et al. 2011). For example, fertilizer management, choice of suitable crops or cultivars, and the use of crop rotation methods are acceptable agricultural practices that could reduce the risk of heavy metal contamination of edible plant tissue, including the spread of heavy metals to higher trophic levels via the food chain (Islam et al. 2007; Lasat 2000; Singh et al. 2011). For example, *Lupinus* (lupine; Fabaceae) has been found to increase Cd levels in wheat grain when grown in a crop rotation before wheat as its roots release citric acid which acidifies soil, thereby increasing the mobility and availability of heavy metals (Singh et al. 2011). Crop rotation is also important because any monoculture will, over time, become more susceptible to pests and pathogenic diseases. However, studies have shown that a monoculture of hyperaccumulator plants could be effective if the contamination is moderate enough to only need around three years of phytoremediation or less (Lasat 2000). Deep tillage could also be an option as it could dilute the distribution of contaminants by blending surface and subsurface soil layers (Singh et al. 2011).

While the approaches outlined here may all be viable in theory, it is difficult to advise farmers to switch from growing edible plants to growing biofuel or fiber crops without additional incentives. There are many personal, cultural, economic, climatic, and other considerations which go into the decision of what plants to grow in agricultural settings. However, phytostabilization using fuel or fiber crops can provide added economic benefits without high input and labor costs. Further, phytoextraction and phytomining using agronomic practices would be less destructive overall than using technological or chemical methods of remediation (Neilson and Rajakaruna 2012; Tang et al. 2012) and have the potential for being more socially acceptable methods of environmental cleanup.

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## 11.7 Potential for Genetic Modification

Hyperaccumulation often results from the over-expression of genes which code for specialized protein transporters and chelators (Chaffai and Koyama 2011; Rascio and Navari-Izzo 2011; Maestri et al. 2010; Verbruggen et al. 2009; Jabeen et al. 2009). Genetic modification has successfully increased the potential for metal accumulation in several species, including those in genera *Brassica* and *Arabidopsis* (Brassicaceae; Gall and Rajakaruna 2013). Genetic modification could also lead to metal tolerance via metal exclusion. Identification of genes that exclude heavy metals from species known to exclude

heavy metals and subsequent transfer of those genes to food crops could be a way to safely grow food plants on contaminated land (Wei et al. 2005). Metal-tolerant plants often exude compounds from their roots, such as citric and malic acids, which can chelate metals in the rhizosphere much like lime or a synthetic chelator would (Lasat 2000), making the contaminants less bioavailable. This characteristic could be useful in limiting translocation of heavy metals to edible tissues. Variation in metal tolerance and accumulation among cultivars of crops (Cutright et al. 2010; Xin et al. 2010; Zhang et al. 2013a, b) could help in breeding for heavy metal tolerance or exclusion; however, this is not an easy task as cultivars must also meet standards of yield, disease resistance, nutritional quality, and commercial viability (Singh et al. 2011).

## 11.8 Conclusions and Future Directions

Although much progress has been made in the exploration of how best to reconcile the growing need for arable land and the simultaneous increase in heavy metal contamination in agricultural soils worldwide, much remains to be learned. More research into how bacteria, fungi, and other soil microorganisms may be exploited for reducing metal transfer into plants and the food chain is an important area of future study. Concerted efforts to establish international standards with respect to heavy metal concentrations in edible plants and other agricultural products and the proper regulation of acceptable levels of heavy metals in food are also vital. Finally, field-based research on eco-friendly soil amendments to reduce bioavailability of metals and increase crop productivity under metal stress and the potential use of crops genetically modified to be tolerant of heavy metals or crop varieties that exclude heavy metals from edible tissue will drive the future of phytoremediation of contaminated agricultural soils.

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