Phytostabilisation and Phytomining – Principles and Successes

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ABSTRACT

Mine and ore beneficiation wastes and smelter contaminated soils often cause phytotoxicity and threaten adverse environmental effects if not remediated. Science has clarified both the risks from soil metals and methods to alleviate those risks that can be applied at low cost. Phytoremediation is a family of plant and agronomy based technologies to deal with environmental aspects of sites requiring remediation. If valid risk assessment indicates that metals comprise risk, phytostabilisation may be used to alleviate that risk for most contaminated sites. In particular, Zn-Pb, Cu and Ni mine and smelter sites are readily remediated by making the soil calcareous and fertile, with added organic and metal sorbent amendments that include soil microbes to 'revitalise' the soil. In each case, the soil fertility and causes of phytotoxicity should be clarified by agricultural soil extractions, and the combination of amendments required to improve fertility and reverse phytotoxicity identified and found locally. In contrast with phytostabilisation, phytoextraction/phytomining uses rare metal hyperaccumulator plants and agronomic management to maximise annual phytoextraction of soil elements into plant shoots for harvest, ashing and use as a metal ore. Plants that accumulate more than two per cent Ni in shoots, and yield 10–20 t ha^{-1} dry biomass yield 200–400 kg Ni ha^{-1}, which has value greater than all common agricultural crops. Considering the value of elements, existence of hyperaccumulator plants and demonstrated agronomic management for Ni phytomining, it is clear that mine sites and Ni mineralised subore-grade serpentine soils can be phytomined economically as an agricultural mining technology. A team developed agronomic methods and improved cultivars of *Alyssum,* which can be profitably grown on temperate zone Ni mineralised or contaminated soils. Plant species for tropical ultramafic soil materials have been identified. Phytoextraction is also strongly needed to remove Cd from rice soils to prevent human disease from soil Cd.

INTRODUCTION

Soils have become contaminated by metals over centuries of human industry. Mining and smelting have caused extensive soil contamination in most countries. Many countries are working to limit environmental and human risks from the contaminated soils under regulatory programs such as the US Superfund. The extent of contamination varies from statistically detectable to severe, such that no plants can grow on the contaminated soils and the contamination erodes to disperse and worsen the environmental effects of the site.

The simplest method to address such sites is to require placing all contaminated soil materials in a secure landfill, usually on-site, and cover the landfill with clean topsoil. For some small areas of contaminated soils, that may be the most cost-effective solution. But for extensive mine waste and smelter contaminated sites, the cost would be massive. The extent of required clean-up would depend on the rules imposed. Although the suggested limit for allowable total Ni in Ontario topsoils

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bore no relation to evidence for phytotoxicity or other adverse effects of soil Ni, the original rule would have required removal of the contaminated topsoil from 29 km^2 at a cost (assuming $1 million/ha) of $2.9 billion (Chaney, Kukier and Siebielec, 2003). But most of this land area was near neutral pH, well vegetated and actively farmed or gardened with no evidence of adverse effects to plants, wildlife, soil organisms or humans. Small areas with >10 000 mg Ni kg^{-1} were removed based on possible soil ingestion risk as a protective measure before any governmental decision about the requirement for soil remediation was completed.

In other locations, huge areas have become contaminated by smelter emissions into acidic forest environments where, ultimately, most vegetation could not persist, erosion followed and sites displayed evident environmental harm. Both Zn-Pb and Ni smelters in several countries have caused extensive destruction of forests due to the solubility of Zn and Ni in acidic soils. If the forest is killed, the whole ecosystem is destroyed (eg Amiro and Courtin, 1981; Bagatto and Shorthouse, 1999; Beyer *et al*, 2010, 2013; Courtin, 1994; Hutchinson and Whitby, 1977; Lautenbach, 1987; McIlveen and Negusanti, 1994; Winterhalder, 1983, 1996).

RISK ASSESSMENT AND REMEDIATION OF METAL CONTAMINATED SOILS

Alternative approaches to remediate such sites have been under investigation for decades and quite effective methods have been developed to attain soil 'revitalisation'. We stress 'revitalisation' as re-establishing a stable diverse living soil and plant system rather than 'ecosystem restoration' because the original ecosystem was destroyed so severely that it may not be possible to restore an equivalent ecosystem if for no other reason than raising soil pH to prevent phytotoxicity alters the ecosystem. But raising soil pH is very effective in reversing phytotoxicity and other risks from soil Zn, Ni and Cu as well as the 'natural' Mn and Al phytotoxicity of strongly acidic soils without contamination.

These new and effective methods for remediation of metal risks from contaminated soils are 'phytostabilisation' and 'phytoextraction/phytomining'. These are agronomic approaches that take into account the effects of soil chemistry and addition of soil amendments on the potential for toxicity of soil metals to all organisms. Risks to plants and soil organisms are obvious because these organisms live in the soil. But protections must be provided for environmental food chains, animals that ingest soil inadvertently or the soil within the earthworms consumed by vermivores. Risk assessment for soil contaminants has progressed greatly in the last few decades such that risks from soil metals to plants, soil organisms, mammals and humans are much better understood. That understanding allows application of agronomic practices to alleviate the risks. Laboratory developed approaches have been proven in field tests at multiple locations in many countries. Some of these tests even involved feeding treated and untreated soils to humans to measure reduction in bioavailability of soil Pb.

PHYTOSTABILISATION OF METAL CONTAMINATED SOILS

As previously indicated, methods to remediate contaminated soils depend on deeper understanding of risks and the chemistry of soil metals. Principles have become evident in risk assessment that provide a basis for inexpensive *in situ* remediation approaches. One principle is the 'soil-plant barrier', which summarises the processes in soils and plants that protect animals from nearly all elements in soils (Chaney, 1983b; Basta, Ryan and Chaney, 2005). Most elements are so insoluble in soil or in plant roots that concentrations in plant shoots are not a risk to the most sensitive livestock class or humans. A second group is the elements that are actually taken up by plants to exceed phytotoxic concentrations. If the plant shoot concentration reached at the point of significant phytotoxicity is not a danger as lifetime chronic feedstuff for the most sensitive livestock class, phytotoxicity protects ecosystems. A third group of elements are not a risk through plant accumulation, but grazing animals ingest some soil and vermivores consume earthworms with internal soil. If the element in ingested soil has significant bioavailability, adverse effects might result (eg Pb, As, F). Only a few elements are not controlled by the soil-plant barrier – Cd for humans (especially subsistence rice farm families with Cd contaminated soils) and Mo and Se in alkaline soils for ruminant livestock (Chaney, 1983b).

This section considers the agronomic aspects of contaminated soils and the agronomic analyses needed to understand actions to achieve remediation. As discussed previously, many mine wastes and soils contaminated by mine wastes and smelting emissions are strongly phytotoxic if acidic. The most common industrial metal phytotoxicity is Zn because of its widespread dispersal and ease of Zn phytotoxicity in acidic soil (Chaney, 1993). One effect of phytotoxicity is to limit root growth, so that short roots cannot absorb the nutrients that are usually absorbed after diffusion from soil surfaces. This includes P, K and most micronutrients. Therefore, metal phytotoxicity can induce P deficiency, especially when the soil is rich in Pb, which reduces phytoavailability of soil P by precipitation. Acidic soils can adsorb and precipitate phosphate more strongly with Fe and Al oxides. Thus, acidic contaminated soils cause so many stresses on plants that it should not be unexpected that sites can become barren or support only a few species that evolved high tolerance to soil metals.

Diagnosis of metal phytotoxicity is best done using agronomic soil analysis methods such as the diethylenetriaminepentaacetate extraction (Lindsay and Norvell, 1978). In this method, the chelating agent DTPA extracts metals in a soil solution matrix buffered at pH 7.3. In order to test contaminated soils, the ratio of solution to soil must be increased markedly. The original method used 20 ml per 10 g of air dry soil. This is fine for diagnosis of potential Fe or Zn deficiency. But for contaminated soils, the metals that are strongly chelated (Fe, Zn, Cu, Pb, Cd, Ni, Mn) can saturate the DTPA causing false low estimates of DTPA-extractable potentially toxic metals. In testing of Zn-Cd contaminated soils at Palmerton, PA, USA, Li *et al* (2000) found that they needed to use 50 ml g^{-1} soil to avoid DTPA saturation and underestimation of available metals. In testing of Ni contaminated soils at Port Colborne, Ontario, Canada, Kukier and Chaney (2001) found that they had to use at least 30 ml g^{-1} soil to avoid saturation.

Although the DTPA extraction is commonly used and convenient, it is not a good predictor of phytotoxicity unless soil pH is included in the prediction equation because the extraction is conducted at pH 7.3 with a buffered solution. In using chelating agent methods, it is important to maintain the ratio of Ca to chelator in the extraction or the results will not be interpretable (Lindsay and Norvell, 1978), so the ratio of solution to soil is varied rather than simply varying the DTPA concentration.

The best method to extract metals highly correlated with existing phytotoxicity risk is the so-called ‘neutral salt’ solutions, such as 0.01 M $Ca(NO_3)_2$ or 0.01 M $Sr(NO_3)_2$. These solutions do not alter soil pH, so the levels of extracted metals are similar to those in soil solution. Kukier and Chaney (2001, 2004) and Siebielec, Chaney and Kukier (2007) showed that Ni extractable by this solution was well correlated with Ni accumulation and phytotoxicity risk to several plant species tested. The correlations were valid across soils as well. Although others have used 0.01 and 0.1 M $CaCl_2$ for similar goals, the inclusion of chloride in extracts increases amounts of any metals that form chloride complexes, especially Cd. If extractable Ni or Zn exceeds levels that are diagnostic of phytotoxicity, no plant test is needed to conclude that the soil is presently phytotoxic. This extraction is highly responsive to soil pH change, and change in extractable metal is well related to change in plant metals and potential for phytotoxicity. Although this extractable soil metals method has very good diagnostic value, the main conclusion will be to raise the pH of the soil to reduce metal phytoavailability.

Fortunately, raising soil pH can increase the adsorption, precipitation and occlusion of metals (Zn, Cu, Ni, Pb, etc) over time. It has long been known that study of metal risks by adding soluble metal salts to soils causes errors in outcomes regarding assessment of risks. When high rates of metal salts are added to soils, metals are adsorbed and protons are displaced causing acidification of the soil. Because lower pH increases metal solubility in soils, the act of adding metal salts enhances metal toxicity (White, Decker and Chaney, 1979; Speir *et al*, 1999). Over time, the Zn and Ni may react with the soil to become strongly adsorbed or occluded or may form new minerals such as the Ni-Al layered double hydroxides, which can limit Ni and Zn solubility depending on pH (Basta, Ryan and Chaney, 2005; Scheckel *et al*, 2009; Smolders *et al*, 2003). If soils are pH near 7 or greater, reactions to reduce metal phytoavailability are maximised. Even chelation of Cu on soil organic matter is strengthened at higher pH and can alleviate Cu phytotoxicity for most plant species.

Several processes tend to acidify soils over time. Acidic rainfall slowly but surely causes soil acidification. Much more important is the use of N-fertilisers, N-fixation and oxidation of N and S in organic amendments applied to soils. Any sulfide in mine wastes can be oxidised to cause extreme soil acidification. So use of phytostabilisation must somehow deal with potential future acidification. The obvious way to counteract future acidification and failure of phytostabilisation is to incorporate more limestone than is needed to simply reach pH 7. One can estimate the limestone requirement to reach pH 7 using standard chemical methods and then apply an additional 50 t ha^{-1} of limestone to make the soil calcareous and provide pH buffering for long periods. At the Leadville site, with 60 cm of pH 2.5 soil materials, 224 t limestone equivalent ha^{-1} was required to provide the pH increase needed for persistent remediation (Brown *et al*, 2005).

Many examples of using alkaline amendments (limestone, wood ash, cyclone ash or other lime rich alkaline by-products) to raise pH of metal phytotoxic soils have been demonstrated in the greenhouse and confirmed in the field. At Palmerton, PA, strong phytotoxicity to lawn grasses was fully remediated by application of a lime-rich biosolids compost (Li *et al*, 2000). This approach was successful at the Bunker Hill Superfund Site in Idaho (Brown *et al*, 2003) and at the California Gulch Superfund site near Leadville, Colorado, USA (Brown *et al*, 2005). The sites represent different challenges and practices needed to attain remediation. At Leadville, mine wastes had been deposited adjacent to a river that had carried mine tailings from Leadville. As much as 60 cm of pH 2.5, very highly metal-contaminated mine wastes had accumulated over decades of uncontrolled releases. In this case, nothing grew on most of the soil. Laboratory testing showed that one could raise the pH to calcareous levels and correct soil fertility limitations by the addition of biosolids. The high P levels added with 224 t ha^{-1} of biosolids dry matter was available to react with Pb in the mine waste/soil. But because of the depth and extreme acidity, heavy equipment was required to mix the amendments with the full depth of contaminated mine wastes. After the pilot program, this method was applied to additional areas along the river where mine wastes had accumulated. With these treatments, lush vegetation grows and is safe for livestock and wildlife consumption (Brown *et al*, 2005). Similar success was achieved by Stuczynski *et al* (2007) in remediation of Zn-Pb smelter slag and smelter contaminated soils in Poland. These studies even included feeding the plants growing on the remediated soil to cattle compared to control soil grown crops and control crop plus metal salts. In Belgium, Vangronsveld, Colpaert and Van Tichelen (1996) showed effective remediation of Zn smelter contaminated sandy soils using amendment with the ash from a coal waste burning facility. Further testing showed the lasting inactivation of metals in the amended soils (Geebelen *et al*, 2006; Ruttens *et al*, 2010).

In other cases, the metals are near the surface and not so severely acidic from pyrite oxidation. The smelter contaminated Bunker Hill site was only mildly acidic and moderately contaminated. But with the death of vegetation soil, erosion had occurred and removed the nutrients needed to sustain vegetative cover. In 1970, Bunker Hill was terraced to limit erosion, but remained mostly barren due to metal toxicity. In previous research on leaching of alkalinity down soil profiles where alkaline biosolids composts were applied, Brown *et al* (1997) showed that the combination of biodegradable organic matter plus alkalinity could achieve leaching of alkalinity down the profile to raise pH of subsurface layers. Alkalinity leaching is more effective on coarse textured soils than fine textured. But seven years after the incorporation of a calcareous biosolids compost on a sandy soil, the strong soil acidity to more than 1 m was brought to pH 7 or higher. Application of limestone to the surface does not achieve neutralisation of soil below the depth of mixing; diffusion rates limit pH adjustment. Some suggest adding gypsum to provide leachable Ca, but that causes soil acidification rather than raising soil pH. Gypsum additions can reduce aluminium phytotoxicity in subsoils because the sulfate can complex Al^{3+} and reduce the activity of free Al^{3+} in the soil solution, reducing Al phytotoxicity.

In another case, the leachability of Ca was critical to remediation and the revegetation of asbestos mine wastes. These wastes are more than 150 ha of ground serpentinite rock from which asbestos had been recovered. They normally contain 2000 mg Ni and Cr kg^{-1} and are rich in Mg silicate (which keeps them alkaline), but severely deficient in Ca and P. Although the high levels of Ni and Cr caused some to believe the mine wastes to be 'toxic', the materials are not phytotoxic because of the high pH, but are severely deficient in Ca, P, N, K and perhaps other nutrients. The asbestos wastes are also coarse textured and contain very low levels of organic matter and soil microbes. Asbestos wastes are a special kind of fertility desert that can be readily addressed using agronomic technologies. The goal of this remediation is to attain a persistent plant cover to prevent erosion of asbestos fibres into air and water, so revitalisation is a sufficient goal to protect the environment. Chaney *et al* (2011) applied a mixture of livestock manure compost, gypsum, limestone and fertilisers to the surface of asbestos mine wastes in northern Vermont, USA, and seeded them with usual revegetation plant species for that region. Highly effective and persistent vegetation followed even on high slopes. In addition, over time more Ca leached into the soil, increasing the rooting depth for normal plant species. As with leaching of alkalinity, surface applied limestone Ca has little benefit because it is not leachable. However, some of the Ca in the compost is leachable, and the gypsum provides slowly leaching Ca. Roots were found as deep as 25 cm within one year after amendment, while on the control plots with simple chemical NPK fertilisers, no plants survived. We recommend the use of composted organic resources so that higher nutrient and stable OM additions can be made without the threat of excessive nitrate leaching, which could occur with manure or digested biosolids.

This unusual benefit of combining biodegradable organic matter (manure, composts, biosolids) with sources of alkalinity (limestone, etc) and any other required nutrients can further the goals of soil revitalisation (Allen *et al*, 2007). Not only can one alleviate all metal phytotoxicity in the tillage depth, one can provide all needed nutrients for persistent plant growth (presuming legumes are included in the cover crops), and provide inoculum of soil microbes often needed in long toxic soils. The high phosphate levels supplied by the organic amendments contributes to reducing the bioavailability of soil Pb to mammals if the soil were ingested.

These recipes for soil revitalisation (Allen *et al*, 2007) require local practitioners to identify and characterise the sources of inexpensive amendments that might be combined on-site to make a mixed amendment to correct all the adverse conditions of the metal contaminated site. Studies of wildlife on such remediated sites has shown protection of wildlife, even of earthworm consuming shrews, which are perhaps the most exposed animals at remediated sites (Brown *et al*, 2002a, 2002b, 2005). See Table 1 for a list of webinars on revitalisation using soil amendments.

PHYTOSTABILISATION/INACTIVATION OF SOIL LEAD

Pb is a common contaminant from mine wastes and smelter emissions and also in urban soils. Excessive soil Pb is a threat to the health of children and wildlife and must be addressed at many sites. Fortunately, much research has been conducted on the risks from soil Pb, and methods have been developed to reduce the bioavailability of Pb in ingested soils. Although plant uptake can occur in phosphate deficient soils, and particular crops may be relatively more effective in accumulating Pb from soils (low growing leafy vegetables, carrots, etc) (Zia *et al*, 2011), the most important risk from soil Pb is through soil ingestion. Whether wind-blown dust from Pb contaminated soils is a significant risk has not been settled, partly because the particle sizes of soil derived dust are not so respirable. Soil ingestion carries all elements of the finer soil particles into the stomach for possible absorption.

Research has shown that the application of phosphate can promote formation of chloropyromorphite ($Pb_5(PO_4)_3Cl$), which has low solubility at the pH of the small intestine. Scheckel *et al* (2013) summarised the science of Pb inactivation. One of the best demonstrations of the power of this approach of *in situ* inactivation of soil Pb was obtained from a field test at Joplin, MO, USA. A long-term smelter had contaminated regional soils with Pb, Zn and Cd. Soil amendments were applied based on practical availability and effectiveness, focusing on phosphate, biosolids compost and iron oxide, and mixed thoroughly into small plots using a rototiller. Some of the phosphate treatments strongly acidified the amended soil, so after a month for reaction, soils were returned to pH 7 with limestone, tilled well and seeded. Lawn grasses thrived on the amended soils despite very high soil Zn and Pb concentrations, and shoots remained low in metals (Brown *et al*, 2004). After three years, soils were fed to rats, swine and humans to test the effectiveness of the Pb inactivation treatments (Ryan *et al*, 2004). Phosphate treatment reduced bioavailability to test mammals by as much as 70 per cent. Scheckel and Ryan (2004) reported that in phosphate treated soils, Pb was converted to pyromorphite extensively. A strong plant cover also reduces the likelihood that soil will be ingested.

The largest need for remediation of soil Pb is urban soils that have often become highly Pb enriched from both automotive and stack emissions and from exterior paint residues. Older parts of cities have higher Pb contamination in general, but soil adjacent to a Pb painted surface can become highly Pb contaminated (>10 000 mg Pb kg^{-1}). Children are exposed to such soils both by play in the soil and by others carrying the soil into homes, where it becomes part of the house dust. House dust is the main

TABLE 1

List of US Environmental Protection Agency (US EPA) webinars (and weblinks) on soil remediation and risk assessment available at the US EPA Clu-In website.

Andersen, K and Chen, C, 2010. Using ecological-based tools and approaches to assess bioavailability [online], United States Environmental Protection Agency archived webinar. Available from: <http://www.clu-in.org/conf/tio/ecoresearch2_063010/> [Accessed: 1 May 2014].
Basta, N, Scheckel, K and Mahoney, M, 2011. Bioavailability-based remediation of metals using soil amendments: considerations and evaluation techniques: part 2 [online], United States Environmental Protection Agency archived webinar. Available from: <http://www.clu-in.org/conf/tio/soilbioavailability2_083111/> [Accessed: 1 May 2014].
Betterton, E, Maier, R and Wilinson, S, 2012. Mine tailings: enumeration and remediation [online], United States Environmental Protection Agency archived webinar. Available from: <http://www.clu-in.org/conf/tio/tailings_011112/> [Accessed: 1 May 2014].
Blaylock, M, Maier, R and Henry, H, 2008. Phytoremediation of metals [online], United States Environmental Protection Agency archived webinar. Available from: <http://www.clu-in.org/conf/tio/phyto3_112508/> [Accessed: 1 May 2014].
Brown, S, Mahoney, M, Pachon, C, Colsman, M and Andersen, C, 2011. Terrestrial carbon sequestration: an ecosystem service provided by using soil amendments for site remediation and reuse [online], United States Environmental Protection Agency archived webinar. Available from: <http://www.clu-in.org/conf/tio/amendments_102711/> [Accessed: 1 May 2014].
Chaney, R, Lipson, G, Zimmerman, M, Compton, H and Mahoney, M, 2013. NARPM presents . . . ecological revitalization using natural materials [online], United States Environmental Protection Agency archived webinar. Available from: <http://www.clu-in.org/conf/tio/Narpmpresents20_051413/> [Accessed: 1 May 2014].
Chaney, R, Sprenger, M and Mahoney, M, 2011. Bioavailability-based remediation of metals using soil amendments: considerations and evaluation techniques: part 1 [online], United States Environmental Protection Agency archived webinar. Available from: <http://www.clu-in.org/conf/tio/soilbioavailability_062211/> [Accessed: 1 May 2014].
Compton, H, Brown, S and Rubin, E, 2006. Jump-starting ecological restoration – soil health [online], United States Environmental Protection Agency archived webinar. Available from: <http://www.clu-in.org/conf/tio/ecorestoration2_100506/> [Accessed: 1 May 2014].
Compton, H, Maier, R and Whitson, L, 2003. NIEHS/EPA metals – remediation [online], United States Environmental Protection Agency archived webinar. Available from: <http://www.clu-in.org/conf/tio/metals_051403/> [Accessed: 1 May 2014].
Daniels, W L, Fredericks, S and Balent, J, 2007. Understanding and reconstructing soil conditions at remediation sites [online], United States Environmental Protection Agency archived webinar. Available from: <http://www.clu-in.org/conf/tio/soilconditions_050207/> [Accessed: 1 May 2014].
Handel, S and Rubin, E, 2006. Jump-starting ecological restoration [online], United States Environmental Protection Agency archived webinar. Available from: <http://www.clu-in.org/conf/tio/ecorestoration4_092106/> [Accessed: 1 May 2014].
Mahoney, M and Sprenger, M, 2011. NARPM presents . . . Ecological revitalization: turning contaminated properties into community assets [online], United States Environmental Protection Agency archived webinar. Available from: <http://www.clu-in.org/conf/tio/NARPMPresents6_031511/> [Accessed: 1 May 2014].
Maier, R and Whitson, L, 2007. Phytostabilization of mine tailings in arid and semi-arid environments [online], United States Environmental Protection Agency archived webinar. Available from: <http://www.clu-in.org/conf/tio/phytostabilization_072507/> [Accessed: 1 May 2014].
Tsao, D, Schnoor, J and Geller, K, 2008. Phytoremediation: the potential is growing [online], United States Environmental Protection Agency archived webinar. Available from: <http://www.clu-in.org/conf/tio/phyto1_101408/> [Accessed: 1 May 2014].

source of Pb ingested by young children, mostly through hand-to-mouth play. Although nearly all Pb poisoning has resulted from interior paint contaminating house dust (Lanphear *et al*, 1998), concern about outdoor soil has encouraged much research on garden soils. Zia *et al* (2011) reviewed studies of urban soil Pb. Using a bioaccessibility extraction developed based on the human feeding tests of Joplin control and phosphate amended soils, they found that Pb in urban garden soils had quite low relative bioavailability. They hypothesised that regular additions of fertilisers and manures, tillage and the growing of crops in gardens has promoted the formation of pyromorphite. Cotter-Howells, Champness and Charnock (1999) observed formation of pyromorphite in the rhizosphere of plants growing in Pb rich soil. As demonstrated by Ryan *et al* (2004), Zia *et al* (2011) found that extraction using 0.1 M glycine at pH 1.5 strongly overestimated the bioavailability of soil Pb, but that extraction at pH 2.5 gave much better correlations. More feeding studies with untreated and remediated soils are needed to calibrate bioaccessibility methods.

Some evidence that high soil As can be inactivated by the presence of hydrous Fe oxides has been reported (Basta, Ryan and Chaney, 2005; Cutler *et al*, 2013). There is clear evidence that As in soils with different properties can have quite different relative bioavailability (Bradham *et al*, 2011; Basta, Ryan and Chaney, 2005; Juhasz *et al*, 2007; 2008). Soil As remediation is important where soils were contaminated by pesticide applications, mine and smelter emissions, etc.

Risk from Cd in contaminated sites from geogenic Cd+Zn sources is usually prevented by the co-contamination with Zn. Soil amendment to prevent Zn phytotoxicity is able to strongly limit food-chain Cd transfer. Zn phytotoxicity occurs at about 400–500 mg Zn kg^{-1} dry leaves; for geogenic Cd with Cd:Zn ratio of 1 g Cd per 100–200 g Zn, the same leaves will be limited to no more than 4 mg Cd kg^{-1} (Chaney, 2010; Chaney, Ryan and Reeves, 2013). As summarised in those papers, rice and tobacco are special cases for Cd risk, such that protecting all other parts of the ecosystem from Zn phytotoxicity does not adequately limit Cd in rice grain, or in tobacco products, where smoking transfers bioavailable Cd so effectively and quite differently from ingested plant Cd sources.

PHYTOEXTRACTION/PHYTOMINING OF SOIL METALS

In contrast with phytostabilisation, where one attempts to convert the soil metals into forms that are not phytoavailable and do not cause excessive uptake by plants, phytoextraction uses unusual plants to achieve removal of significant amounts of the contaminant from soils. Chaney (1983a) introduced the concept, which has become widely studied since. As shown in Table 2, crop plants (eg maize silage) do not accumulate high enough concentrations of metals in their shoots to achieve appreciable removal of metals from the field, even when they are suffering significant Ni or Zn phytotoxicity. In contrast, rare plants called 'hyperaccumulators' may accumulate 100 to 1000 times higher concentrations of a few elements than crop plants at the point where crop plants suffer metal phytotoxicity. Harvesting hyperaccumulator plant biomass may allow high annual removal of some elements from contaminated soils. A recent review (van der Ent *et al*, 2013b) established levels of Zn, Cd, Ni, Pb, Mn, As, etc, that are sufficiently unusual to be called hyperaccumulators. These plants hyperaccumulate one metal (Ni, Zn, As, Co, Tl) or several closely related metals (Zn and Cd) into their shoots, so the phytoextraction concept has narrow element applications.

TABLE 2

Estimated Ni phytoextraction by maize (*Zea mays* L.) shoot biomass versus *Alyssum murale* grown as a phytomining crop; assume control soil contains 25 mg Ni kg^{-1} and the Ni-rich soil contains 2500 mg Ni kg^{-1} = 10 000 kg Ni (ha 30 cm)$^{-1}$; for line 2, assume soil is acidic enough that Ni causes 50 per cent yield reduction compared to corn grown on similar soil without Ni mineralisation or with higher pH. Research has shown that unimproved *Alyssum murale* can easily yield 10 t ha^{-1} with fertilisers, and selected cultivars can exceed 20 t ha^{-1} with appropriate soil and crop management on serpentine soils. Most crop plant species suffer 25 per cent yield reduction when the shoots contain 50–100 mg Ni kg^{-1} dry weight.

Species	Soil		Ni in the crop			
		Yield (dry t ha^{-1})	mg kg^{-1}	kg ha^{-1}	% of soil	Ash-Ni (%)
Maize	Control	20	1	0.02	0.01	0.002
Maize (50% yield decrease)	Ni-rich	10	100	1	0.01	0.20
Wild *Alyssum* in pasture	Ni-rich	3	10 000	30	0.3	10–15
Wild *Alyssum murale*	Ni-rich	10	20 000	200	2.0	20–25
Alyssum murale cultivar	Ni-rich	20	25 000	500	5.0	25–30

In the case of using hyperaccumulators to remove soil contaminants to achieve soil decontamination, the process is called 'phytoextraction'. The removal of the element gives biomass very rich in the element, but the metal-rich biomass may have little economic value depending on the price of metals. For Cd and As, and probably Zn, the biomass will have to be disposed of safely in a landfill or burned and the fumes recovered for recycling or disposal. Fortunately, these specific elements are relatively volatile and could be separated from the rest of the plant ash during incineration (Ljung and Nordin, 1997).

Much of the early interest in phytoextraction arose from the claims of the Raskin research group at Rutgers University. Unfortunately, this work caused great confusion and waste of resources because it claimed that Pb phytoextraction was possible (Kumar *et al*, 1995), which is clearly not valid. It only observed high Pb in the shoots of *Brassica juncea* because it grew the plants with very low supply of phosphate and sulfate and provided soluble $Pb(NO_3)_2$ in the uptake test period with no phosphate. Pb was accumulated and killed the plants. But when they tested this and other species on actual Pb contaminated soils, little Pb phytoextraction occurred. Only by the addition of chelating agents such as ethylenediaminetetraacetate to the soil could they obtain soluble PbEDTA and harm the roots such that PbEDTA could leak into the plants and reach the shoots with transpiration (Blaylock *et al*, 1997). The addition of EDTA to soils is not acceptable in the open environment (see review by Nowack, Schulin and Robinson, 2006). More Pb leaches down the soil than is accumulated in the plant shoots. Further, application at 10 mmol kg^{-1} soil would cost about $21 500 ha^{-1} using bulk prices for commercial EDTA. This method was soon prohibited in the US and the European Union. Unfortunately, many scientists and garden groups have tested using *Brassica juncea*, sunflower and other diverse species to phytoextract soil Pb all without success. More discussion of these issues is included in the paper by Chaney, Broadhurst and Centofanti (2010).

PHYTOEXTRACTION OF SOIL CADMIUM TO PROTECT FOOD SAFETY

In two kinds of soil contamination, the important risk is to food-chain safety at least for rice (Chaney, 2012; Chaney, Ryan and Reeves, 2013). Although most crops do not accumulate appreciable amounts of As in their edible tissues, because rice is grown in flooded soils and arsenite is produced in the anaerobic soil, it can accumulate substantial amounts of As on its silicate transporter (Ma *et al*, 2008). For most soils, As risk is through soil ingestions and, in those cases, the speciation of soil As is important in risk, as discussed previously under phytostabilisation. A number of fern species have been found to hyperaccumulate As, some to above one per cent in shoot dry matter such that phytoextraction could remove As. In addition, the mixing of surface soil where contamination accumulated with subsurface less contaminated soil during tillage for growing of the phytoextraction crop also reduces risk from ingestion of soil. This technology has been successfully applied in the field in the US (Blaylock, Elless and Pulley, 2011).

In the case of rice soils, where there has been contamination from industrial or geogenic sources, grain can be considerably increased in As. One approach to prevent the production of rice grain with high levels of inorganic As (the chemical form that comprises the greatest risk to humans) is to grow the crop in aerobic (non-flooded) soil. Aerobic production limits formation of arsenite and can greatly limit uptake of As by rice (Arao *et al*, 2009; Linquist *et al*, 2014). But aerobic production also increases uptake of Cd into grain (see Chaney, Ryan and Reeves, 2013). Because of extensive soil Cd contamination in Japan, China and several other rice producing countries, any attempt to reduce rice grain inorganic As may increase grain Cd to unacceptable levels.

Cd phytoextraction has been researched by numerous scientists, but commercial application of the technologies has yet not proceeded. The evident reason commercialisation has not progressed is that few land owners are required by government agencies to remediate soil Cd contamination problems. In Japan, only about 4000 ha have actually been remediated to reduce Cd in rice, while over 40 000 ha would cause excessive Cd if soils were not kept flooded until grain was mature. With no market need for the technology, little investment has been made beyond research. Recent progress was reported by Simmons *et al* (in press) on Cd phytoextraction using southern France races of *Noccaea caerulescens* in Thailand, where climate made growth of this temperate zone species difficult. By application of a fungicide, planting on raised beds and lowering soil pH to promote metal accumulation (see also Wang *et al*, 2006; Yanai *et al*, 2006), the improved agronomic management protected the plants against fungal pathogens. In another setting of high Cd supplied by a Cd-rich biosolids with high cumulative applications, soil Cu made growth of *Noccaea caerulescens* difficult, but a maize inbred with unusual Cd accumulation and good growth on the biosolids rich soil allowed significant annual Cd removals (Broadhurst *et al*, 2014). Another promising Cd phytoextraction system for rice paddy soils is a mutant rice that accumulates high levels of Cd in shoots rather than roots (Murakami *et al*, 2009). Although this system may phytoextract only low amounts of Cd per year compared to true hyperaccumulators, the mutant rice grows well in tropical rice soils. As discussed in other papers (Chaney *et al*, 2011), other Cd phytoextraction systems are being researched for the extensive tropical Cd-contaminated rice land in Asia.

Another approach to Cd phytoextraction is the use of bioenergy crops with relatively high Cd accumulation, but that are clearly not hyperaccumulators (eg willow). The bioenergy value of the crop could drive the economics of soil remediation and the ash could be placed in landfills (Witters *et al*, 2012). Basic understanding of Cd phytoextraction continues to be researched, and a recent paper reported the regulatory genes and gene copy number for key genes that achieve high Cd accumulation by southern France *Noccaea caerulescens* (Milner *et al*, 2014).

PHYTOMINING OF NICKEL AS A COMMERCIAL TECHNOLOGY

In consideration of the land area rich in Ni, both serpentine soils and contaminated soils, which could serve as substrates for commercial Ni phytomining, and the existence of Ni hyperaccumulator plants that are tall enough for convenient production and accumulate over one per cent Ni in dry shoots, Chaney (1983a) introduced the concept of Ni phytomining using *Alyssum* species. Over time a cooperative research and development agreement was established to support the research needed to develop phytomining, including selection of an appropriate species for domestication, collection of diverse germplasm (seeds), testing of the agronomic requirements to grow the species, field evaluation of yield and Ni accumulation ability of the genotypes, breeding improved cultivars for commercial phytomining and recovery of Ni from the biomass. Research has been reported (Angle *et al*, 2001; Chaney *et al*, 2007; Li *et al*, 2003a, 2003b) on the development of the practical phytomining technologies that were patented by the authors' institutions (eg Chaney *et al*, 1998). We established the fertiliser requirements to produce full biomass on serpentine soils and tested the ability of *Alyssum* species to accumulate Ni from diverse serpentine soils from Maryland and Oregon, finding that *Alyssum* was self-incompatible and that recurrent selection would be required to breed improved cultivars. Li *et al* (2003a) showed the wide variation in Ni concentration accumulated by nearly 200 *Alyssum* accessions in a serpentine soil in OR. One of the most interesting findings contradicted the expected relationship of soil pH to accumulation of Ni by *Alyssum* compared with crop plants. For all crop plants studied, increasing soil pH reduces the solubility of Ni in the soil solution and reduces Ni uptake by the plants. When a soil causes Ni phytotoxicity, liming the soil and correcting infertility can fully remediate any phytotoxicity risk from soil Ni (eg Crooke, 1956; Halstead, 1968; Kukier and Chaney, 2001, 2004; Siebielec, Chaney and Kukier, 2007). This normal effect of soil pH on solubility/extractability of Ni in diverse serpentine soils is shown in Figure 1. But when we grew *Alyssum* species on these soils with fertilised versus acidified and fertilised treatments, lowering pH decreased Ni accumulation by *Alyssum* from nearly all of the soils. Only soils with higher levels of Fe oxides and higher pH failed to show *Alyssum* having higher shoot Ni with higher soil pH (Figure 2). Figure 3 shows the relationship between *Alyssum* Ni and soil pH, clearly showing the unexpected positive relationship. For *Alyssum*, solubility is not related to phytoavailability.

As noted previously, other researchers estimated the potential for Ni phytoextraction by extracting various soils using 1.0 M NH_4-acetate, a common extractant for 'exchangeable' soil metals. Estimates of depletion of soil Ni were made based on repeated extractions using NH_4-acetate (Robinson *et al*, 1999). But as Figures 2 and 3 show, *Alyssum* shoot Ni has a very opposite reaction to soil pH and exchangeable Ni than that found for crop plants.

Estimating the possible value of phytomining crops is complex. Estimating costs of production requires understanding of the fertiliser requirements of this crop on serpentine or Ni-contaminated soils and the yield potential under rainfed or irrigated management. Over a period of years, Bani *et al* (in press) tested accumulation of Ni by *Alyssum* growing on a natural serpentine soil in Albania, a field that was used for grazing and had in some past years been used to produce low yields of wheat (due to serpentine infertility issues). At first they only harvested the unfertilised wild *Alyssum* plants growing in the field and estimated biomass yield at 0.3 t ha^{-1} and biomass Ni of 10 kg t^{-1}. In subsequent years, they applied fertilisers then fertilisers plus herbicides to limit competition and water use by other species. Subsequently, they tilled the soil, added fertilisers and used herbicides to grow a seeded *Alyssum* crop rather than the naturally occurring crop. With the last iteration, which tested rainfed Ni phytomining on one field in Albania, they harvested 9 t dry *Alyssum* biomass ha^{-1}, which contained 105 kg Ni ha^{-1}. As noted above, Li *et al* (2003a) bred improved cultivars that accumulated higher Ni than the parent genotypes, had high yields in irrigated fields in OR and retained their leaves into flowering. Some wild genotypes start to drop Ni-rich leaves at the first sign of flowering. If plants retained their leaves into flowering, several more weeks of biomass production could occur before the crop would be harvested at a point where the seeds were not yet viable. The combination of agronomy improvements and genetic improvements allowed up to 20 t ha^{-1} yield with over 20 kg Ni t^{-1} dry biomass of *Alyssum* shoots. As we reported (Chaney *et al*, 2007), *Alyssum* biomass ash was processed in an electric arc furnace at the Copper Cliffs smelter, Sudbury, Ontario, and it was a valuable Ni ore. In contrast with usual Ni ores, biomass ash has little Fe, Mn or silicate to interfere with Ni recovery. Ash contains plant nutrients rather than ore ingredients. There is no

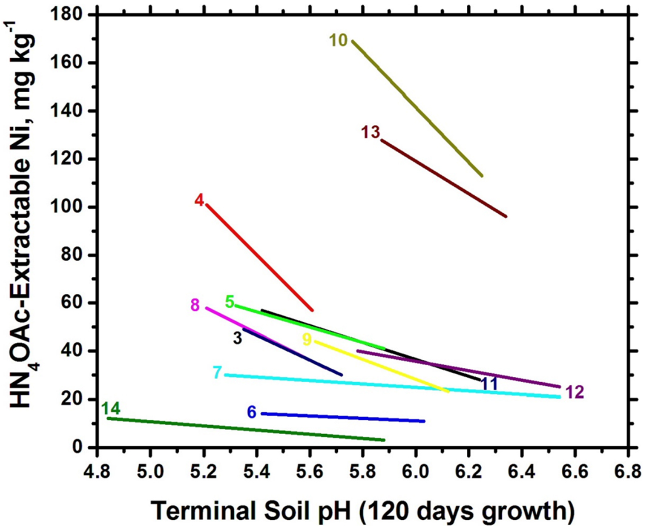

FIG 1 – Effect of soil variation and soil pH alteration on 1.0 M MH$_4$-acetate extractable (exchangeable) NI in diverse serpentine soils. Numbers on lines indicate specific serpentine soils used in the test (Chaney, Li, Roseberg, Brewer, Angle, Baker and Reeves, unpublished).

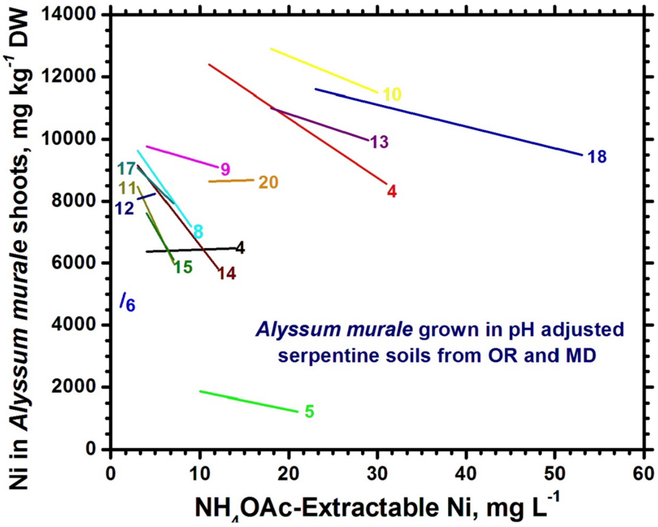

FIG 2 – Effect of terminal soil NH$_4$-acetate extractable Ni on *Alyssum* accumulation of Ni from serpentine soils. Numbers on lines indicate specific serpentine soils used in the test (Chaney, Li, Roseberg, Brewer, Angle, Baker and Reeves, unpublished).

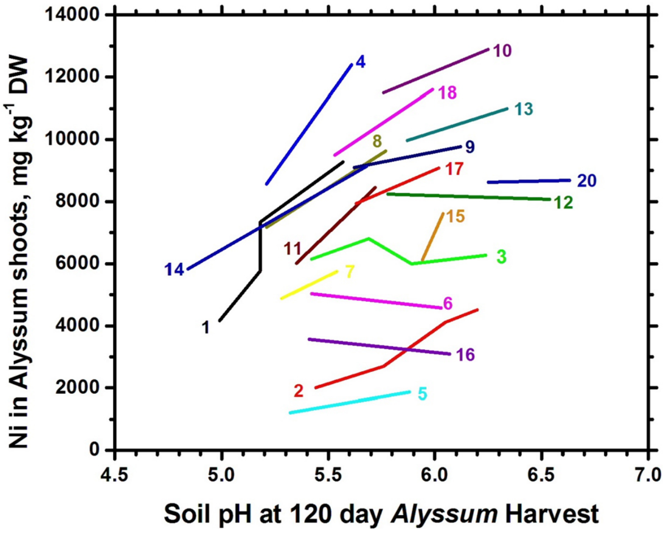

FIG 3 – Effect of terminal soil pH and soil variation on *Alyssum* accumulation of Ni from serpentine and smelter contaminated soils. Numbers on lines indicate specific soils used in the test (Chaney, Li, Roseberg, Brewer, Angle, Baker and Reeves, unpublished).

need for hot concentrated sulfuric acid under pressure to release Ni from the ash as is required for ores at many facilities. *Alyssum* plant ash is probably the richest and easiest Ni ore to recover pure Ni from ever offered for sale, showing the commercial value of the biomass ash as Ni ore. Barbaroux *et al* (2012) tested the production of another Ni product, $Ni(NH_4)_2(SO_4)_2$, which appears to have more value per unit Ni than Ni metal. Hunt *et al* (2014) suggest the possible production of 'green' products from hyperaccumulator biomass, such as catalysts or nanoparticles.

If growing improved *Alyssum* cultivars with improved agronomic practices allows production of 400 kg Ni ha^{-1} and the current value of Ni metal is \$18 kg^{-1}, the Ni value of the Ni in the crop would be \$7200 ha^{-1}. That value of Ni would have to pay for the land rent, fertilisers, growing and harvesting of the crop, hauling the crop to a processing facility to produce ash and transporting the ash to a smelter, which would process the ash into Ni metal or other Ni products and market the products. Considering that most agricultural crops net no more than \$1000 ha^{-1}, and for serpentine soils net crop value is often less than \$300 ha^{-1} because of the infertility and higher fertiliser requirements of serpentine soils, Ni phytomining appears especially promising for commercialisation. The failure of the patent licensee to commercialise the technology is hard to understand because Ni industry firms attempted to do joint ventures to conduct phytomining on land they controlled, without success. With the expiration of the patents in 2015, the opportunity to commercialise this technology is open again.

Although *Alyssum* species are adapted to temperate serpentine soils, tropical soils offer very different ecological situations. A test crop of *Alyssum* in Sulawesi was much less successful than production in OR or Albania. Some nations will require either a native Ni hyperaccumulator species or a sterile genotype of an exotic (non-native) species to allow growing for Ni phytomining. Reeves (2003) and van der Ent *et al* (2013a; 2013b) have discussed several species that might be useful on tropical serpentine soils. In order for those species to be used in phytomining, their agronomic production needs will have to be established, and improved cultivars selected or bred to assure predictable high yield of Ni in biomass.

CONCLUSIONS

Progress in understanding risks from metals in contaminated soils, and the chemistry of contaminated soils and soil amendments has led to the development of *in situ* phytostabilisation (revitalisation) for nearly all mine wastes and smelter-contaminated soils requiring remediation. These methods are quite inexpensive compared to soil removal, and we can only hope that industry will use the phytostabilisation technologies on the large number of hazardous sites around the globe. In addition, phytoextraction offers the ability to alleviate soil Cd risks from the few crops and soils that cause actual Cd risk to humans or the environment. Lastly, for the few elements where the value of metals in biomass of farmed hyperaccumulator species is high enough, commercial phytomining offers a new way to produce high value Ni ores. It is time for industry to start adopting phytotechnologies.

ACKNOWLEDGEMENTS

The US Environmental Protection Agency has not subjected this manuscript to internal policy review. Therefore, the results presented do not necessarily reflect agency policy. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

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