Presented at: US-EPA's Conference "Phytoremediation: State of the Science Conference", *May 1-2, 2000, Boston, MA.*

"Progress in Risk Assessment for Soil Metals, and In-situ Remediation and Phytoextraction of Metals from Hazardous Contaminated Soils.

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ABSTRACT

Mining and smelting of Pb, Zn and Cd ores have caused widespread soil contamination in many countries. In locations with severe soil contamination, and strongly acidic soil or mine waste, ecosystems are devastated. Research has shown that Zn phytotoxicity, Pb-induced phosphate deficiency, Cd risk through uptake by rice or tobacco, and Pb risk to children, livestock or wildlife which ingest soil are the common adverse environmental effects at such contaminated sites. Improved understandings of soil metal risks to the environment have been developed which examine risk to all possible exposed organisms through soil, plants, animals, or water exposures. This review summarizes information about soil Cd risk to food-chains, explaining that when Cd is present at the usual 0.005-to-0.02 ratio to Zn in the contaminated soil, only rice and tobacco allow Cd to be transferred from the soil in amounts which can harm humans over their lifetime. Zn inhibits plant uptake of Cd, and inhibits intestinal absorption of Cd, protecting animals from Cd in most situations. Pb risk to children or other highly exposed organisms results from ingestion of the contaminated soil, and absorption of Pb from the soil into the blood where adverse health effects occur at 10-to-15 μg Pb/dL blood. Soil Pb has much lower bioavailability than water Pb, and if ingested with food has even lower bioavailability. Research has shown that if high phosphate levels are added to Pb contaminated soils, an extremely insoluble Pb compound, chloropyromorphite, is formed in soils from all known chemical species of Pb which occur in contaminated soils. It had earlier been learned that adding adsorbents such as hydrous Fe oxides and phosphate to Pb contaminated soils inhibited Pb uptake by crops, and combined with the evidence that these materials could reduce the bioavailability of soil Pb to children, feeding tests were conducted with rats and pigs in several laboratories. A new approach to remediation of severely disturbed Pb/Zn/Cd contaminated soils has been developed which uses mixtures of limestone equivalent from industrial byproducts such as woodash (to make soil calcareous and prevent Zn phytotoxicity), phosphate and Fe from biosolids and byproducts (to precipitate Pb and with Fe, increase Pb adsorption), organic-N from biosolids and manures and other beneficial components which correct the infertility of contaminated and eroded soils. Composting can stabilize the organic matter and slow N release to allow higher application of remediation amendments. Highly effective revegetation has resulted at four field test locations where this

approach was tested, Palmerton, PA; Katowice, Poland; Bunker Hill, ID; and Leadville, CO. All plants tested were readily grown on the amended soil even with soil contained over 1% Zn and 1% Pb. Plant analysis indicates that these plants may be consumed safely by wildlife and livestock, although soil ingestion should be minimized at such sites. Although mining and smelting contamination has caused severe environmental harm in many locations, this method of soil metal remediation allows effective and persistent remediation at low cost, and should be applied to prevent further dispersal of the contaminated soil materials at many locations.

The potential use of metal hyperaccumulator plants to phytoextract soil metals is a new method of remediation under development. Combining improved cultivars of these accumulator plants, agronomic management practices to maximize yield and metal accumulation, burning the biomass to generate power, and recovery of metals from the ash appear to offer an economic technology compared to soil removal and replacement.

INTRODUCTION

Mining or smelting of Pb-Zn ores generates mine tailings rich in Pb, Zn, and Cd. Some of these tailings contain dolomitic limestone, and others contain pyrite which generates acidity when oxidized. Smelting of Pb, Zn, and Cu ores has commonly caused emission of Zn, Cd and Pb at levels which can cause adverse effects in the terrestrial environment. Strongly acidic Zn rich mine wastes and smelter contaminated soils cause severe Zn phytotoxicity (Chaney, 1993), and can prevent all plants from surviving on the soil (e.g., Beyer, 1988). This paper is a summary of the key evidence that such mine and smelting wastes cause phytotoxicity of Zn, potential Cd risk to humans if rice or tobacco are grown on the contaminated soil, and Pb risk to children who may ingest the mine wastes or contaminated soils or housedust generated from these contaminated soil materials. Adverse environmental effects of these metals have resulted in many nations where older industrial technologies were used in mining or smelting.

On the other hand, there has been important progress in risk assessment methodology for soil metals, and research on methods to remediate Zn, Cd, and Pb contaminated soils and sediments. New practical approaches for both *in situ* remediation by addition of amendments which reverse Zn phytotoxicity and Pb risk from soil ingestion have been demonstrated in recent years. Practical, inexpensive methods are available to revegetate such contaminated soil materials, and support vegetation which can be safely consumed by wildlife, livestock, and humans. Also, phytoextraction research has illustrated the potential of growing unusual metal hyperaccumulator crops on contaminated soils to remove some metals, and provide biomass power and an ash which can be recycled to reduce the costs of remediation.

A full discussion of present-day risk assessment and soil metal remediation methods would take a book. Thus, the goal of this paper is to give an overview of these ideas, with references to full papers and book-chapters which more fully report the science which allows the improved risk assessment and practical soil metal remediation. One of the most important advances in soil metal remediation is our development of using phosphate rich, high Fe biosolids and composts, and lime rich woodash and other lime-containing byproducts to make “Tailor-Made” Remediation Biosolids Mixtures and Composts and readily achieve effective revegetation and ecosystem restoration at such metal contaminated sites (see Chaney, Ryan and Brown, 1999; Stuczynski et al., 1997; Li and Chaney, 1998; Daniels et al., 1998; 1999; Brown et al., 1998b; Siebielec et al., 1999).

Improved Risk Assessment for Soil Metals. When present at high enough concentrations, Pb, Zn, and Cd in soils can cause adverse effects on plants, soil organisms, wildlife, livestock and humans through Pathways which involve soil ingestion by children or livestock, ingestion of foods grown on the soil, ingestion of animals which ingested plants which grew on the soil, or from leaching of metals to drinking water or streams where Zn harms fish (Table 1). Extensive research and evaluation of the literature were conducted over the last decade to develop quantitative limits for metals in land-applied biosolids (municipal sewage sludge), and for characterization of the potential hazards which a soil could cause (see Chaney and Ryan, 1994; US-EPA, 1993). And research was conducted to find methods to amend or treat contaminated soils to reduce the risk of soil metals in a persistent manner such that the hazardous nature would be reversed or remediated.

Table 1. Pathways for risk assessment for potential transfer of biosolids-applied trace contaminants to humans, livestock, or the environment, and the Highly Exposed Individuals to be protected by a regulation based on the Pathway Analysis (US-EPA, 1989a, 1993; Chaney and Ryan, 1994). Each Pathway presumes 1000 t dry biosolids ha^{-1} and/or maximum allowed annual application of biosolids as N fertilizer.

	PATHWAY	HIGHLY EXPOSED INDIVIDUALS
1	Biosolids➜Soil➜Plant➜Human	Individuals with 2.5% of all food produced on amended soils.
2	Biosolids➜Soil➜Plant➜Human	Home gardeners with 1000 t ha^{-1}; 60% garden foods for lifetime.
3	Biosolids➜Human	Ingested biosolids product; 200 mg d^{-1}.
4	Biosolids➜Soil➜Plant➜Animal➜Human	Farms; 1000 t/ha; 45% of "homegrown" meat.
5	Biosolids➜Soil➜Animal➜Human	Farms; 1000 t/ha; 45% of "homegrown" meat.
6	Biosolids➜Soil➜Plant➜Animal	Livestock feeds; 1000 t/ha; all from amended land.
7	Biosolids➜Soil➜Animal	Grazing Livestock; 1.5% biosolids in diet.
8	Biosolids➜Soil➜Plant	"Crops"; strongly acidic amended soil (1000 t/ha), but with limestone to prevent natural Al and Mn toxicity.
9	Biosolids➜Soil➜Soil Biota	Earthworms, microbes, in amended soil.
10	Biosolids➜Soil➜Soil Biota➜Predator	Shrews (*Sorex araneus* L.); 33% earthworms diet, living on site.
11	Biosolids➜Soil➜Airborne Dust➜Human	Tractor operator.
12	Biosolids➜Soil➜Surface Water➜Human	Subsistence fishers.
13	Biosolids➜Soil➜Air➜Human	Farm households.
14	Biosolids➜Soil➜Groundwater➜Human	Well water on farms; 100% of supply.

The formal risk assessment method uses 14 or more Pathways to estimate the effect of soil metals on Highly Exposed Individuals (HEIs) which are humans who live on the soils, livestock pastured on the soil, crops grown on the soil, soil organisms in the soil, etc. (Table 1). For the biosolids risk assessment, it was assumed that 1000 t/ha of dry weight of biosolids would be applied over many years (centuries) of biosolids use as a fertilizer or soil conditioner. In risk assessment for hazardous soils, the contaminated soil is considered as is. One important change in the approach to risk assessment is the inclusion of valid measurements of “bioavailability” of soil metals to the HEI organism under consideration (child, adult, livestock, plant, etc.). And for the use of field-derived metal transfer coefficients from soil to plants, soil to livestock, soil to humans, etc.

The importance of using field-derived plant uptake slopes for the biosolids-amended soil is highly evident from examination of the literature. First, one needs to consider the effect of the chemical form of, and recency of metal salt additions on phytoavailability and bioavailability of metals added to soils. When metal salts are added to soil, or metal salts added to biosolids which are then mixed with soil, many errors can occur (e.g., Cunningham et al., 1975a; 1975b; 1975c). All of these errors increase plant uptake and bioavailability of added metals compared to field-contaminated soils. If pure metal salts are mixed with soil, it takes a considerable time for the added metals to reach a quasi-equilibrium with the soil (Singh and Jeng, 1993). And other constituents of a metal source (Fe and Mn oxides, phosphate, organic matter, etc.) are not applied when metal salts are used to model the risk of contaminated soils (Corey et al., 1987; Logan and Chaney, 1983; Chaney and Ryan, 1994). This has caused important confusion regarding Cd phytoavailability because Fe and Mn oxides present in biosolids can increase the selective or specific metal adsorption ability of the amended soil, but addition of metal salts cannot have this effect (Figure 1). Fig. 1 shows models of the patterns of plant uptake of Cd and Zn in relation to soil Cd and Zn concentrations found in studies of long-term biosolids application compared to those for metal-salt treated soils. In Fig. 1, all lines start at the linear slope usually found for added Cd-salts, and represent equal Cd additions in different forms, to one soil. Curve A represents the linear response to small additions of Cd salts found in nearly all studies in the literature. In curve B, the pattern is of increasing plant:soil slope at increasing Cd applications because Zn is also added, at 100-times the Cd additions, and the added Zn competes for the stronger adsorption sites in the soil. These first two patterns have been repeatedly observed in many studies, and are illustrated well by the data in White and Chaney (1980). In contrast to patterns found when Cd salts are applied, model slope C in Fig. 1 is for biosolid applied Cd, which causes decreasing slope toward a plateau with the X axis. This response is believed to result from the addition of adsorbent (Fe, Mn, Al oxides) for metals along with the metals when complex biosolids are applied to soils.

Effects of biosolids-applied Cd in the long term is the fundamental question which requires an answer. Does applied Cd remain plant available or become occluded in soils and have reduced availability? “Aging” reactions can reduce phytoavailability of applied Cd without occlusion. Several studies have shown substantial decline in Cd uptake by cereal crops after biosolids applications cease in an experiment with repeated applications (e.g., Chang et al., 1982; Bidwell and Dowdy, 1987). Such large reductions in plant Cd uptake after ceasing biosolids applications have seldom been observed for dicot crops; part of the effect is known to result from rapid biodegradation of organic matter added in the biosolids. In the studies in which cereals had much lower Cd concentrations after applications ceased, higher than N-fertilizer application rates were being applied in a research study. When applications are limited to regulated N-fertilizer supply for the crop to be grown, effects on uptake are seldom observed when high quality biosolids are utilized. Further, phytosiderophores secreted by roots of *Poaceae* species may play a role in the apparent difference between cereals and dicots in these responses.

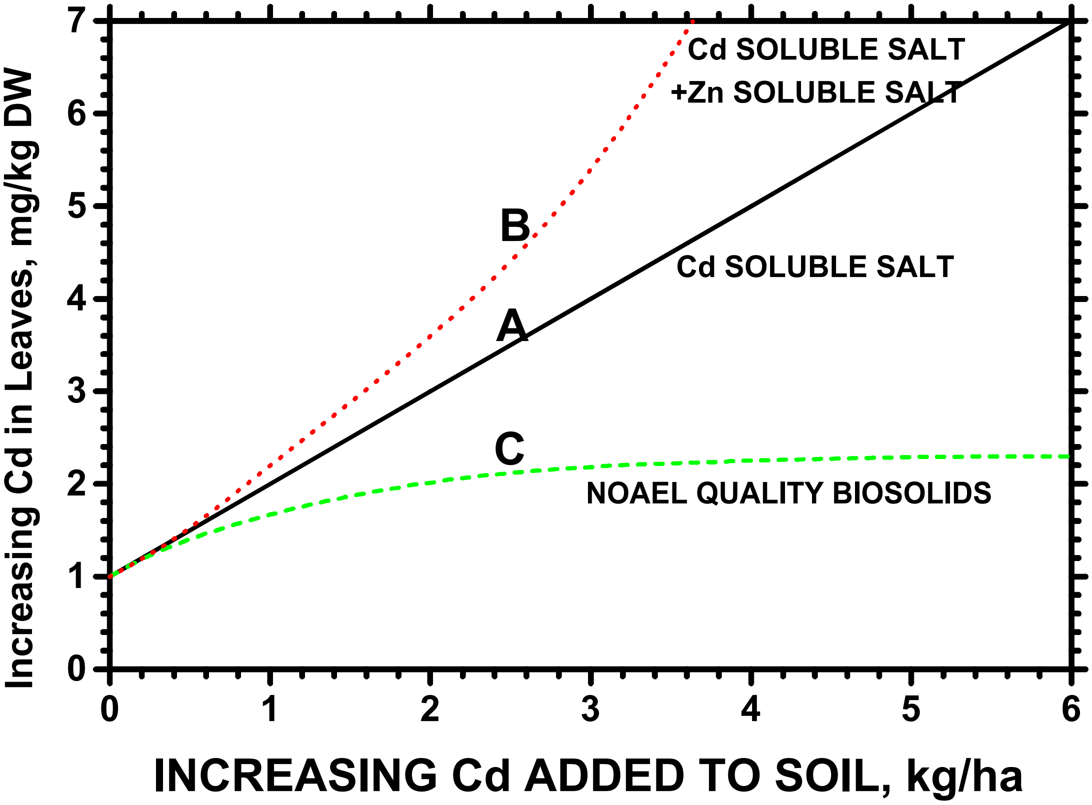

Figure 1. Hypothetical models of increasing plant Cd concentration in response to increasing total soil Cd concentration: A) From addition of a soluble Cd-salt; B) From addition of a soluble Cd-salt with 100 times more Zn as a soluble Zn-salt; and C) From addition of NOAEL quality biosolids, after organic matter stabilization to background levels.

We were able to examine the long-term effects of biosolids applications and salt-Cd additions to a soil in experiments at Beltsville. Evaluation of Cd uptake by lettuce grown on a soil amended with a Cd salt or Cd-rich biosolids in 1976 to 1979, showed that biosolids-applied Cd had low uptake slopes even when most of the organic carbon applied in the biosolid was biodegraded (Brown et al., 1998a). Even though soil pH declined over time due to application of N-fertilizers and normal acidic rainfall, uptake of Cd from the biosolids plots declined while uptake of Cd from the Cd-salt plots increased. While on plots where a high quality high Fe biosolid was applied, no increase in phytoavailability of Cd was observed.

In plots on a different soil series where high rates of high quality alkaline biosolids were applied in 1976, the high pH and low soil Mn supply allowed the alkaline biosolids to induce Mn deficiency by 1990 (Brown et al., 1997c). In this study, where the maintained calcareous pH aided sorption and occlusion of metals in the high Fe biosolids matrix, the Zn concentration in diagnostic leaves (of Mn fertilized treatments which regained crop yields) was barely adequate for plant growth. This effect, the continued control of metal phytoavailability even when added organic matter has been biodegraded, is now understood to result from the specific metal adsorption of biosolids-applied materials such as Fe and Mn oxides, and from the quasi-equilibrium reached in biosolids before application to the land. Research has repeatedly confirmed the existence of slow “aging” reactions of metals with soil surfaces and organic matter, and the increasing occlusion of metals in Fe and Mn oxides (e.g. Bruemmer et al., 1988; Corey et al., 1987). Further, study of laboratory prepared hydrous Fe oxide fails to observe the substantial increase in adsorption capacity and strength when phosphate is present along with the Fe, Zn, and Cd (Kuo, 1986). This aging response of added metals is more important for Ni and Zn than for Cd due to the selectivity of metal adsorption by soil Fe and Mn surfaces (Singh and Jeng, 1997).

Another clear evidence of biosolids-applied adsorbent was found in studies by Mahler et al. (1978) in which paired untreated and biosolids-amended soils were collected from long-term biosolids utilization farms at several locations. The researchers added 0, 5, and 10 mg Cd/kg to each soil to measure the slope of plant response to added salt-Cd as a bioassay on Cd phytoavailability, and made both soils calcareous so that simple difference in soil pH between untreated and treated soil did not confound the comparison. Fig. 2 shows the results for two locations where appreciable amounts of biosolids and metals had been applied over time. The Cd uptake slope for freshly added salt-Cd by Cd accumulator crop Swiss chard on the biosolids-amended soils was lower than for the non-amended soils. In general, when unamended and biosolids-amended soils are compared at equal pH long after biosolids were applied, their ability to limit solubility and plant uptake of salt-Cd and salt-Zn applications are reduced compared to non-amended soils. In examining this sorption relationship in biosolids-remediated contaminated soils, Siebielec and Chaney (1999) reported that high Fe added with a biosolids-compost to a Zn-phytotoxic soil maintained amorphous Fe oxides at increased levels in the soil, and reduced Cd and Zn in soil solution type extractions with 0.01 M $Sr(NO_3)_2$.

One of the most insidious errors of using metal salts is the displacement of adsorbed protons from soil cation binding sites when metals are added, which lowers the pH of the amended soil; the higher the metal application, the greater the reduction in soil pH (White et al., 1978). Thus the researcher sees greater harm at higher metal concentration, the expected result, but fails to recognize that the study was confounded by pH lowering proportional to metal salt application.

Another serious error in study of biosolids Cd risk is addition of chloride in one metal salt being tested, which can substantially increase the plant uptake of Cd due to formation of chloride complexes which increase mobility of Cd in soils, and allow a complexed form of Cd to leak into roots (McLaughlin et al., 1994). Low soil pH promotes metal solubility and phytoavailability such that pH is a almost always more important factor in metal uptake and phytotoxicity than is the amount of metals added. But high chloride can overwhelm the effect of limestone in reducing phytoavailability of soil Cd (e.g., Li et al., 1997).

Another source of error in risk assessment for soil metals is the greenhouse vs. field error illustrated by the work of deVries and Tiller (1978). These researchers compared uptake of metals by lettuce and onion grown on soil-biosolids mixtures at several rates of application, when the plants were grown 1) in large pots in a greenhouse, 2) in outdoor lysimeters in which the biosolids were incorporated 10 cm deep, and 3) in growers fields in which the biosolids were incorporated 10 cm deep. As has been long known, if plants are grown in pots of contaminated soil, phytotoxicity and uptake are higher than if grown in the same soil in the field where the metal rich soil is present only in the surface soil layer. In pots, the roots cannot escape to subsurface less contaminated soils. Further, some aspect of greenhouse culture which appears related to water use or salt concentrations in the soil solution promote metal solubility and uptake by plants. The full requirement of fertilizer nutrients are usually applied to pots before starting the plants, promoting high ionic strength and hence solubility of soil metals, worse with smaller than larger pots. Other errors result from the temperature of soil in pots in a greenhouse compared to soils in the field, and water transpiration in greenhouse compared to field.

In a similar way, when the bioavailability of metals in ingested soil is measured by soil feeding studies, Pb absorption by rats declined when Pb was mixed with soil (Chaney et al., 1984; Chaney and Ryan, 1994). Similar effects of soil sorption of metals reducing bioavailability to mammals has been shown for As (Freeman et al., 1995) and Cd (Schilderman et al., 1997), and is evident in biosolids feeding tests (e.g., Decker et al., 1980). Considering the role of adsorption at the neutral pH of the small intestine where most microelement cations are absorbed by animals, it should not be a surprise that adsorption of metals on dietary soil can reduce Pb and other element uptake by animals in a manner somewhat like the reduction in absorption by plants (see Freeman et al., 1992; Chaney and Ryan, 1994).

Looking at mine wastes and smelter contamination processes in relation to these selective soil adsorption processes, what are the implications for risk assessment and soil remediation? If high Fe in biosolids can sorb metals persistently, biosolids metals can have low phytoavailability and bioavailability compared to metal salts. But smelter-emission contaminated soils will have received only the more volatile elements emitted by a smelter stack. Even here, Zn which accompanies emitted Cd can provide a persistent reduction in potential plant uptake of Cd by competition at root uptake sites, and also reduce translocation to plant shoots and storage tissues (e.g., McKenna et al., 1992b; Chaney et al., 1999a). Mine wastes may have very high Fe levels from pyrite in the ore, so Fe would accompany the metals. But if ore sulfides are allowed to oxidize, soil pH is lowered severely which greatly increases metal toxicity risk. We have measured pH of surface soil in farmer's fields which had become covered by alluvial deposits of mine waste where sulfide oxidation lowered pH to < 3. In such a case (often found in Zn-Pb ores from the Rocky Mountain area such as Butte, MT and Leadville, CO), the extreme acidity is the key feature of the contaminated site. Until this extreme acidity is neutralized, solubility of Zn will prevent plant survival.

Another important principle of soil metal risk assessment is the "Soil-Plant Barrier" to element transfer to cause food-chain risk to animals. Chaney (1980; 1983) summarized three major processes which limit risks from most elements in soils to animals through the food-chain Pathway. First, precipitation or adsorption of metals by soil particles, or in the fibrous root system hinders uptake of most elements (Pb, Cr, Sn, Ti, Fe, Hg, Ag, F, etc.). Second, phytotoxicity of the common phytotoxic elements (Zn, Cu, Ni, Mn, etc.) occurs at concentration of these elements in the plant shoots which do not comprise risk to livestock or humans chronically exposed to the metals. The third process involves interactions between elements which hinder uptake, translocation or bioavailability of soil metals. For example, Zn is normally present at 50-200 times higher concentration than Cd in Zn-Pb ores. And Zn metal products are treated to remove most Cd for separate marketing and to protect the quality of the Zn in certain industrial applications. When galvanized metal corrodes, Zn is very high and Cd low such that plant Cd is hardly increased when Zn reaches severely phytotoxic concentrations (Jones, 1983). Because Zn and Cd are commonly absorbed and translocated at about the ratio found in the soil the plant is growing on, and because Zn phytotoxicity occurs at about 400-600 mg Zn/kg dry plant shoots, co-contaminating Zn normally limits shoot Cd to less than 5-10 mg Cd/kg dry weight. Coupled with Zn inhibition of Cd absorption by animals, soil Cd risk is alleviated (see below) because Zn phytotoxicity alerts the gardener to the problem.

The Soil-Plant Barrier fails to provide complete protection for only a few elements, Se and Mo which are widely known to poison ruminant livestock, and Cd under circumstances which separate Cd from Zn (Table 2). The Soil-Plant Barrier for Co could also theoretically fail because ruminant livestock cannot tolerate the concentrations of Co (injury to ruminant livestock begins at approximately 10 mg Co/kg dry forage) which can be reached in plants when Co is phytotoxic (25 mg/kg or higher in plant shoots). Cd risks to humans is discussed below. Se is not only a risk to livestock, but can harm humans who consume only foods locally grown on contaminated soils (Yang et al., 1984).

Table 2. Maximum tolerable levels of dietary minerals for domestic livestock in comparison with levels in forages.

Element	"Soil-Plant Barrier"	Level in Plant Foliage[A]		Maximum Levels Chronically Tolerated[B]			
		Normal	Phytotoxic	Cattle	Sheep	Swine	Chicken
		--mg/kg dry foliage--		---------------mg/kg dry diet---------------			
As, inorg.	yes	0.0I-I	3-I0	50.	50.	50.	50.
B	yes	7-75	75	150.	(150.)	(150.)	(150.)
Cd[C]	Fails	0.I-I	5-700	0.5	0.5	0.5	0.5
Cr^{3+}	yes	0.I-I	20	(3000.)	(3000.)	(3000.)	3000.
Co	Fail?	0.0I-0.3	25-100	10.	10.	10.	10.
Cu	yes	3-20	25-40	100.	25.	250.	300.
F	yes?	1-5	-	40.	60.	150.	200.
Fe	yes	30-300	-	1000.	500.	3000.	1000.
Mn	?	15-150	400-2000	1000.	1000.	400.	2000.
Mo	Fails	0.1-3.0	100	10.	10.	20.	100.
Ni	yes	0.1-5	50-100	50.	(50.)	100.)	(300.)
Pb[C]	yes	2-5	-	30.	30.	30.	30.
Se	Fails	0.I-2	100	(2.)	(2.)	2.	2.
V	yes?	0.I-I	10	50.	50.	(10.)	10.
Zn	yes	15-150	500-1500	500.	300.	1000.	1000.

[A] Based on literature summarized in Chaney (1983).

[B] Based on NRC (1980). Continuous long-term feeding of minerals at the maximum tolerable levels may cause adverse effects. Levels in parentheses were estimated (by NRC) by extrapolating between animal species.

[C] Maximum levels tolerated were based on Cd or Pb in liver, kidney, and bone in foods for humans rather than simple tolerance by the animals.

Another case where livestock and wildlife can be harmed by metals is the case in which high emissions of Zn or other elements from a smelter cause extensive contamination on the surface of plants by deposition from the aerosol source. In this case, plants can reach much higher concentrations without phytotoxicity than possible by root uptake if the metals were in the soil. For elements which have low uptake slopes, or for which phytotoxicity protects the food-chain (e.g. Zn, Cu, Pb, As, F, Fe), deposition can cause plant metals to reach levels which can poison sensitive livestock (e.g., Chaney et al., 1988). Zn on forages has killed young horses (foals) at many Zn smelter locations because apparently healthy plants can contain over 1000 mg Zn/kg, but if the Zn had been absorbed by roots, visible signs of Zn phytotoxicity would have occurred by 500 mg Zn/kg shoots. Different livestock are sensitive to different metals, for example ruminants are sensitive to induced Cu deficiency and Pb, As and F toxicity, while young horses are especially sensitive to excessive ingested Zn.

Another aspect of soil metal risk has received much attention in recent years, the potential for soil metals to harm soil organisms. However, our experience has indicated that metal sensitive plants such as lettuce and white clover are visibly harmed at soil metal concentrations below those required to harm soil microbes or earthworms, etc. (Chaney, 1993; Ibekwe et al., 1998). Further, the errors from adding metal salts are potentially much more important for soil organisms than for plants because the organisms are present at the moment when soluble metals are mixed with the soil. And many ecotoxicology studies use artificial soils with addition of metal salts, and cause much more severe toxicity to earthworms and soil microbes than found with biosolids or stack emissions cause soil contamination with Pb, Zn, and Cd (e.g., Spurgeon and Hopkins, 1996). Concerns about harm to the rhizobium for white clover from biosolids-applied Zn have been clarified by comparisons of the toxicity of Zn and Cd to the rhizobium, compared to toxicity to the plants (Ibekwe et al., 1996; 1997a; 1997b; 1998; Angle and Chaney, 1995; Angle et al., 1993). If nodules are formed before testing metal toxicity, Zn and Cd had no effect on N fixation before yield of the plant had been sharply reduced by metal phytotoxicity. And testing of microbial metal tolerance with controlled chemical activity of Zn and Cd showed that the microbes were much more tolerant of these elements than were plants. The most sensitive step appears to be the rhizobium infection of root hair process rather than survival of the microbes in soil. Even arguments about microbial genetic diversity in relation to soil metal enrichment appear to result from study of highly contaminated biosolids, or unusual soils, since Ibekwe et al. (1997b) found that low soil pH reduced survival of white clover rhizobium on both control and metal rich soils, and the rhizobium survived with good diversity when soil pH was maintained at levels needed to produce legumes. We have observed nodulated white and red clover growing on soils with very high levels of Zn (> 3000) if pH is maintained and phosphate is supplied at levels required for legume production (see below discussion of ecosystem restoration)

Soil Cd Risk Assessment. Although great concern has been expressed about Cd poisoning of humans from smelter emissions and mine wastes, research has now clarified the situations where such Cd food-chain poisoning may occur. Cd is important regarding chronic toxicity -- acute toxicity is prevented by regulations to limit chronic toxicity of Cd emissions and discharges. In mammals, Cd accumulates over one’s lifetime in the proximal tubules of the kidney cortex; if a toxic concentration is reached, a renal proximal tubular dysfunction will occur (this is not “kidney failure” as this term is commonly used). Ordinarily, kidney Cd accumulates in humans until about age 50, and then starts to decline over time. If one has ingested insufficient bioavailable Cd over that 50 years, no disease results. Smoking cigarettes commonly doubles kidney cortex Cd for persons who smoke one pack per day, compared to non-smokers, because Cd enters the mainstream smoke and is well absorbed in the lung (e.g., Elinder et al., 1976). Average non-smokers today have only 10-15 mg Cd/kg fresh weight of kidney cortex, far lower than the 200 mg/kg fresh weight required for the tubular dysfunction of sensitive individuals in the population.

Because soil Cd (from dispersed mine and smelter wastes) caused human disease in Japan and China (Kobayashi, 1978; Tsuchiya et al., 1978; Cai et al., 1990), and aerosol Cd in the workplace has harmed industrial workers at many factories which used pure Cd salts such as Cd-Ni battery manufacturing, much research has been conducted to improve our understanding of Cd risk to humans. In the case of soil Cd, agronomy is very important is understanding the risk to humans, not just toxicology and medicine (Chaney et al., 1999a). Although soil Cd caused human Cd disease in subsistence rice farmers, much higher soil Cd had no adverse effects on persons exposed to Zn+Cd rich soil and dust, garden foods or western grains (Shipham, UK -- Strehlow and Barltrop, 1988; Stolberg, Germany -- Ewers et al., 1993; Palmerton, PA, USA -- Sarasua et al., 1995). Because of the chemistry of flooded soils, ZnS is formed and persists for some time after a flooded rice soil is drained, but CdS is quickly transformed to more phytoavailable forms, and pH drops making the soil Cd more phytoavailable. Rice growers drain their fields at the start of flowering to optimize yield of grain. Cd absorbed by rice during grain filling is readily translocated to grain while Zn is not increased in grain even though the soil had 100 times more Zn than Cd, similar to western soil contamination cases (e.g., Takijima and Katsumi, 1973). Further, polished rice grain contains insufficient Fe, Zn and Ca to supply the amounts needed for humans (Chaney et al., 1999a).

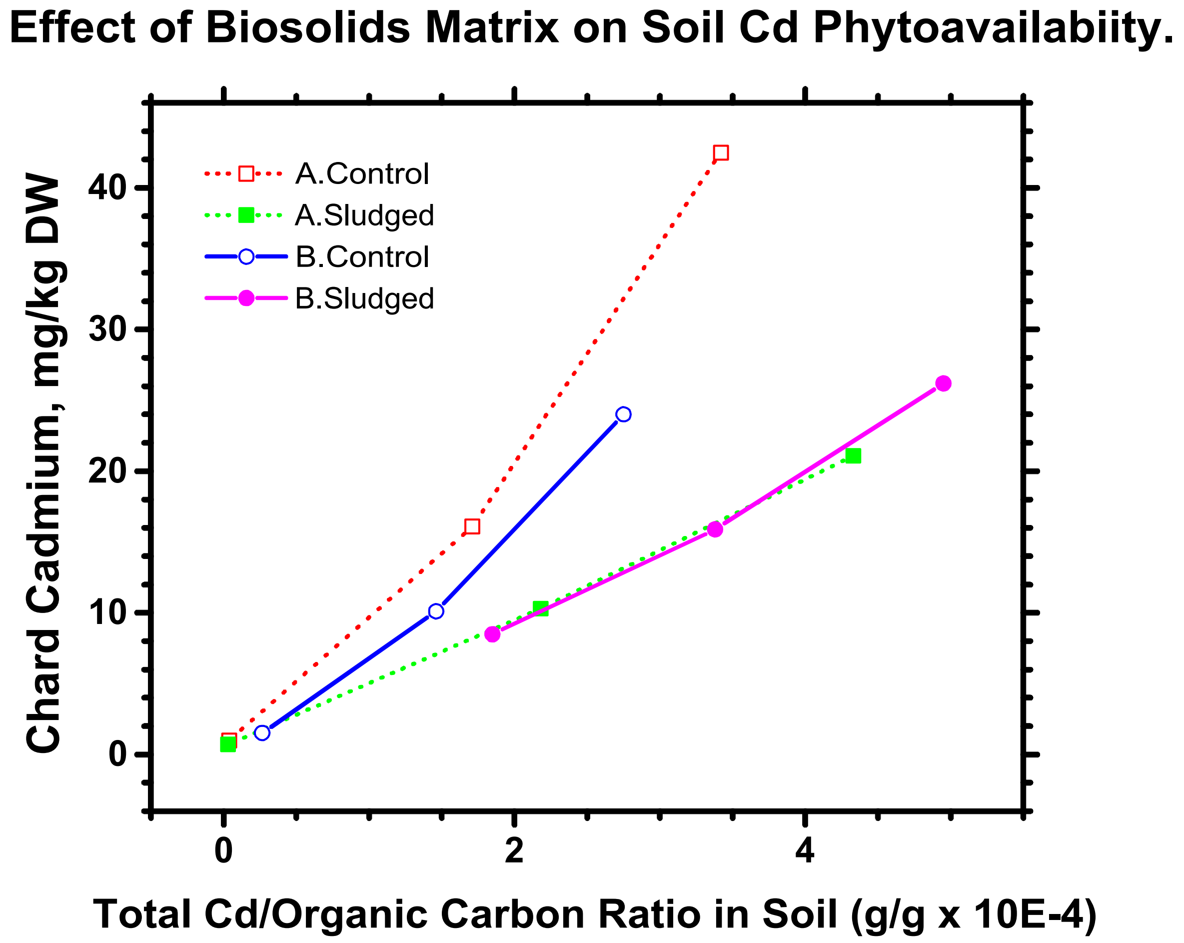
Effect of Biosolids Matrix on Soil Cd Phytoavailabiity.

Figure 2. Linear response of chard Cd concentration to added salt-Cd on long term biosolids amended or non-amended soils. Carbon levels in the biosolid-amended soils are no longer above levels in the non-amended soils, and soil pH levels were made equivalent by making all soils calcareous (based on data from Mahler et al., 1987). Soil A was Morely, and B was Wea.

Subsistence rice farm families are commonly Fe and Zn deficient if they do not obtain adequate Fe and Zn from other dietary sources. And deficiency in Fe, Zn, and Ca promote Cd absorption in the human intestine (Fox, 1988; Fox et al., 1984), promoting risk from Cd in rice grain. One of the first experimental findings which illustrated that rice Cd risk was qualitatively different from other foods was a study of New Zealand oyster fisherpersons who consumed up to 500 μg Cd/day in high Cd oysters, but had no evidence of renal tubular dysfunction from these high levels of Cd, as high as the Japanese rice consumers who had a high incidence of renal tubular dysfunction (Sharma et al. 1983) Further examination of these oyster consumers revealed that their kidney Cd was hardly increased by oyster-Cd, but responded strongly to smoking (Sharma et al., 1983; McKenzie-Parnell and Eynon, 1987; McKenzie-Parnell et al., 1988). Many other errors have resulted when toxicologists tried to predict Cd risk on the basis of injected Cd, or adding Cd salts to purified diets. And in interpretation of diagnostic information of secretion on low molecular weight proteins in urine by normal humans compared to persons which suffer frank tubular disease from dietary Cd (see Chaney et al., 1999a).

Wheat and vegetables have been found to have very different soil-plant-animal relationships for Cd and Zn compared to rice. These crops are grown in aerobic soils where both Cd and Zn are plant available during growth, and Zn inhibits both uptake of Cd from soil, and transport of root Cd to edible tissues of the plant. And Zn is translocated to all plant tissues where Cd accumulates so it is simultaneously present with Cd in any foods and in the intestine (Table 3) (see also McKenna et al., 1992a). Although corn is also a poor source of bioavailable Fe, when western crops are grown in soils enriched in both Zn and Cd, corn grain has increased Zn levels somewhat proportional to the increased Cd, and the Zn in the such corn grain satisfies the human Zn requirement and inhibits absorption of Cd in the intestine much more effectively than found for rice grown on such contaminated soils.

Table 3. Bioavailability of Cd in biosolids-fertilized Swiss chard fed at 28% of diet to Guinea pigs for 80 days (Chaney et al., 1978b).

Treatment	Biosolid Rate	Soil Cd	Soil pH	Cd in Chard	Zn in Chard	Cd in Kidney	Cd in Liver
	t/ha	μg/g		--------- μg/g dry weight ----------			
Control	0	0.04	6.0	0.5	70	14.9 a	3.1 a[‡]
High Metal Biosolids	56	0.32	5.7	1.5	950	14.5 a	2.7 a
Blue Plains Digested	112	0.94	5.5	2.7	580	14.5 a	2.7 a
Blue Plains Compost	224	0.89	6.6	1.4	257	15.8 a	3.6 a

[‡] Means followed by different letters are significantly different at $P < 0.05$).

It is difficult to overstate the importance of Zn in a crop in inhibiting animal absorption of Cd from that crop. Table 3 shows the accumulation of Cd and Zn by Swiss chard (*Beta vulgaris* L. var. *cicla*) grown on soil treated with normal chemical fertilizers vs. different biosolids products used as fertilizer. For one of the biosolids, chard leaf Cd was increased by 5-fold in the strongly acidic soil, but Zn had a corresponding increase. Guinea pigs were fed the chard at a high fraction of diet for a long period, yet there was no significant increase in Cd in kidney or liver. In this situation, although the soil contains significantly increased levels of Cd, it has zero bioavailability to the guinea pigs.

When livestock are fed crops grown on Zn+Cd contaminated soils, Cd is very poorly absorbed by cows, sheep, pigs and chickens. The usual 100 Zn:1 Cd ratio prevents accumulation of Cd in animal tissues used for food, and strongly limits accumulation in kidney and liver. For example, in the feeding study of Kienholz et al. (1979) in which 3 or 10% biosolids were mixed with cattle diets and fed for 90 days, the fraction of ingested Cd which remained in the carcass including liver and kidney was < 0.1%. Thus animal agriculture usually prevents Cd risk in humans who consume "homegrown" meat. When high quality biosolids with low Cd:Zn ratio are used on land, no increase was found in kidney or liver Cd (Decker et al., 1980). When biosolids with high Cd levels and high Cd:Zn ratios were fed to cattle, kidney and liver Cd levels were significantly increased (e.g., Johnson et al., 1981). A rare exception to this rule that Zn prevents food-chain transfer of Cd is found in Australia and New Zealand where "cape weed" selectively accumulates Cd relative to Zn on pasture soils. The soils had become somewhat Cd enriched due to use of high Cd (and high Cd:Zn ratio) phosphate-fertilizers. Capeweed could thus increase Cd transfer to sheep liver and kidney, which prevents sale of these organs in Europe for animals over 2 years of age (it is likely that even this Cd does not comprise risk because of Zn supplied in liver and kidney along with Cd; market rejection of such liver and kidney is based on Cd concentration alone, ignoring interactions which affect bioavailability of food Cd).

Soil Lead Risk From Ingested Soils. Study of soil contamination by automotive and industrial Pb emissions clearly showed that aerosol Pb accumulated in plant leaves when air Pb was high in previous years. But high soil Pb concentrations increase Pb levels in most crops weakly. As other sources of Pb to soils were considered, an important role of house paint Pb in contaminating soils near painted walls became evident (see Chaney et al., 1984; Chaney and Ryan, 1994). We have measured up to 5% Pb in houseside soil in a remote rural home. Because of these multiple soil Pb contamination sources, a number of scientists studied uptake of Pb by garden crops which a family might grow in a home vegetable garden. A few crop types do respond to increasing soil Pb with appreciable uptake, particularly the low growing leafy vegetables such as lettuce. Potatoes and other root vegetables which can carry soil particles on their "skins" can bring higher Pb from contaminated gardens.

However, as Pb risk to children was increasingly recognized, and found to occur at lower blood Pb concentrations than previously considered toxic (Centers for Disease Control, 1985), the ingestion of soil and housedust by young children became recognized as the predominant route of soil Pb risk to children rather than plant uptake from contaminated soils. Pb risk is complex, and children become Pb poisoned from drinking water pipes with acidic water, from Pb-rich glazes on pottery, from ingestion of paint chips, from Pb in the solder which closed food cans for many decades, etc. Each of these sources can cause "undue Pb absorption" in 1-7 year-old-children such that over 5% of the population exceeds 10 μg Pb/dL whole blood. Above this level, sensitive children begin to show evidence of some Pb health effects on hearing and balance, and as Pb rises more and more above this level, populations of children show lower IQ levels (ATSDR, 1988). If housedust is enriched to high levels of Pb from paint or smelter sources, high blood Pb is commonly found, while mine wastes which cause equivalent increase in Pb ingestion cause little increase in blood Pb (e.g., Steele et al., 1990). Thus the source of Pb contamination of soil may influence the risk of this Pb. Many researchers believe this results because different sources of Pb have either different solubility or bioavailability, or physical mobility to children. One source of confusion about risk from soil Pb results from the use of fasted animals in study of Pb risk. When Pb-acetate is administered to fasted animals, it remains essentially 100% soluble and bioavailable upon ingestion. But when food in present in the stomach and intestine, human absorb as low as 1% of diet Pb compared to 60-80% absorbed when human adults are tested in the fasted condition (e.g, James et al., 1987). Soil acts somewhat like food by buffering pH and binding Pb. Thus the risk from soil Pb may be qualitatively different from Pb in paint dust or smelter emissions where little adsorbent accompanies the Pb (see Chaney and Ryan, 1994).

High soil Pb is found at many locations in most countries. As noted above, housepaint is a very common source of high soil Pb. And leaded gasoline caused high soil Pb near heavily trafficked roads. Pb smelters, including secondary Pb smelters such as battery recycling factories, cause extensive dispersal of highly bioavailable PbO in communities if housing is near to smelter stacks. Mine wastes have often increased soil Pb, but have lower bioavailability as shown in many tests.

The first approach to protection of children from excessive soil Pb was soil removal and replacement by clean soil. For urban homes, soil removal and replacement is quite expensive. And studies have shown that in most cases soil Pb concentration is much higher near the foundation of domiciles. Paint residues fall onto the soil. And automotive and stack emission Pb in particulates are collected on the surfaces of houses by surface tension, and then washed onto the soil. Over time these Pb sources are altered to forms controlled by soil chemistry, adsorbed Pb on Fe oxides, or pyromorphite (e.g., Cotter-Howells and Thornton, 1991; Zhang, Ryan and Yang, 1998).

An important aspect of soil Pb risk was identified during a large US-EPA study evaluating removal and replacement of Pb contaminated soil around houses. In these studies, part of the children were assigned to soil replacement immediately after characterization of population blood Pb, while other children were assigned to have their soil replacement one year later, after characterization of blood Pb in the two populations one year after the initial measurements (about 9-10 months after soil replacement). In the Boston, MA, study, the soils replaced averaged about

1950 mg Pb/kg, but blood Pb was only slightly (but significantly) reduced due to the independent effect of soil removal and replacement (Weitzman et al., 1993). Many other studies of children exposed to soil and housepaint Pb have affirmed that soil Pb has lower risk than paint Pb, which we believe should at least partially be attributed to the adsorption of Pb by soil particles in the digestive tract. Pb in house paint is the principle Pb risk to children today, not the Pb in contaminated soils.

Guidance for Beneficial Utilization of Biosolids and Biosolids Composts. With the development of the 40 CFR 503 Rule for land application of biosolids, a risk-based estimation of allowable cumulative biosolids element applications was provided (US-EPA, 1993; Chaney and Ryan, 1993; Ryan and Chaney, 1993). This rule included the “Alternative Pollutant Limit” (APL) which allowed marketing of higher quality products. This reflects the increasing evidence that regulation of biosolids quality would provide more protection than regulation only of the cumulative application of elements in biosolids. This pattern results from the adsorption or precipitation of these elements by the mineral constituents of the biosolid, as discussed above.

Table 4 shows the limits of the 503 Rule, the USDA “No Observed Adverse Effect Level” (NOAEL) biosolids limits, and concentrations we consider “attainable” by good pretreatment of industrial wastes, and reduction of corrosivity of drinking water. Because these lower levels of trace elements can commonly be attained by good practices, some want to require that all biosolids and composts be regulated at the lower “attainable” levels. We find this argument un-persuasive. The APL and cumulative metal application limits of the 503 Rule are protective under the very conservative risk assessment model, 1000 t/ha, for highly exposed individual with lifetime exposure at this cumulative application rate. On the other hand, we feel it appropriate to advise biosolids generators and composters that lower concentrations of these elements can be readily attained if they work at it. Higher quality products will create higher demand in the market, and bring in higher economic return for the marketed products. We view this as best practice, but not needed to achieve the protections expected by citizens which are the basis of the 503 Rule.

In the case of “yard debris” or “green wastes” composts, lower element levels can be attained than found in biosolids and biosolids composts. And composts prepared from pre-separated Municipal Solid Waste (MSW) can contain lower concentrations than found in biosolids composts (Epstein, et al., 1992). Pre-composting separation of glass, metal and plastic from other MSW constituents minimizes concentrations of elements in the compost products, but there is little evidence that this difference is so great that only pre-separation should be allowed for MSW composting. Pre-separation of MSW compostable fraction is most important for removal of glass, plastic, and metal particles which reduce acceptability to consumers.

Table 4. Limits of the 40 CFR 503 biosolids Regulation (EPA, 1993) *vs* USDA recommended biosolid quality for long-term use on farmland, and attainable quality biosolids and composts. Deletion of Cr limits from the 503 Rule is discussed by Chaney, Ryan and Brown (1997).

Element	Ceiling 99th	Cumulative =APL, mg/kg	NOAEL (1993)	Percentile of NOAEL(1993)	Attainable Quality
	mg/kg	kg/ha	mg/kg		mg/kg
As	75	41	54	98	<25
Cd	85	39	21	91	<5-10
Cd/Zn	-	-	1.5	87	<1.0
Pb	840	300	300	90	<100
Hg	57	17	17	93	<5
Mo	75	35	54	98	<50
Se	100	36	28	98	<15
Cr	3000	1300	-	-	-
Cu	4300	1500	1500	89	<500-750
Ni	420	420	290	98	<100
Zn	7500	2800	2800	91	<1500-2000
PCBs	-	-	8.1	99	<0.5

Further, without inclusion of biosolids or manures in yard debris or MSW-composts, they are poor nutrient sources, and have little value as fertilizers or in remediation of contaminated soils. Although some individuals may believe it important to impose tight regulations on contaminants in these different kinds of composts, to require each to be as clean as possible, risk assessment should continue to be the basis of regulations (as recommended by Hornick et al., 1983). Labeling of composition, including nutrient value and trace element levels in relation to the US-EPA limits, will provide consumers the basis for choice of soil amendments. Composting or heat drying can provide the pathogen kill needed for biosolids and livestock manure, and yard debris composts, to be safely used on lawns and gardens where humans will have exposure. Perspective on risk of elements in these many compost type consumer products is needed when considering development of restrictive regulations. If the Cd and Pb in high quality biosolids composts and MSW compost products cause no increase in human or environmental risk, similar to other commercial organic amendments including yard debris composts, there is no legitimate basis for claiming such products have different Cd or Pb risk. The high Fe and phosphate of high quality biosolids products can provide a solution for soil Pb environmental risks as noted above, not add to Pb risk of children.

***In situ* remediation or inactivation of soil Pb.** An alternative to soil replacement to reduce soil Pb risk to children has been developed, the use of soil amendments to precipitate soil Pb, or otherwise reduce the bioavailability of soil Pb based on animal feeding tests. These strategies are complementary, in that high phosphate can hasten formation of chloro-pyromorphite $[Pb_5(PO_4)_3Cl]$ an extremely insoluble Pb mineral, and mixtures of Fe and phosphate can increase the Pb-adsorption capacity of a soil, to reduce bioavailability in the intestine by stronger binding to ingested soil particles. Some very elegant work by Ma, Ryan, Logan, and cooperators (Ma et al., 1993; Zhang et al., 1997; 1998; 1999a; 1999b) showed that pyromorphite can be formed from all chemical species of Pb found in soils, and that different Pb chemical species react at different rates. Both Pb and phosphate have limited solubility at normal soil pH, which tends to slow the reaction. But when phosphate amended soil enters the acidic stomach, the pH condition favors rapid formation of pyromorphite.

The use of biosolids to reduce soil Pb bioavailability was developed based on studies of Pb absorption by livestock which were exposed to, or fed, biosolids with different levels of Pb (e.g., Decker et al., 1980), and on the reduction in Pb uptake by lettuce when soils were amended with composted biosolids (Sterrett et al., 1996). These feeding studies were conducted to evaluate risks to livestock and wildlife of Pb in biosolids. As summarized by Chaney and Ryan (1994), until biosolids exceed 300 mg Pb/kg, there was no net retention of Pb by test animals. For some biosolids with stronger Pb adsorption ability, even higher Pb concentration in the biosolid, fed at 3-10% of dry diet, had no effect on blood or bone Pb. Both mechanisms could be at play in this case because biosolids are rich in P, and when Fe is added during wastewater treatment to improved phosphate removal, the biosolid has even higher P levels along with high Fe (up to 10% compared to typical levels of 1-2% Fe in dry digested biosolids in the absence of Fe additions during sewage processing). In a comparison of different biosolids processing technologies effect on the ability of the biosolids products to inactivate soil Pb, Brown et al. (1997b) found that all products from one treatment works could reduce Pb bioavailability, but those higher in Fe and phosphate were most effective. Any products to be used where children might be exposed to the soil must be treated to kill pathogens; and high rates of application are desired to achieve a high reduction in bioavailability with a single treatment. So composted biosolids rich in Fe are favored for remediation of soil Pb around houses. Such composted materials are also very effective in alleviating soil compaction, and Zn phytotoxicity in acidic urban soils, and improve soil physical properties and soil fertility. Thus lawn grasses usually grow very well on compost amended urban soils, providing a physical barrier to soil ingestion by children.

Because application of composted biosolids rich in Fe and P substantially reduced Pb uptake by lettuce and other plants (Sterrett et al., 1996), and the Pb in biosolids had very low bioavailability when ingested by beef cattle (Decker et al., 1980), we tested the incorporation of different biosolids products to reduce the bioavailability of soil Pb to mammals (see Chaney and Ryan, 1994; Brown et al., 1997b). To date our cooperators have conducted 3 separate studies in which soil Pb bioavailability was reduced 50% or more (within 30 days of mixing) by incorporation of 10% biosolids in a high Pb urban soil, or smelter contaminated soil.

Remediation and Ecosystem Restoration using Tailor-Made Biosolids Mixtures and Composts. With the finding that adding high Fe and phosphate to soils reduced Pb uptake by crops, and reduced soil Pb bioavailability to animals which ingested the soil, we considered using such biosolids plus other byproducts or “wastes” to achieve a comprehensive remediation of the usually barren soils surrounding long term Zn or Pb smelters. Such soils often contain 1% Zn, 100 mg Cd/kg, and 100-30,000 mg Pb/kg (e.g., Chaney et al., 1988; Brown et al., 1998). Smelters often emitted SO_2 in large amounts, which caused local soil acidification near the smelter as sulfuric acid was formed. In the case of mine wastes, if the mine tailings contain high levels of pyrite (FeS), when the tailings become aerobic the sulfide was oxidized generating sulfuric acid. Soil pH could be lowered below 2, causing severe phytotoxicity from many metals (Zn, Cd, Al, Mn). And when tailings or smelter emissions are rich in Pb, part of the soil Pb is converted to pyromorphite, greatly reducing the plant availability of native soil phosphate. Even if these soils are limed to pH 5.5-6, if high Zn levels are present the soil can remain severely Zn-phytotoxic. Low P availability due to the presence of Pb interacts adversely with high soil Zn because high Zn shortens roots thereby reducing P uptake ability of roots. The combination of soil acidity, high soil Zn, high soil Pb and low soil phosphate make a very difficult soil condition to remediate. One can revegetate such soils only if one remediates the P deficiency, the Zn phytotoxicity, and the potential for acid generation over time.

Considering this combination, we initially tested use of high Fe, calcareous, biosolids compost from Washington, DC, to remediate the severely Zn phytotoxic soil at Palmerton, PA (Li and Chaney, 1997; Li et al., 2000). Accumulated soil Zn made survival of Kentucky bluegrass difficult, and many homes were surrounded by barren soils; homeowners even gave up on trying to grow grasses and covered their soil with mulch. In tests we conducted, the application of limestone to reach pH 6.5 or higher, along with normal application of N, P, and K fertilizers to establish lawns, allowed grasses to germinate and start to grow. But when the plants were stressed by cold, heat, or drought, the lawn grasses died. We found that the highly Zn-resistant ‘Merlin’ red fescue performed well with this intermediate pH and phosphate levels, but tall fescue and bluegrass simply died on the control fertilized soil, or the limestone plus fertilizer treatment (Li et al., 2000).

With the application of 224 t/ha of composted high Fe biosolids which contained 30% limestone equivalent, the soil immediately became calcareous (and had lots of pH buffering capacity), and high phosphate status (Li et al., 2000). Further investigation of these soils by Siebielec and Chaney (1999) revealed that the higher Fe in the biosolids-compost-amended soil increased metal adsorption, lowering soil solution Zn and Cd concentrations better than limestone addition alone. This same compost was highly effective in reducing soil Pb bioavailability to rats in several feeding studies (see Chaney and Ryan, 1994; Brown et al., 1997b).

Not all biosolids contain high limestone equivalent, or high Fe levels. But there are many industrial, urban, and agricultural byproducts which can provide the Fe and limestone equivalent to make a remediation product. Composts have a special value for application in cities where children would be exposed to the amended soil because composting kills pathogens in biosolids. Composts are also preferred when contaminated stream side soils are to be remediated. Chaney, Walker, Brown, et al. noted that one could combine different manures and byproducts to make a mixture which aided remediation of metal contaminated soils. The mixture needs to contain limestone equivalent, phosphate, adsorbent, and slow release organic N, as well as microbes in order to achieve effective remediation of soil Pb, Zn, and Cd. This approach has been called "Tailor-Made Remediation Biosolids Mixtures and Composts" to stress that if one searches one's region, one can find different wastes or byproducts which have little value for commercial use or are disposed in landfills at substantial cost, but which when combined and applied to metal contaminated soils, can inactivate soil Pb, prevent Zn phytotoxicity, improve soil fertility and physical properties, and supply energy, nutrients and inoculum for soil microbial populations. Limestone equivalent can come from wood ash, from lime wastes, from sugar beet waste lime, from fly ash and other alkaline byproducts if the levels of other contaminants in the byproduct would not prevent use of these materials on cropland. These materials usually contain levels of Zn, Cd, As, and some other elements higher than found in background soils, but not at levels which would cause risk through plant uptake on home gardens, or through soil ingestion.

Using such mixtures has been shown to provide a "one-shot" persistent remediation and revegetation of metal contaminated sites such as Palmerton, PA (Li and Chaney, 1998), Katowice, Poland (Stuczynski et al., 1997; Daniels et al., 1998), and Kellogg, ID (Brown et al., 1999), where mine wastes and smelter emissions killed ecosystems. Plants growing on the remediated sites contain levels of Zn and other elements which are safe for lifetime consumption by livestock or wildlife. Further, in the work to establish a demonstration experiment at Kellogg, ID, Henry, Brown et al. (1998b) found that certain biosolids spreading equipment was highly effective in applying a mixture of biosolids, wood ash, and logyard debris to strongly sloping barren soils on Bunker Hill. Non-composted mixtures are considered appropriate for such remediation because composting provides a value-added product which needs to cost more than a simple mixture of biosolids plus byproducts. Compost would be preferred to control N-mineralization so that higher cumulative rates of application can be made to improve the likelihood of full remediation of the contaminated soil, although including cellulosic byproducts in the Tailor-Made mixture can limit soil nitrate leaching potential.

Individuals need to show considerable creativity in searching for byproducts from many sources, near to the site where remediation would be conducted, to find a cost-effective combination of remediation agents and fertilizers, control the rate of N mineralization to protect groundwater and preserve the remediation, and support the growth of plants adapted to the region. When revegetation is desired "out of normal season" for planting a site, one can use large-seeded cereals, and then overseed with more expensive but more tender native grasses, legumes, etc.

Another aspect of the combination of limestone equivalent with biodegradable organic matter in the Tailor-Made Remediation Mixture is the formation of chemical forms of Ca and Mg which move down the soil profile and neutralize subsurface acidity. This effect was reported by several researchers, and confirmed for four kinds of biosolids or composts in a long term field study by Brown et al. (1997a). The less well aerobically stabilized the organic matter of the product, the more extensive was the leaching of limestone equivalent down the soil profile. In the absence of this benefit of biodegrading organic matter, surface-applied limestone slowly neutralizes soil depth by diffusion of Ca and Mg between soil particles and replacement by dissolution of the limestone material. It is possible that the high surface area of amorphous byproduct limestone materials aids in the reaction rate as well.

Although the focus of this paper is on Pb-Zn-Cd mining and smelting contamination of soils and remediation of soil metals risks, many of the same principles apply to As contamination (Chappell et al., 1997). Risk assessment for soil As must consider bioavailability, chemical speciation, etc., and high Fe additions may reduce risks of soil As.

Web site with photographs and data from studies of the use of Tailor-Made Biosolids Mixtures to remediate Zn-Pb-Cd contaminated soils.
Readers may find more details about the soil remediation research described above at a web site prepared by cooperators C.L. Henry and S.L. Brown at the University of Washington; the files contain color photographs and details of several studies in which Tailor-Made remediation methods were used to remediate severely phytotoxic soils at smelter and mine waste contaminated sites in the western US. The addresses for these sites are: http://faculty.washington.edu/clh/bunker.html (Bunker Hill, Kellogg, ID); http://faculty.washington.edu/clh/leadville.html (adjacent to Arkansas River downstream of Leadville, CO); and http://faculty.washington.edu/clh/wet.html (Page swamp wetland site near Kellogg, ID).

Phytoextraction of Soil Metals. Phytoextraction uses plants to remove metals from soils. Several approaches have been studied. We have been working to develop the method which uses natural metal hyperaccumulator plant species. These rare plants are selected by evolution on mineralized soils where they have an advantage over plants which exclude metals because the metals can help the plant reduce the effect of chewing insects and plant disease organisms on its ability to reproduce. Table 4 lists hyperaccumulators species for several trace elements, which achieve over 1% metal in plant shoots when grown in soils where the plants evolved. Phytoextraction can be a “green” technology for soil remediation, but commercial systems are still in development.

Our research team has developed effective metal hyperaccumulator plants for Ni+Co, and for Zn+Cd (Brown et al., 1994; Li et al., 1997; Chaney et al., 1999b). Table 5 illustrates the important role of hyperaccumulation and hypertolerance of metal by these plants in the annual rate of removal of metals from the soil. Normal plant species such as corn (*Zea mays* L.) do not remove appreciable amounts of metals even when suffering phytotoxicity from the metal they accumulate from phytotoxic soils. *Thlaspi caerulescens*, on the other hand, has poorer yield than corn, but hyperaccumulated 2.5% Zn in field tests. Further, Li et al. (1997) have examined Zn and Cd accumulation from a field test plot by a number of genotypes of this species collected at different locations in Europe, and found substantial variation in Cd hyperaccumulation in the presence of the normal 1 g Cd:100 g Zn. All strains accumulated 1-2% Zn, but differed in Cd hyperaccumulation (Figure 4). These remarkable genotypes offer an effective technology for phytoextraction of Cd from soils with little Zn contamination, not possible with the ‘Prayon’ strain of *T. caerulescens* used in most research on *Thlaspi* (Chaney et al. 1999b). And require only the same nutrients as crop plants to achieve this remarkable metal uptake and tolerance. Because lower soil pH increases solubility of Zn and Cd, *Thlaspi caerulescens* accumulates higher Zn and Cd concentrations if soil pH is lowered by agronomic management practices. We believe that cultivars of *T. caerulescens* could be bred to combine higher yields, and the Super-Cd-accumulator trait, and be used to quickly clean up soils where rice or tobacco can cause human health effects. In this case, the value of Cd in the crop would not affect the need to produce the crop to decontaminate a soil; rather, phytoremediation services and the value of Zn in the crop would need to pay for the costs of crop production and processing. Phytoextraction with *T. caerulescens* cultivars would be remarkably less expensive than soil removal, and offers the only practical solution for Cd contaminated soils which comprise risk to humans.

Table 4. Examples of plant species which hyperaccumulate Zn, Ni, Se, Cu, Co, or Mn to over 1% of their shoot dry matter in field collected samples (about 100-times higher than levels tolerated by normal crop plants).

Element	Plant Species	Max. Metal in Leaves	Location	Reference
Zn	*Thlaspi calaminare*[1]	39,600	Germany	Reeves & Brooks, 1983b
Cd	*Thlaspi caerulescens*[1]	1,800	Pennsylvania	Li et al., 1997
Cu	*Aeollanthus biformifolius*	13,700	Zaire	Brooks et al. 1978
Ni	*Phyllanthus serpentinus*	38,100	N. Caledonia	Kersten et al., 1979
Co	*Haumaniastrum robertii*	10,200	Zaire	Brooks, 1977
Se	*Astragalus racemosus*	14,900	Wyoming	Beath et al., 1937
Mn	*Alyxia rubricaulis*	11,500	N. Caledonia	Brooks et al. 1981b

[1] Ingrouille and Smirnoff (1986) summarize consideration of names for *Thlaspi* species; many species and subspecies were named by collectors over many years(Reeves and Brooks, 1983a; 1983b; Reeves, 1988).

Genetic engineering is being used to develop new plants for phytoremediation. One successful example is the transfer of microbial mercuric reduction genes to higher plants, which allows the plants to reduce soil mercuric ion to mercury metal which can be evaporated from the soil and reduce risk (Rugh et al., 1996). Methylated mercury is the dangerous form of Hg in the environment; it is lipophilic and biomagnified especially in aquatic food-chains. Plants with both the methyl mercury hydrolase and mercuric ion reductase have been developed by Rugh et al. (1996). Other fundamental aspects of developing phytoextraction technologies are summarized by Chaney et al. (1997; 1999b).

Table 5. Estimated removal of Zn and Cd in crop biomass of a forage crop (corn), compared to an existing Zn+Cd hyperaccumulator or an improved Phytoextraction cultivar. Presume the soil contains 5,000 mg Zn/kg and 50 mg Cd/kg dry weight (or 10,000 kg Zn/ha·15 cm) and 50 ppm Cd (or 100 kg Cd/ha·15 cm). Crop is presumed to have 10% ash of the dry matter.

Crop	Yield	Zn in Shoots			Zn in Ash
	t/ha	mg/kg	kg/ha	% of Soil	%
Corn, Normal	20	25	0.5	0.005	0.025
Corn, Zn-Toxic	10	500	5.0	0.025	0.50
Thlaspi	5	25000	125.	0.62	25.
REMED CROP	20	25000	500.	2.5	25.

Crop	Yield	Cd in Shoots			Cd in Ash
	t/ha	mg/kg	kg/ha	% of Soil	%
Corn, Normal	20	0.5	0.010	0.005	0.0005
Corn, Zn-toxic	10	5	0.05	0.025	0.005
Thlaspi	5	250	1.25	0.62	0.40
Super-Cd *Thlaspi*	5	2500	12.5	6.2	4.0
REMED CROP	20	250	5.0	2.5	0.40
Super-Cd CROP	20	2500	50.0	25.0	4.0

Some researchers have criticized use of hyperaccumulator plants because many have small biomass yield (e.g., *Thlaspi caerulescens* where a good yield is 5 t/ha-year). Some stress that crop plants can accumulate 1000 mg Zn/kg in some cases with little yield reduction, and compare Zn accumulation by *T. caerulescens* under the conditions which kill the crop plants. In our view, this is not a valid comparison. One must characterize how high metals can reach when each crop is managed to attain maximum levels without yield reduction. Corn, oat, and Indian mustard have only normal metal tolerance, and are greatly reduced in yield with 500 mg Zn/kg. If *Thlaspi* can accumulate 25-100 time more shoot Zn than corn under valid comparison conditions (Table 4), it seems obvious that plant species with normal metal tolerance offer little value for phytoextraction.

Unfortunately, natural plants do not accumulate concentrations of plant Pb needed to achieve significant phytoextraction of soil Pb (Chaney et al., 1999b). Some researches have shown that if one applies strong chelating agents such as EDTA, soil Pb can be dissolved, and the root membranes weakened enough to promote uptake of PbEDTA with the water moving into roots (Blaylock et al., 1997; Huang et al., 1997; Wu et al., 1999). Transpiration carries the PbEDTA from soil into plant shoots (Vassil et al., 1998). When high Pb levels are reached, the crop plants tested to date are not tolerant of the accumulated Pb, and growth ceases.

Concerns have been raised about application of EDTA to soils to achieve chelator-induced phytoextraction because of the experience the Department of Energy had with leaching of chelated radionuclides at their facilities (Means et al., 1978). Soil-applied chelators dissolve metals based on the activity of soil metals and the selectivity of metal binding by the chelator. Non-target elements can be dissolved and leach down soil profiles if fields are irrigated, or in humid regions.

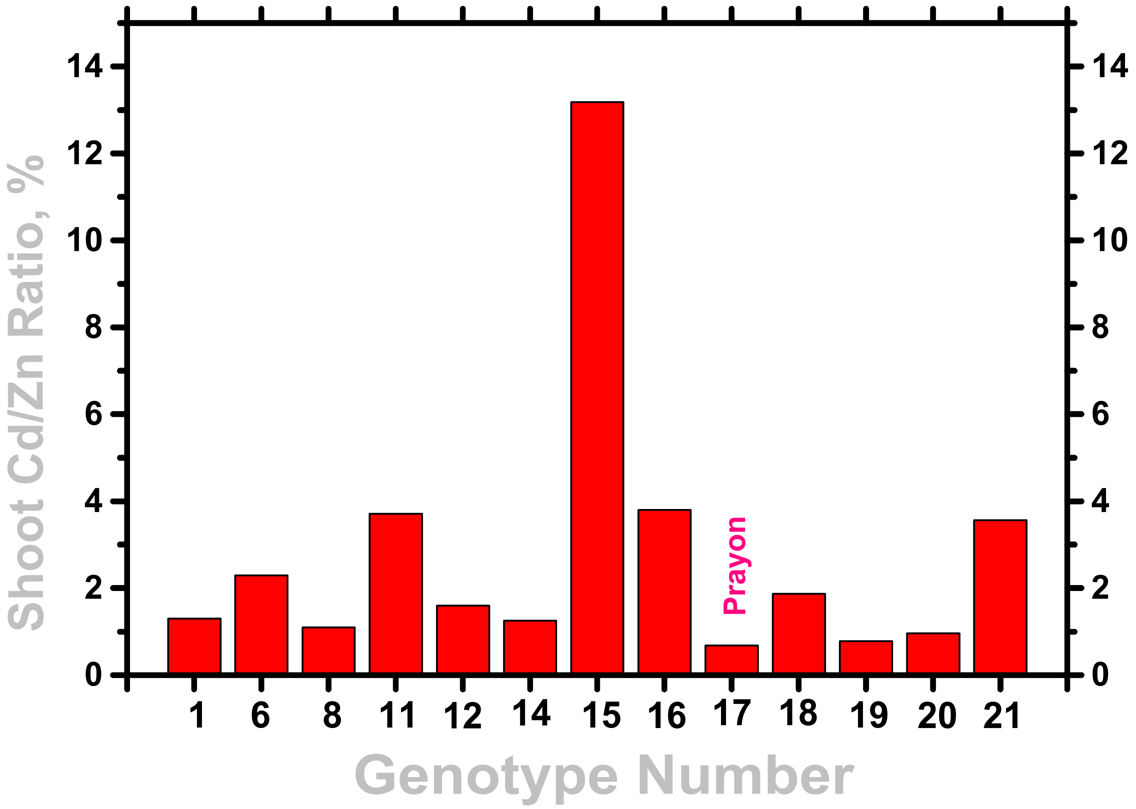

Figure 4. Variation of *Thlaspi caerulescens* genotypes in shoot Cd:Zn ratio; all accumulated 10,000-20,000 mg Zn/kg, but Cd transported to shoots reach very high levels in selected genotypes (Li et al., 1996).

Chelator-induced phytoextraction may not work for all metals or all crops. Robinson et al. (1999) tested NTA and EDTA with *Berkheya coddii*, a South African accumulator of Ni, and found that added chelating agents actually inhibited uptake by the plants. Perhaps the special property of Indian mustard which allowed high accumulation of PbEDTA does not commonly occur in other species.

However, if such a chelate-induced phytoextraction technology were practiced with the soil over a plastic liner to prevent leaching of the EDTA chelates into the subsurface soil, it might be an effective technology. But with the need for liner and EDTA in large quantity, the method is expensive compared to the use of natural hyperaccumulators as is possible with Zn and Cd, or Ni and Co. Because of discussions about chelate-induced phytoextraction, we calculated the cost of applying EDTA at rates found to optimize Pb uptake in the work by Blaylock et al. (1977) and Huang et al. (1997), 10 mmol/kg soil. The price of technical grade EDTA ($1.95/pound) was obtained from a major US manufacturer in early 2000. Assuming 15 cm depth of soil Pb contamination, one application of EDTA at 10 mmol/kg soil costs $30,000/ha. Thus this method is very expensive as well as comprising risk to ground water contamination if liners are not used. With the highly effective *in situ* inactivation of soil Pb noted above, it seems clear that inactivation of soil Pb is the more desirable approach for remediation of soil Pb.

Some have criticized phytoextraction using hyperaccumulator plants based on presumed risk to wildlife which might ingest the crop. Because the crop is usually always high in metals which it can hyperaccumulate, the assumption was that animals would be at risk wherever this technology was practiced. However, field observation of livestock in areas where hyperaccumulators occur naturally indicates that sheep, goats and cattle avoid the *Alyssum* and *Thlaspi* metal hyperaccumulators. The seeds of these species are small, and comprise little feed value. Further, it is very unlikely such animals will choose to ingest only a diet of hyperaccumulator plants considering the avoidance of metal rich leaves in the studies of Boyd and Martens (1994) and Boyd and Moar (1999). Chronic exposure to intrinsic plant metals has never been reported, and would be a valuable topic of study to settle whether wildlife or livestock may be at risk from fields of farmed hyperaccumulator crops. In general, birds and large mammals have large ranges, and would be unlikely to consume much hyperaccumulator plant biomass unless it were attractive (not found in practice). Small mammals such as field mice or other herbivore wildlife with a small range could live within a phytoextraction field, and would be expected to be harmed by the plant metals if they consumed only those plant tissues. Whether field mice would avoid these plants as found for sheep and goats is unknown at this time.

Mechanisms used by natural hyperaccumulators or metal tolerant plants in storage and tolerance of metals:

Research on both natural metal hyperaccumulators, and evolved metal tolerant plant species or ecotypes has shown that tolerance relies on vacuolar storage of metals rather than formation of chelates with soluble ligands, especially those containing P (phytate) or S (phytochelatins, or metallothioneins). The work on *Silene vulgaris* by Verkleij, Schat, Ernst, et al., has illustrated this relationship very strongly (Schat and Kalff, 1992; Harmens et al., 1993; Chardonnens et al., 1999). And studies on hyperaccumulators have shown this vacuolar storage to play a very significant role in natural hyperaccumulators (Lasat et al., 1998; Küpper et al. 1999; Verkleij et al., 1998). Also, attempts to use protoplast fusion to build plants with higher biomass but natural hyperaccumulation ability have proved unsuccessful (Brewer et al., 1999)

Phytoextraction with hyperaccumulator offers great promise for soil remediation:

Metal hyperaccumulation by plants offers a new cost effective approach for soil remediation. Further, the crop can be harvested as a biomass crop, air dried like “hay”, and burned in a biomass power generator. For metals which have commercial value, the ash is a high grade ore, very different from the traditional metal ores of commerce. For Zn and Cd, the value of biomass energy and metals for recycling appears to be a profitable opportunity (MacDougall et al., 1997), and for more valuable metals, hyperaccumulation may be more cost effective than mining technologies. Phytoextraction and phytomining technologies require extensive research and development. One is essentially domesticating a new crop, a difficult task. Cost effective metal phytoextraction is sufficiently promising that several research teams are working to develop practical phytoextraction systems (improved plant cultivars, and agronomic management practices needed for cost effective metal hyperaccumulation) (see Chaney et al., 1999b).

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