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Immobilization of Heavy Metals in Soil Using Natural and Waste Materials for Vegetation Establishment on Contaminated Sites

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Contaminated land is increasingly becoming an important issue worldwide. Many contaminants are persistent in soil for a large number of years. With the increase in public awareness regarding the consequences of contaminated soil, many researchers are concentrating on developing cost-effective and socially acceptable soil remediation technologies. Soils of many sites, which have been left derelict after industrial decline, harbor a broad suite of metal and organic contaminants. Land where such contaminants are deemed to pose a significant risk to receptors is considered contaminated under modern guidance. Remediation to break identified pollutant linkages would precede reclamation and plant establishment. One approach to break the pollutant receptor linkage is to utilize materials that effectively create soil conditions that immobilize contaminants whilst providing essential plant growth properties in terms of nutrition and water holding capacity. Materials that may achieve this include: 1) composts derived from materials such as sewage sludges and other municipal sources; 2) natural or synthetic zeolites; or 3) industrial by-products such as red-mud or other iron-rich materials such as iron grit or iron oxyhydroxides. Remediation techniques that utilize such materials may be cost-effective compared to more traditional methods and may effectively divert materials from the waste stream and could thereby make a dual contribution to sustainable development.

Keywords contaminated soils, organic soil amendments, zeolites, iron-rich compounds, compost

Introduction

It is estimated that there are about 20000 contaminated sites in England and Wales that may need treatment (Environment-Agency, 2004). These sites may present significant risks to human health and to the wider environment. Most of the governments in the European countries have made the sustainable reuse of land an important priority in their sustainable development strategy. For example, in the UK, more than 50% of the development occurs on previously developed land, and the UK government has set a target for at least 60% of new homes to be built on such brownfield sites by 2008 (National Land Use Database, 2004). Remediation and reclamation of contaminated brownfield land is considered a sustainable activity because it helps to conserve land as a resource, prevents the spread of pollution to

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air and water, and reduces the pressure for development on Greenfield sites (Bardos and Vik, 2001).

To improve the development of brownfield sites, considerable efforts have been made towards developing appropriate remediation technologies for treating contaminated soils. Soil excavation used to be the most preferred choice, but recently more attention has been given to the use of *in-situ* treatment techniques as they avoid expensive excavation, minimize social and ecological disturbance, require no transport of soil, and avoid transferring the problem to another site, which future generations may have to deal with (Rabinowitz, 1993; Yang et al., 2001). As one of the major groups of contaminants, heavy metals in soil pose a threat to the environment as they are not degraded and can persist for long periods in the soil. One approach for remediating heavy metal contaminated soils is through immobilization, which transforms heavy metals into less bioavailable forms. In this way the pollutant linkage between the contaminant and receptors can be broken and a site can be redeveloped.

As an alternative for the building of houses, brownfield sites in the urban environment are also increasingly considered for the development of greenspace. Green space redevelopment in urban areas has prominent benefits such as restoring ecological value, improving the environmental quality of air, water, etc., improving the urban appearance, and providing space for recreation. Various researchers (Hough, 1994; Hough et al., 1997); Thompson and Sorvig, 2000; Kalpan, 1993, 2001; Fried, 1982; Kuo et al., 1998; Cackowski, 1999; Shafer et al., 2000) have found that the provision of urban greenspace improves the social well being of people through providing a sense of well being and causing stress reduction, and can also lead to enhanced economic investment in an area.

Various soil amendments have been suggested for their ability to immobilize heavy metals and arsenic whilst providing conditions essential for plant growth. Such materials include organic soil amendments (Williamson and Johnson, 1981; Abbott et al., 2001; Walker et al., 2004; Cao et al., 2003, 2004; Clemente et al., 2003), minerals such as zeolites (Ming and Mumpton, 1989; Tsitsishvili et al., 1992; Shanableh and Kharabsheh, 1996; Lin et al., 1998; Edwards et al., 1999) and iron-rich compounds (Browner, 1995; Brunoi et al., 2005; Parek and Goldberger, 1976; Friesl et al., 2003; Summers et al., 1996). The purpose of this paper is to review the use of these material types for revegetating heavy metal and arsenic contaminated soils. An overview of current knowledge on the immobilization capacities of these materials as well as their influence on plant growth is presented.

1. Use of Composted Organic Soil Amendments as Remediating Agents for Polluted Soil

Addition of organic matter to contaminated soils has been used for many centuries to improve soil fertility, enhance revegetation and decrease the plant availability of toxic metals (Williamson and Johnson, 1981; Abbott et al., 2001). The addition of organic amendments to soils can reduce the heavy metal bioavailability by changing them from bioavailable forms to the fractions associated with organic matter or metal oxides or carbonates (Walker et al., 2004). Organic amendments can also improve soil aeration, water and nutrient holding capacities. Different kinds of organic amendments that have been used for the remediation of contaminated soil include manures, biosolids, sawdust, and wood ash, composts derived from different source materials, sewage sludge, bark chips and woodchips. In the case of manure, only aged manure is used for soil remediation purposes as fresh manure can harm plants due to high ammonia levels (Davis and Wilson, 2005).

The use of a range of composted organic soil amendments (Municipal solid waste compost, biosolid compost, mature compost, cow manure, etc.) for restoring heavy metal and arsenic contaminated soils has been tested by various researchers (Cao et al., 2003; Cao and Ma, 2004; Clemente et al., 2003; Cala et al., 2005; Walker et al., 2004; Kiikkilä et al., 2002; Rate et al., 2004). For most of these experiments the uptake of heavy metals and arsenic by plants was reduced by the addition of composted materials to the soil.

For example, Cao and Ma (2004) used carrot (*Daucus carota* L.) and lettuce (*Lactuca* sativa L.) for their pot experiments grown for 10 weeks in arsenic-spiked soil with or without compost in pot experiments. They showed that biosolid compost application (10% w/w) reduced plant uptake of arsenic in carrot by 79–88% and in lettuce by 86–96% compared to untreated soil. Arsenic was adsorbed by the organic matter from the compost and the fractionation analysis performed showed a reduction of arsenic in soil water soluble, exchangeable and carbonate fraction by 45%.

Similarly, Cao et al. (2003) reported that dried municipal solid waste and biosolid compost amendments to As spiked contaminated soil, at a ratio of 50g/kg soil, reduced water soluble As and the uptake of arsenic by Chinese brake fern (*Pteris vittata* L.) grown on these soils. The authors hypothesized that arsenic adsorption onto the organic matter was responsible for the observed reductions.

Previous studies have also demonstrated immobilization of heavy metals through amendment of contaminated soils with a range of organic materials (Kiikkilä et al., 2002; Walker et al., 2004; Castaldi et al., 2005). Kiikkilä et al. (2002) in their laboratory studies used nine different organic materials (composted sewage sludge, compost of organic household waste, mixture of compost and woodchips, mixture of compost and bark chips, garden soil, birch leaves, bark chips, humus or peat) amended to a soil contaminated with Cu 1600 mg/kg; and having Fe 6100 mg/kg; Zn 160 mg/kg; Pb 130 mg/kg. Copper immobilization, changes in microbial mass, microbial respiratory activity was studied. Exchangeable copper concentration was found to decrease after mulched treatment with garden soil (GS), sewage sludge (SS), compost (C) and compost mixed with bark chips and woodchips (C-B, C-W, respectively), but not in the treatments with bark chips, humus or peat, or control. The authors explained the probable reason for this was formation of complexes with particulate organic matter carried down into the underlying soil from the mulch. They assumed that significant amounts of particulate organic matter were released from SS, C, C-W, C-B and GS when pH was above 6. Other studies have examined the effects of compost produced from olive leaves, olive husks and olive mill wastewater on metal mobility and plant availability (Walker et al., 2004; Castaldi et al., 2005). Compost produced from olive leaves and olive mill wastewater and cow manure were applied to pyritic (sulphide rich) soil contaminated with Cu 133 mg/kg; Zn 521 mg/kg; and Pb 220 mg/kg, and containing 45713 mg/kg of Fe. The effect of heavy metal bioavailability and vegetation growth was studied in their pot experiments in which *Chenopodium album* L. was grown. Air dry compost and cow manure were added at the rate of 27 and 26 g per kg dry soil, respectively. Their results showed that the compost amendment to the soil lowered tissue concentrations of Pb, Zn, Fe and Mn, although Zn and Mn were still toxic. Cow manure application reduced shoot concentrations of the heavy metals especially Zn and Mn by 91% and 95%, respectively compared to non-amended control soils. The cow manure was effective in decreasing heavy metal bioavailability, as it increased the soil pH, and supplied essential plant nutrients. Castaldi et al. (2005) studied the effect of a 10% (w/w) amendment of compost produced from olive husks (50%), sewage sludge (25%) and vegetal waste (25%) in pot experiments on soil contaminated with very high total concentrations of Pb (19 663 mg kg^{-1}), Cd (196 mg kg^{-1})

and Zn (14 667 mg kg^{-1}). The amendment resulted in an 87% decrease in concentration of Pb in the aerial part of the plant grown-white lupin (*Lupinus albus* L.) compared to the control samples. The concentration of Zn in the aerial part of plants grown in the compost amended soil was 31% lower than in the control sample.

Petruzzelli et al. (1998) demonstrated the use of sludge derived from a paper industry water treatment system for the *in situ* attenuation of heavy metals in soil of an old landfill both at laboratory and field scales. The paper mill sludge was composed of 50% organic matter and talc, $CaCO_3$, and clay from the paper production units. Paper mill sludge was mixed with soil at a rate of 30% (w/w). Heavy metal mobile fractions, before treatment and six months after sludge application to the soil, were determined by sequential extraction procedures allowing evaluation of the water soluble, exchangeable, adsorbed and complexed metals in soil. After six months, the results of the EDTA part of the sequential extraction showed a decrease of 30-50% in the heavy metal mobile fractions. Reductions in concentration were: Cu, 35%; Zn, 42%; Ni, 30%; Pb, 51%; Cd, 38%. The authors explained that the sorption sites were available on the solid phase of soil after sludge application. The authors concluded that the reduction of heavy metal mobility in the field was due to the increase in sorption ability of the soil matrix when it was amended with paper mill sludge.

In contradiction to the research described above where organic matter reduces bioavailability of heavy metals, some of the results from various authors show mobilization of metals and an increase in plant metal uptake after application of composted organic amendments. Cao et al. (2003) reported that when biosolid compost was added to either acidic or neutral soil the adsorption of As was increased by the organic matter in the compost resulting in a reduction of water soluble As. Dried municipal solid waste and biosolid compost, however, were mixed with Chromated-copper-arsenate (CCA) soil and As spiked contaminated (ASC) soil at a ratio of 50g/kg soil. In this case, both municipal solid waste compost (MSW) and biosolid compost (BC) added on CCA contaminated soil with a neutral pH induced an anaerobic environment in the soil, which favoured the conversion of As (V) to mobile As (III) and facilitated the arsenic uptake by the fern. The fraction/concentration of As (III) in solution was increased from 9.7 to 20% and 24% for MSW and BC, respectively.

Similarly, Rate et al. (2004) observed an increase in concentrations of plant available metals in soil amended with biosolids (sewage sludge derived material). Biosolids were applied at 0, 10, 25 and 50 dry t/ha (0, 17, 43 and 87 dry g/kg dry soil) and soil was limed to pH 6. Ryegrass (*L. rigidum*) and subterranean clover (*T. subterraneum*) were used for greenhouse experiments. Results showed that with increasing biosolid application, Cd concentration in both plant roots and shoots increased significantly. A similar trend was observed with As, Co, Cr, Cu and Pb.

These two examples demonstrate that care should be taken before contemplating application of organic soil amendments to metal contaminated soils. In the first case, the increased plant uptake of As can be subscribed to the onset of anaerobic conditions but in the latter case no specific mechanism for the increased uptake is presented. This supports the need for more research to determine the mechanisms involved in metal mobilization and immobilization when organic soil amendments are added to As and metal contaminated soils.

Apart from the mobilization of heavy metals and arsenic, it is also important that the addition of organic soil amendments increases the biomass production of plants on contaminated soil. The following cases clearly indicate the potential beneficial effects of organic amendment on plant growth. Cow manure was shown to increase the biomass of *C. album* grown on a pyrite-contaminated soil (Walker et al., 2004). Similarly, biosolid compost amendment to a copper, chromium and arsenic contaminated soil has been shown to increase the biomass of carrot and lettuce by 3–5 times compared to the control (Cao and Ma, 2004). Other studies have shown an increase the biomass production in *Rosmarinus officinalis* L. and an increase in plant micro and macro nutrient status (Cala et al., 2005). The compost (made of (v/v) olive husks (50%), sewage sludge (25%) and vegetal waste (25%) increased the above ground plant biomass of white lupin (*Lupinus albus* L). by a factor of 3.6 whilst root biomass increased by a factor of 5.6. (Castaldi et al., 2005). Municipal biosolids, woody debris, pulp and paper sludge has also been shown to increase plant biomass from 0.004 mg acre^{-1} in the control to a mean of 1.4 mg acre^{-1} in the amended plots (Brown et al., 2003). Rate et al. (2004) found that the total dry plant matter yield of ryegrass (*Lolium rigidum*) and subterranean clover (*Trifolium subterraneum*) was increased by the application of biosolids applied in the topsoil than the residue clay/sand.

The important observations by various researchers on the use of composted organic waste can be seen in Table 1. It is very clear from the experiments that soil organic amendments discussed above play a significant role in reducing the plant bioavailability of heavy metals and arsenic. In the discussed cases, organic matter present in the amendments adsorbs the metals with the probable cause for the observed decreases in exchangeable metal concentration being due to the formation of complexes with particulate organic matter. Application of sewage sludge onto metal contaminated soil resulted in not only immobilization and thereby reduction of bioavailability of metals to plants, but also improved soil quality and enhanced sorption capacity of the soil matrix. pH also plays a significant role in metal plant availability and mobility in soils. A general trend observed is that acidic soil conditions favor the mobility of metals and that the addition of amendments such as manures and composts increase soil pH, which reduces metal availability. An onset of anaerobic condition has been shown to cause As to become more plant available whereas heavy metals are likely to produce reduced complexes with a low plant availability. For the latter reason, it can be recommended that for every soil, a potential organic amendment should be tested on its metal mobilizing or immobilizing behavior before it is applied in the field at large scale.

2. Use of Zeolites for Remediation of Contaminated Soil

A group of minerals that have been widely tested for their capacity to immobilize heavy metals in soils are zeolites. Zeolites are naturally occurring crystalline, hydrated aluminosilicates of alkali and alkaline earth cations. They are formed in nature when water of high pH and high salt content interacts with volcanic ash, causing a rapid crystal formation. They have a silicate framework consisting of interlocking tetrahedrons of SiO_4 and AlO_4 (Fig. 1). To be classified as a zeolite the molar ratio $(Si + Al)/O$ must equal $1/2$.

Positively charged cations are attracted towards the negatively charged alumino-silicate structure within giving the zeolite high cation exchange capacity (CEC). The large vacant space in the zeolites allows space for large cation groups (sodium, potassium, barium and calcium) and even relatively large molecules and cation groups (water, ammonia, carbonate ions and nitrate ions) to enter. These spaces are interconnected in some zeolites and form wide channels of varying sizes depending on the type of mineral. These channels allow the easy movement of the resident ions and molecules into and out of the structure. One of the important characteristics of zeolites is their ability to both lose and absorb water without damage to their crystal structures. These characteristics make zeolites useful compounds for soil remediation purposes. Clinoptilolite, chabazite, and phillipsite are natural zeolites that have been evaluated as sequestering agents for environmental cleanup (Ming and Mumpton,

Table 1
Observations on metal immobilising capability of composted organic waste.

Immobilising agent	Application rate	Observation
Biosolid compost *Cao and Ma (2004)*	10%	69–88% reduction in arsenic uptake by carrot and 56–96% in lettuce. Biomass of carrot and lettuce increased by 3–5 times.
Composted sewage sludge (SS) Compost of organic household waste Compost + woodchips (C + WC) Compost + barkchips (C + BC) Gardens soil (GS) Birch leaves Humus or peat *Kikkilä et al. (2002)*	—	Exchangeable copper concentration decreased with SS, GS, C + BC,C + WC.
Cow manure Compost from olive leaves/olive mill wastewater *Walker et al. (2004)*	2.7% dry compost 2.6% cow manure	Cow manure was effective in reducing bioavailability of metals as it increased the pH of soil helping in immobilising metals. Tissue concentrations of Pb, Zn, Fe and Mn were reduced.
Compost from olive husk (50%) Sewage sludge (25%) Vegetal waste (25%) *Castaldi et al. (2005)*	10%	87% reduction in Pb in aerial parts of the plant *Lupinus albus*. Zinc was 31% lower than the control sample in the aerial parts of the plant. The biomass above ground was increased by a factor of 3.6 after adding the amendment.
Paper mill sludge *Petruzzelli et al. (1998)*	30%	Decrease in heavy metal mobile fractions: Cu, Zn, Ni, Pb and Cd-35%, 42%, 30%, 51% and 38% respectively.
Dried municipal waste and biosolid compost. *Cao et al. (2003)*	5%	Due to an increase in water soluble arsenic and conversion of As (III) to As (V), mobilisation of arsenic was observed.
Biosolids *Rate et al. (2004)*	1.7%, 4.3%, 8.7%	As, Co, Cu, Pb and Cr uptake by the plant increased. With liming, metals in plant tissues were lower than unlimed soil. This was due to decrease in bioavailability of metals due to liming (increase in pH) or metal adsorption onto organic matter in biosolids.

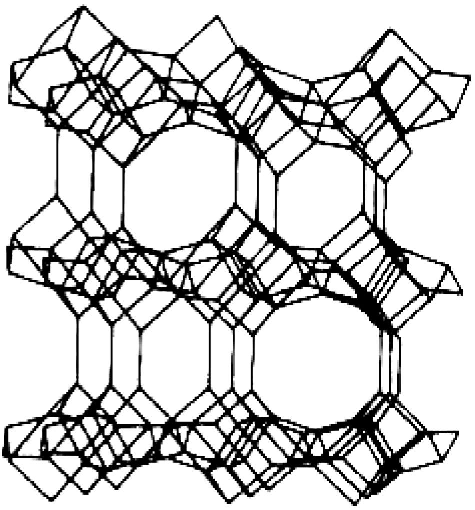

Figure 1. Framework of Clinoptilolite. Reprinted from Manley and Holmes (1989). Copyright (1989), reprinted with permission from New Scientist.

1989; Tsitsishvili et al., 1992). The ability of these materials to immobilize contaminants in polluted soils has been extensively tested (Shanableh and Kharabsheh, 1996; Edwards et al., 1999) and waters (Pansini et al., 1991; Ruiz et al., 1997; Moreno et al., 2001; Ouki and Kavannagh, 1999). As they tend to have a high CEC, zeolites have been identified to be good candidates for the remediation of metals in soils and effluents (Shih and Chang, 1996; Curkovic et al., 1997; Chang and Shih, 2000; De Gennaro et al., 2003).

Haidouti (1997) used rye grass (*Lolium perenne L.*) and alfalfa (*Medicago sativa L.*) as indicator plants for evaluating the applicability of natural zeolite, clinoptilolite, on soil contaminated with mercury. The application of the zeolite at 1–5% (w/w) addition reduced plant uptake of the mercury by up to 58% in the roots and 86% in the shoots. Shanbleh and Kharansheh (1996) reported the use of TCLP tests (Toxicity Characteristics Leaching Procedure) for evaluating the stabilization of Pb, Cd and Ni by fajuasite and phillipsite in an artificially contaminated soil. The results showed that the leaching of the metals was reduced by 40–97% for Pb, 50% for Ni and 60% for Cd. The sorption capacity (especially for Pb) of the zeolite was affected by the competition among the metals in solution, with a 5–35% w/w application of the zeolite required to reduce Pb leachability below the TCLP acceptable limit. Similarly, Moirou et al. (2001) investigated the stabilization of Pb, Zn, and Cd by the natural zeolite clinoptilolite. The contaminated area selected was a former lead-zinc mining district and the metal concentrations found were Pb (120–11350 ppm), Zn (140–11400 ppm) and As (18–1180 ppm). Batch experiments were conducted for one month using pot experiments with varying soil-zeolite mixtures. US EPA leaching tests were followed for evaluation purposes, mainly TCLP, EPT test (Extraction Procedure Toxicity) and SPLP (Synthetic Preparation Leaching Procedure). According to the TCLP procedures followed, moderate solubility reductions were observed for Pb 38%, Zn 33% and Cd 32%. The EPT test, however, showed a 55%, 74% and 46% reduction in Pb, Zn and Cd, respectively. The authors have observed that Pb solubility could not be decreased below the permissible level of 5 mg/l, even at 25% (w/w) addition of the zeolite. This was attributed to the presence of Na competing ions, which were originating from the TCLP leaching solution. The SPLP did not produce any measurable values for Pb, which was probably due to the use of inorganic acids and test pH value of 5. For Zn, the reduction in solubility was significant for all three leaching tests (74, 81 and 33% in the EPT, SPLP and TCLP tests respectively). In all three instances, a significant decrease was observed with a 10% zeo lite addition. In the case of Cd, zeolite addition improved the soil by immobilizing 32% and 46% of leachable Cd from the TCLP and EPT test results, respectively. In addition, Moirou et al. (2001) also conducted column studies that showed that 50–60% of Pb was immobilized with the 20% (w/w) zeolite amendment.

Ponizovsky and Tsadilas (2003) compared the retention of lead by a sandy loam soil from Greece and the zeolite clinoptilolite in their lab studies. The soil was slightly acidic and had low content of phosphorus and organic matter. Batch sorption tests were carried out to produce sorption isotherms. Comparison of the isotherms of lead retention by the soil and the zeolite showed that clinoptilolite adsorbed more Pb than the soil and the amount adsorbed was independent of pH. It was concluded that clinoptilolite adsorbed 10–20 times more Pb than soil and sorption by the zeolite was independent of pH. It was also noted that 1% (w/w) zeolite addition could retain 750 mg Pb kg^{-1} in the soil. Similarly, Zorpas et al. (2000) used clinoptilolite for the immobilization of heavy metals (Cd, Cr, Cu, Fe, Mn, Ni, Pb and Zn) from sewage sludge, when it was used as a bulking agent during composting. Their results demonstrated that by using 25–30% of clinoptilolite during composting, 100% of Cd, 28–45% of Cu, 10–15% Cr, 41–47% Fe, 9-24% Mn, 50–55% Ni and Pb, 40–46% of Zn were adsorbed out of solution. Cholpecka and Adriano (1996) showed that by adding a lower dosage of zeolite, 15 g/kg, there was significant decrease in uptake of metals Pb and Cd by maize (*Zea mays*) and barley (*Hordeum vulgare*).

Synthetic zeolites equally have potential for metal immobilization. Faujasite type (also called Zeolite Y) and ZMS-5 zeolites have most commonly been tested. In addition, it has been demonstrated by several researchers that the addition of synthetic zeolites to contaminated soils can improve the quality of plant growth and reduce soil phytotoxicity.

Zeolites, synthesized from fly ash, were studied for their ability to stabilize cadmium in a contaminated soil (Lin et al., 1998). The zeolite was produced from fly ash from a coal-fired power plant by addition of NaOH and being heated to 90°C for 24 hrs.

Two kinds of soils were used for their experiments: real contaminated soil and an artificially contaminated soil. Varied portions of the zeolite were added to the contaminated soil samples, ranging from 0.5 to 16 g/100 g of soil. The soil samples were collected from various locations: Pinchen, Jente, Erlin and Chengchung. Their results showed that without zeolite addition, the leachate Cd concentration was approximately 3.9 mg/l for Pinchen soil and 2.3 mg/l for Jente soil; yet only 0.25 and 0.1 mg/l for Erlin and Chengchung soil samples, respectively. The authors hypothesized that the differences in Cd leachability were due in the main to the differences in the initial soil pH since the soils had similar CEC values. They observed that the addition of synthetic zeolite inhibited the leaching of cadmium from all of the soil samples. Amendment with 16 g zeolite/100g soil resulted in leachate cadmium concentration of the samples being reduced to <0.05 mg/l. The cadmium concentration in leaching solution was found to be inversely proportional to the rate of addition of the zeolite. It was concluded that the higher cation exchange capacity of the zeolite/soil mixture and higher pH were the conditions favoring stabilization of cadmium in contaminated soil. The authors suggested a zeolite dosage of approximately 0.1–0.2 g/mg Cd/100 g soil to reduce the concentration of Cd in leachates from all studied soils below 0.05 mg/l.

Gworek (1992) conducted experiments with the synthetic zeolites 4A and 13X to determine their effects on the mobility of cadmium when amended to a contaminated loamy soil. 1% (w/w) amendments of each zeolite were added to the soil and lettuce (*Lactuca* *sativa*) was grown in pots to determine the effects on plant metal uptake and biomass. The results showed a reduction in cadmium concentrations of up to 86% in the leaves of the lettuce when compared with the control (with no added zeolites).

Similarly, Edwards et al. (1999) used amendments of 1% of zeolite 4A, 0.5% of zeolite P and 5% of zeolite Y (w/w) or 1% lime and found a similar resulting reduction in metal content of mobile fraction of Cd of between 42–70%.

Despite promising results for immobilization of metals by zeolites, several studies have demonstrated that zeolite addition failed to promote satisfactory growth of plants grown in contaminated soils (Geebelen et al., 2002; Coppola et al., 2003; Nishita et al., 1968; Stead, 2002). Geebelen et al. (2002) investigated lead immobilization on soils spiked with increasing concentrations of Pb in which lettuce (*Lactuca sativa L.*) was grown as a test species. 0.5% w/w zeolite (13-X type) was added along with other organic and inorganic amendments. The zeolite slightly increased the soil pH 4.91 to 6.65 and at the highest concentration of Pb tested (2000 mg Pb kg-^{1}) the amendment caused a 71% decrease in extractable Pb. A significant reduction in the root growth and leaf area was observed independent of soil Pb concentration. The authors noted that zeolite had caused a dispersed soil structure, which was due to the addition of sodium ions that can also cause direct plant toxicity. The resulting reduced plant growth led to a reduced uptake of Pb by the plants. Similarly, Coppola et al. (2003) reported a negative effect on plant growth due to high amendment rates of zeolite to soils. An organo-zeolite conditioner was used to study the remediation of soil contaminated with 4.2 mg kg^{-1}and 220 mg kg^{-1} of Cd and Pb, respectively. The organo-zeolite conditioner was prepared from Neapolitan Yellow Tuff (NYT), which had a zeolite content of 54%, phillipsite 37%, Chabazite 17% and pellet manure (PM). The NYT/PM (1:1 w/w) mixture was added at the rate of 0%, 25%, 50% and 75% (w/w). Wheat (*Triticum vulgare L.*) was grown on the soil mixtures. The dry matter of shoots harvested from experimental pots with 0% addition was 2.7 g pot$^{-1.}$ With 25% conditioner, there was a significant increase in the dry matter of shoot to 5 g pot^{-1}, which was thought to be due to nutrient supply from the conditioner. In contrast, at 50% and 75% conditioner addition, there was a strong decrease in the dry plant biomass and almost no plants survived in the pots with a 75% conditioner addition. This was explained by the observed increase in the electrical conductivity of the soil highlighting increased soil salinity and Na toxicity, which had an adverse effect on plant growth.

Nishita et al. (1968) also observed a 10% decrease in the yield of bean (*Phaseous vulgairs L.*) when Na-clinoptilolite was used as a soil amendment. This was due to high sodium ion released into the soil, causing osmotic and toxicity problems. Stead (2002) also reported a similar negative effect on plant growth by the addition of a sodium-zeolite. Rye grass ((*Lolium rigidum*) and clover (*Trifolium subterraneum*) grown in 5%, 10, 20% pots contained long, thin stems, yellow leaves and short toot depth. This impact was due to high sodium exchanged from the zeolite.

The important observations by various researchers on the use of zeolite can be seen in Table 2. This shows that zeolites can considerably reduce the solubility of metals in soil, thereby their uptake by plants with few exceptional cases where it had detrimental effect on plant growth. All of the studies that found negative effects of zeolite amendment on plant growth had used zeolites with high sodium content. The use of zeolites with high sodium content as soil amendments is therefore not recommended. The immobilization of metals in soil is due to an increase in soil cation exchange capacity and pH by the addition of zeolites. The increase in soil pH favors adsorption of metals onto zeolites' surface and the formation of insoluble metal hydroxides. The adsorption and ion exchange capacity of the zeolites depends on the pH conditions, the concentration of heavy metal cations, and also

Table 2

Observations on metal immobilising capability of zeolites.

Immobilisation agent	Application rate	Observation
P, 4A and Y synthetic zeolite. *Edwards et al. (1999)*	0.5%, 1%, 5%	Reduction in mobile metal fraction between 42–70%. Reduced phytotoxicity.
Synthetic zeolite from flyash. *Lin et al. (1998)*	0.5%–16%	Cd concentration in the leachate soil sample was less than 0.05 mg/l. Higher zeolite to soil mixture with high pH favoured Cd stabilisation.
Clinoptilolite *Haidouti (1997)*	1-5%	Hg solubility reduction up to 58% in roots and 86% in shoots of alfalfa and ryegrass.
Synthetic zeolite 4A, 13X *Gworek (1992)*	1%	Reduction in Cd concentration in leaves of lettuce up to 86% compared to the control. Good plant growth.
Clinoptilolite *Moirou et al. (2001)*	0–10%	Solubility reductions were 38% for Pb, 33% for Zn, 32% for Cd using TCLP procedures. 55% for Pb, 74% for Zn and 46% for Cd with ETP test.
Fajuasite and phiilipsite *Shanbleh and Kharnsheh (1996)*	5–35%	Leaching of Pb reduced by 40-97%, Ni by 50%, and Cd by 60%.
Alfisol and clinoptilolite *Ponizovsky and Tsadilas (2003)*	1%	1% zeolite added retained 750 mg Pb kg^{-1}soil
Clinoptilolite *Zorpas et al. (2000)*	25–30%	Used for immobilising Cd, Cr, Cu, Fe, Mn, Ni, Pb and Zn from sewage sludge. 100% Cd, 28–45% Cu, 10–15% Cr, 41–47% Fe, 9–24% Mn, 50–55% Ni and Pb, 40–46% of Zn were retained by the zeolite (from metals bound in carbonate and exchangeable fractions).
13X type zeolite *Geebelen et al. (2002)*	0.5%	Lettuce was grown as bioindicator 71% decrease in extractable Pb was observed. Significant growth reduction in root and leaf area was observed.
Organo-zeolitic conditioner *Coppola et al. (2003)*	25%, 50%, 75%	The dry matter of wheat plant (shoot) was 2.7 g/pot was observed at no addition. With 25% addition it was 5 g/pot, at 50% there was a strong decrease in dry matter. Practically no growth was observed at 75% addition.
Clinoptilolite *Nishita et al. (1968)*	—	10% decrease in the yield of bean plant was observed with clinoptilolite.
Clinoptilolite *Stead (2002)*	5%, 10%, 20%	Rye grass and clover were grown in the pots showed long thin stems, yellow leaves and short root depth.

the grain size of the zeolite used. It is suggested that the long-term effectiveness of zeolite amendment should be evaluated by aging studies, desorption studies and plant growth tests before large-scale application in the field.

3. Use of Industrial Waste By-Products for the Remediation of Contaminated Soil

Various researchers have studied the use of industrial waste by-products for soil remediation. The reuse of such materials would not only solve the problem of waste disposal but may also provide a financially lucrative market for the material as a useful product. Metal sorption experiments have been carried out using waste by-products such as berengite, red-gyspum, phosphogypsum and cyclone ashes. Other materials like iron-rich biosolids, oxyhydroxides and lime have also been tested for the remediation of heavy metal contaminated soils. In this section we discuss the use of iron oxides, phosphogypsum and red gypsum. Red mud has extensively been studied and therefore will be presented in a different section.

A. Red Gypsum and Phosphogypsum

Lombi et al. (2004) and Illera et al. (2004) tested red gypsum (RG) and phosphogypsum (PG) as soil amendments for the remediation of metal-contaminated soils. Phosphogypsum ($CaSO_4.2H_2O$) is an industrial by-product of phosphoric acid manufacturing. It is produced when phosphate rock is treated with sulfuric acid to produce the acid. Phosphogypsum is identical to naturally occurring gypsum and has some impurities, which differs from place to place. Phosphogypsum can be used as a soil amendment to increase fruits and vegetable yield.

Red gypsum is a by-product of the titanium dioxide pigment manufacturing industry and contains about 35% iron oxides. Titanium is extracted from a type of sand, called ilmenite, using sulfuric acid which leads to an iron sulfate waste, which is neutralized with lime to give red gypsum.

Lombi et al. (2004) used a combination of water treatment sludge, red mud and red gypsum for the remediation of As and Cu contaminated soils. They tested amendment with two different water treatment sludges (WTS-A and WTS-B), two red muds and red gypsum, all rich in iron oxyhydroxides at 2% (w/w) on a soil contaminated with As and Cu. Rye grass and lettuce were grown on the soils amended with the above mixtures. It was observed that only WTS-A improved lettuce growth. With the exception of WTS-A, the other soil amendments improved the growth of rye grass. Concentration of As in soil pore water and extractable As decreased only in WTS (A and B) and red mud gypsum treatments, whereas Cu concentration decreased in all treatments by more than 84%.

Acidification of the treated soil showed that the concentration of extractable As and Cu increased in the treated soils compared with untreated ones.

Illera et al. (2004) used redgypsum (RG) and phosphogypsum (PG) for the immobilization of Cu, Pb and Cd in an acidic soil. For both products a 1% w/w amendment increased the soil's retention of lead, cadmium and copper. The initial concentration of metals used in solution (1:5 soil: solution) were 10, 25, 50, 100, 250, 500 and 1000 mg l^{-1} of Cd, Cu and Pb. Application of PG or RG showed a 98% reduction in Pb concentration in the solution. The effects on copper were less dramatic, with RG reducing copper concentration in solution by 9% whilst PG showed no effect ($<1\%$). Cadmium concentration in solution was reduced by 2.4% and 6.5% by PG and RG, respectively. In summary, the addition of

RG and PG was more effective at reducing the concentration soluble Pb than that of Cd or Cu. A similar result has been reported by Garrido et al. (2005), who tested the use of RG and PG, dolomite residue and sugar foam for immobilization of Pb, Cd and Cu in metal spiked acid soil. The sequential extractions and single (DTPA) extraction used in this study showed that sugar foam and dolomite residue were effective in reducing the mobility of Cd and Cu and, to a lesser extent, Pb, whereas RG and PG were found to immobilize Pb more effectively than the other two metals.

It has been suggested that the increase in lead retention by the addition of PG and RG is due to the formation of anglesite minerals. Metal retention by DR was due to the formation of laurionite type minerals and also Cd and Cu hydroxy-chlorides. It has been shown elsewhere that application of PG on orange groves can also improve tree growth and increase calcium levels in the leaves and the bark of the trees (Stanley, 1992). PG and RG applications may have the additional benefit of increasing yield of crops on acidic soils by ameliorating aluminium toxicity and supplying additional calcium.

B. Iron Bearing Additives

Products rich in iron oxides have been successfully used for the reduction of metal mobility in soil. The sorption behavior of iron is related to pH (with a range of 5-8) and each ion has its own optimum pH range for heavy metal adsorption. It is reported that iron in a cubic yard of natural soils is capable of adsorbing from 0.22–2.2 kg of soluble metal cations, anionic complexes or a similar amount of organic biodegradation products (Vance, 2002). Ferric salts have been recognized as an effective scavenger of heavy metals and studies were performed on their application and underlying metal sorption mechanisms. In addition, iron oxides have been widely used as agents for in-situ remediation of arsenic in polluted soils. At neutral to alkaline pH, ferric salts precipitate as amorphous hydrated oxide or oxyhydroxide, which has stable properties. Gradually the precipitate transforms into the crystalline iron oxide (Goethite) form (Murphy et al., 1976; Voges and Benjamin, 1996).

Addition of ferrous sulfate to contaminated soil for removing / reducing heavy metal mobility is also a valid method of remediation. The added ferrous sulfate precipitates into iron oxides under field conditions. Hartley et al. (2004) and Warren and Alloway (2003) used iron bearing additives and proved that they are effective at adsorbing heavy metals including arsenic. The amendments used were goethite (alpha-FeOOH), iron grit (particle size 2–4 mm diameter), iron (II) sulfate heptahydrate (98%) + lime, iron (III) sulfate pentahydrate + lime and lime on its own. These compounds were added at 1% w/w to contaminated soils. Results showed that iron oxide decreased the soluble arsenic concentration and the efficiency of arsenic adsorption was in the order $Fe^{+3} > Fe^{+2} >$ iron grit > goethite > lime. Untreated soil leached 3077 μg kg^{-1} arsenic that was reduced to 524 μg kg^{-1} in iron (III) amended soil. Similarly, the leachate arsenic concentration was reduced from 18331 μg kg^{-1} to 2330 μg kg^{-1} with addition of iron (III) in another soil. Warren and Alloway (2003) used the vegetables beetroot, spinach, calabrese, cauliflower, lettuce, potato and radish for pot experiments with a 0.5% w/w Fe oxides as ferrous sulfate amendment applied to a soil contaminated with 577 mg As kg^{-1}. The results showed a prominent reduction in the bioavailability of arsenic. When the rate of application of ferrous sulfate was increased from 0.5% to 1% it did not give any further significant decrease in arsenic bioavailability. With the exception of spinach, the authors observed that ferrous sulfate treatment caused a reduction in bioavailability of As in some part of the crops. A 0.2% iron oxide application provided as ferrous sulfate in solution caused an average 22% reduction in As uptake. The authors have observed a side effect on application of ferrous sulfate as it liberated H_2SO_4 when it reacted to form Fe oxides. This induced mobilization of manganese from the two trial soils. Lime was applied to counter the generated acidity in order to avoid excessive mobilization of soil manganese.

In summary, these studies demonstrate that iron-rich compounds are effective at immobilizing arsenic in the soil. Ferrous sulfate and amorphous iron oxide have a proven high adsorptive capacity for soil arsenic. It has been showed that the application of iron oxides, especially from ferrous sulfate, which precipitates to give hydrous Fe oxides, was shown to reduce extractable arsenic from contaminated soils. Use of different combinations of iron compounds with other materials such as lime and zeolites has also been shown to immobilize metals and is worthy of future research.

C. Red Mud

Another industrial waste by-product that could potentially be used for remediation of heavy metals is red mud. Red mud is produced during the refining of bauxite to alumina through the Bayer's process. It is highly alkaline in nature and is composed of hematite (Fe_2O_3), boehmite (-AlOOH), quartz (SiO_2), sodalite ($Na_4Al_3Si_3O_{12}Cl$) and gypsum ($CaSO_4.2H_2O$).

The high iron oxide content in red mud makes it efficient in removing the toxicity and reducing the mobility of heavy metals. Due to the residual caustic soda used in the extraction process, red mud has a very high pH (>11), which causes strict constraints on disposal. One possibility for its utilization is its application to agricultural land, especially where soils are very sandy and have poor phosphorus retention capabilities. It has been shown (Vlahos et al., 1989) that red mud could be neutralized with gypsum (from phosphate industry) or ferrous sulfate (from titanium dioxide industry) and then used for controlling phosphorus leaching. Brunoi et al. (2005) have also shown that red mud can be used for the remediation of contaminated land after adequate neutralization. The use of red mud on contaminated soils for promoting plant growth and reducing the bioavailability, mobility and plant toxicity of heavy metals has been studied by various researchers (Brunoi et al., 2005; Friesl et al., 2003; Summers et al., 1996; Zhao et al., 2004; Hartley et al., 2004; Warren and Alloway, 2003; Illera et al., 2004; Lombi et al., 2004).

Brunoi et al. (2005) studied the immobilization capacity of red mud using metal trapping studies and leaching experiments on the trapped metals. For metal trapping studies, the concentration of elements in the solution was: As $500\mu g\ l^{-1}$, Cd 450 $\mu g\ l^{-1}$, Cu 550 $\mu g\ l^{-1}$, Mn 1200 $\mu g\ l^{-1}$, Ni 700 $\mu g\ l^{-1}$ and Zn 4200 $\mu g\ l^{-1}$. Solution pH was maintained at 5 throughout the leaching experiments and two solid/liquid ratios (2 g l^{-1} and 10 g l^{-1}) of treated red mud were studied. Both unwashed and washed treated red mud were used for metal trapping studies. Their results demonstrated that using a 2 g l^{-1} amendment of treated red mud caused a reduction in solution of $>99\%$ Zn and Cd, $>94\%$ Ni, Co, Cu and up to 80% Mn. However, only 30% As removal was observed. No marked difference was observed between the washed and unwashed treated red mud materials. The metal immobilization capacity increased with increase in concentration of treated red mud in solution with the 10 g l^{-1} amendment removing up to 70% arsenic as opposed to 35% with the 2 g l^{-1} amendment. Surface chemical adsorption was thought to be the responsible mechanism for As removal, as it is present as an oxy-anion in solution. In the second set of experiments deionized water was added to the dried red mud powder (Liquid/Solid ratio = 8) from the trapping studies and the metal concentration in the supernatant was analyzed after 15 and 60 minutes. In both treated and untreated red mud, less than 6% of As, Cd and Cu and 10–30% of Mn and Zn were leached. This confirmed the hypothesis that the metals that are sorbed are not easily exchangeable.

Table 3
Observations on metal immobilising capability of industrial waste-by products

Immobilisation agent	Application rate	Observation
Red mud *Brunoi et al.* (2005)	1% 10 g/l	Zn and Cd in excess of 99%; Ni, Co and Cu in excess of 94% and 80% of Mn were immobilised. 70% arsenic was removed as opposed to 35% with 2 g/l.
Red mud Zeolite Lime *Friesl et al. (2003)*	1% 2% 3%	Metal extractability due to red mud was 70% for Cd, 89% for Zn, 74% for Ni and plant uptake in the treatment was reduced by: 38–87% for Cd, 50–81% for Zn, 66–87% for Ni when compared to the control.
Red mud *Zhao et al. (2004)*	3% 5%	Complete grass cover observed on 5% treated pots. Decrease in metal concentration of Ni, Cu, Zn and Cd.
Water treatment sludges A and B (WTS-A&B) Red mud Red gypsum *Lombi et al. (2004)*	2%	WTS-A improved lettuce growth. WTS-B, red mud and red gypsum improved rye grass growth. Extractable copper concentration decreased by 84%.
Ferrous sulphate *Warren and Alloway (2003)*	0.5%	Vegetables grown for bioavailability test were spinach, beetroot, calabrese, cauliflower, lettuce, potato and radish. With 0.2% addition, arsenic bioavailability reduced by 22% in all except spinach.
Phosphogypsum Red gypsum Dolomitic residue *Illera et al. (2004)*	1%	Red gypsum and phosphogypsum showed 98% reduction of Pb from the metal spiked solution. Red gypsum showed a 9% decrease in copper and phosphogypsum showed less than 1% decrease in copper concentration from the solution. Cd concentration was decreased by 2.4% and 6.5% by phosphogypsum and red gypsum respectively.

Similarly, Zhao et al. (2004) reported a significant decrease in Zn, Ni, Cd, Cu of grass grown on soil treated with red mud. The soil was contaminated with Zn (3954 mg/kg), Pb (3776 mg/kg), and Cd (78 mg/kg) and was supporting very sparse vegetation. Red mud was applied to the top soil at either 3% or 5% (w/w) and compared with both lime (applied to give a similar soil pH) and the control (no amendment). Grass was grown and metal concentration in leaves was measured. Complete grass cover was observed on the 5% red mud treated plots with a significant decrease in Zn, Ni, Cd, Cu in grasses of the treated soil compared to the untreated control. Similar improvements in plant growth were also observed by Summers et al. (1996) using red mud untreated or treated with gypsum at 0, 10, 20, 40 and 80 t/ha added to an uncontaminated subterranean clover (*T. subterraneum*) and rye grass (*L. rigidum*) paddock. The authors noted that an application of 40 t/ha of red mud increased hay (subterranean clover and rye grass) production by 24%.

Apart from using red mud as a single amendment, research has also been undertaken using a combination of waste and naturally occurring materials (Illera et al., 2004; Lombi et al., 2004; Friesl et al., 2003). Friesl et al. (2003) studied the effect of red mud (10 g kg^{-1}), zeolite (20 g kg^{-1}) and lime (3 g kg^{-1}) on metal lability in soil and its uptake by the grass fescue (*Festuca rubra* L.) and amranthus (*Amaranthus hybridus* L). Soil samples were collected from various sites in Austria, out of which one site was a former Pb-Zn smelter polluted with Pb (12300 mg kg^{-1}), Zn (2713 mg kg^{-1}) and Cd (19.7 mg kg^{-1}). Other non-contaminated soils were spiked with Zn (700 mg kg^{-1}), Cu (250 mg kg^{-1}), Ni (100 mg kg^{-1}), V (100 mg kg^{-1}) and Cd (7 mg kg^{-1}). The plants were grown for 15 months and an ammonium extraction (1 M) was used in a soil: solution ratio of 1:2.5 for detecting the influence of the soil amendments on the labile nature of metals. The results showed that the metal extractability due to red mud was 70% for Cd, 89% for Zn, and 74% for Ni in the spiked sandy soil and plant uptake in this treatment was reduced by 38–87% for Cd, 50–81% for Zn, and 66–87% for Ni when compared to the control.

The important observations by various researchers on the use of red mud can be seen in Table 3. In summary, it was evident from the above experiments that iron-rich compounds are a potential source of remediating metal-contaminated soils. Red mud is one such compound, which is receiving a great deal of attention from researchers for its ability at decreasing metal lability in soils and thereby reducing plant uptake of heavy metals. Red mud has a number of flocculants and potential adsorbents and consists of abundant fine Fe particles. The alkalinity and the solid phases in it are responsible for adsorption and fixation of metals in soil. Red mud as used for metal-trapping studies shows that the trapping mechanism was different for different metals, which is dependant on factors like the speciation of metal in solution, formation of oxyanions, formation of complexes, etc. It was also clear from the leaching experiments conducted on the red mud that it is safe for reuse as the metals sorbed by the red mud are not easily exchangeable. Care should be taken that alkalinity is reduced before it is used for soil remediation as high alkalinity affects stability of organic matter through oxidation. Application of untreated alkali red muds may therefore promote the leaching and increase the solubility of the metals that formed stable complexes with organic matter.

4. Conclusion

Application of organic wastes (sewage sludge, biosolid compost and green waste) has been shown to immobilize metals and increase the above-ground biomass of plants. Lime and manure, when added with composted organic amendments, increase the soil pH, which favors metal immobilization.

Natural zeolites also have potential for metal immobilization due to their high ion exchange capacities and highly porous structures. Most published research showed that clinoptilolite was most effective in immobilizing lead and cadmium in soils. Care should be taken when using zeolites with high sodium content as they have been shown to increase soil salinity and exchangeable sodium concentrations, which could cause plant toxicity.

Synthetic zeolites have been shown to be effective at reducing soil phytotoxicity and improving plant growth. Zeolite used as a soil conditioner can reduce the need for fertiliser whilst improving plant growth.

Soil amendment with red mud and other iron-rich compounds has been shown to immobilize labile metals. At higher concentrations, red mud has been shown to be especially effective at reducing arsenic bioavailability and improving plant performance.

Red gypsum and phosphogypsum showed a good ability to adsorb Pb more than any other metal. Similarly, phosphate-based amendments, especially apatites, have been shown to be very good at immobilizing Pb from soil. Overall, iron-rich compounds are found to immobilize arsenic better than any other soil amendment. This gives us a scope to explore the potential of other iron-rich industrial waste-by products for metal immobilization and greening application purposes.

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