Use of inorganic and organic wastes for in situ immobilization of Pb and Zn in a contaminated soil

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Abstract
The effectiveness of five waste materials (blast furnace slag, water treatment sludge, red mud, sugar mill mud and green waste compost) as metal immobilizing agents in a Pb- and Zn-contaminated soil was investigated. Materials were incubated with the soil for a period of 12 weeks at rates of 5 and 10% w/w. Addition of blast furnace slag, water treatment sludge and red mud markedly reduced EDTA-extractable Zn levels, while additions of water treatment sludge, red mud and mill mud reduced EDTA-extractable Pb concenbtrations. A sequential extraction procedure revealed that reductions in acetic acid-extractable (exchangeable and adsorbed) Pb induced by additions of mill mud and compost were accompanied by increases in the oxidisable (organic) and residual Pb fractions. For Zn, reductions in the percentage present in the exchangeable/adsorbed and organic fractions following additions of water treatment sludge, red mud and mill mud were accompanied by increases in the percentages present in the residual fraction. Materials such as water treatment sludge, red mud, mill mud and blast furnace slag showed good potential as immobilizing agents.

Key Words
Metal immobilization; metal fixation; heavy metals; lead; zinc.

Introduction
Contamination of soils with heavy metals is of environmental concern because the accumulated metals may adversely affect soil ecology, agricultural production, product quality, animal and human health as well as groundwater quality (Adriano *et al*. 2001). Indeed, unlike organic contaminants, most heavy metals do not undergo microbial or chemical degradation and therefore total concentrations and ecotoxicological effects persist for very long periods after their introduction to the soil. The traditional method of treating metal-contaminated soil is to excavate it and transport it to landfill. In addition, processes have been developed for removing metals from soils including solute extraction, ion exchange and electrode deposition (Virkutye *et al*. 2002; Khan *et al*. 2004; Dermont *et al*. 2008). Such methods are generally expensive, can be environmentally invasive, may generate additional risks to operators and may produce secondary waste. Low cost, non-invasive, technologies are required for large areas of metal-contaminated soils. A major driving force for the need for removal techniques is that, in general, throughout the world, acceptable metal limits in soils are based on total metal concentrations. However, there is a trend towards the development of new approaches based on site-specific risk assessment, in which the necessity for remediation is linked to human health and/or ecological risks associated with the contaminated site. Within such new regulation frameworks, in situ immobilization is an attractive remediation option.

In situ immobilization relies on the addition of an amendment to a contaminated soil which increases the proportion of total metal burden within the intransigent solid phase, either by increased metal precipitation or sorption, thereby reducing the soluble and exchangeable metal fractions. That is, the contaminant metals are not removed from the site but rather transformed into forms less biologically available. Waste materials trialled as immobilizing agents include fly ash, blast furnace slag, steel slag, red mud, bark/sawdust, composted wastes and animal manures (Martin and Ruby 2004; Guo *et al*. 2006; Kumpiene *et al*. 2008). The purpose of this study was to investigate the effectiveness of five waste materials (blast furnace slag, water treatment sludge, red mud, mill mud and green waste compost) as immobilizing agents for Pb and Zn in a metal-contaminated soil.

Materials and methods
The study soil, classified as a Calcarosol, was excavated from the 0-10 cm layer in the Port Pirie region of South Australia. It had a pH of 8.1, EC of 183 uS/cm and a sand, silt and clay content of 78, 11 and 11 % respectively. It was contaminated with Pb and Zn which originates from airborne particles from a Pb/Zn

smelter nearby. The air-cooled blast furnace (BF) slag was sourced from Bluescope Steel, alum water treatment (WT) sludge from SEQWater (Mt Crosby Station), seawater-neutralized bauxite processing residue mud (red mud) from Virotech International, sugar mill mud from the Millaquin Sugar mill (Bundeburg Sugar) and greenwaste compost from Phoenix Power recyclers.

The five materials were added to the soil (3 replicates per treatment) at 5 and 10% w/w. Amendments were thoroughly mixed with soil samples (1L), placed in 2 L plastic containers and rewetted to 70% of water holding capacity. The containers were arranged in a randomized block design and incubated at room temperature (24-30 ºC) for 12 weeks. Containers were opened and mixed each week to ensure adequate aeration. At the end of the incubation time samples were randomly taken from each container and air-dried prior to chemical analysis.

Total metal content of soils was analysed by microwave digestion in HNO_3, HF and HCl (5:3:2 ratio) and Pb and Zn were analysed by ICP-AES. The extractable fraction of Pb and Zn were extracted with 0.5 M EDTA (1:5 soil:solution ratio for 1 h) and metals in the extracts were analysed by ICP-AES. A three-step modified BCR sequential fractionation procedure was applied to the soils as described by Rauret *et al.* (1999). This extracted the "exchangeable and weak acid soluble fraction" (0.11 M acetic acid; 1:40 soil:extractant ratio for 16 h.), "reducible fraction" (0.5 M hydroxylammonium chloride; 1:40 soil:extractant ratio for 16 h.) and the "oxidisable fraction" (digested twice with 8.8 M hydrogen peroxide; 1:10 soil:extractant ratio). Amounts of metals present in the residual, non-extractable, fraction were calculated by subtraction of the total extractable metals from the total soil metal contents.

Results and discussion
For BF slag (predominantly calcium silicate; akermanite/gehlenite), water treatment sludge (mainly amorphous hydroxyl Al) and red mud (predominantly iron oxide; hematite with some sodalite) the main mechanisms of immobilization of metals are through specific adsorption/surface precipitation onto their inorganic surfaces. Mill mud (filter press mud) is produced when $CaCO_3$ is added to heated sugar cane juice as a flocculant and precipitated organic matter is then filtered in presses. Thus, immobilization may occur through adsorption to $CaCO_3$ surfaces and complexation with organic matter. For compost the main mechanism will be complexation to humified organic matter. Although a liming effect can be an important immobilizing reaction, the study soil already had a high pH (i.e. pH_{CaCl_2} = 8.1) so such an effect was probably not of great significance. Nonetheless, additions of BF slag and red mud did raise pH. That is, values for pH_{CaCl_2} at the 10% level of addition for the BF slag, WT sludge, red mud, mill mud and compost treatments were 8.7, 7.7, 8.9, 8.4 and 7.7 respectively.

In interpreting the results of this study it is important to note that Pb is sorbed to inorganic soil colloids (e.g. Fe and Al oxides) by specific adsorption more strongly than Zn and, in addition, Pb has a much greater affinity for organic soil colloids (e.g. humic material) than Zn (McBride 2000; Bradl 2004). Thus, acetic acid (which extracts metals mainly from inorganic fractions) extracted a greater amount of Zn than Pb whilst EDTA (an organic matter extractant) extracted a greater amount of Pb (Figures 1 and 2). Because the two extractants extract metals from different pools they did not necessarily show the same trends with addition of different amendments. That is, both EDTA and acetic acid extractable Zn were decreased by additions of BF slag, WT sludge and red mud, but while acid-extractable Zn was reduced by mill mud additions, EDTA extractable Zn was not (Figures 1 and 2). This may be due to EDTA extracting Zn held to organic fractions on the mill mud surfaces. Similarly, mill mud and compost were effective agents for decreasing acid-extractable Pb. However, when EDTA was used as an extractant, these agents (particularly compost) were much less effective since EDTA extracts Pb from organically - bound fractions. Nonetheless, EDTA-extractable Pb was also appreciably reduced by additions of WT sludge and red mud.

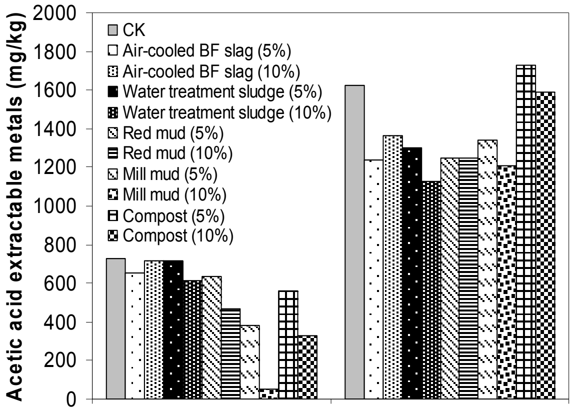

Figure 1 Effect of incubation of a contaminated soil with five waste materials on EDTA-extractable Pb and Zn

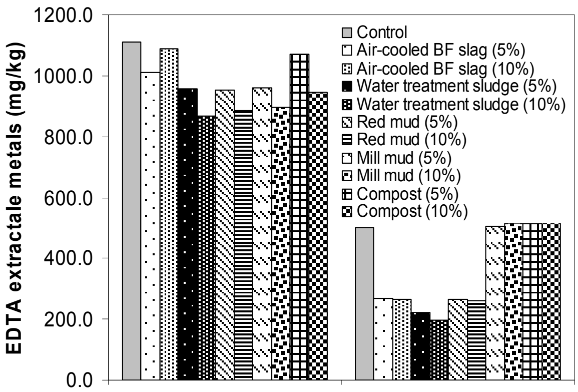

Figure 2 Effect of incubation of a contaminated soil with five waste materials on acetic acid-extractable Pb and Zn

Many limitations surround sequential fractionations since they are semi-quantitative and not completely selective, open to redistribution and only operationally defined. They are, however, considered the best available method of gaining knowledge on the forms in which metals are present in soils. The simple fractionation procedure used here showed that for Pb, large reductions in the percentage present in exchangeable/adsorbed (acetic acid extractable) fraction when mill mud and compost were added were accompanied by concomitant increases in those present in the organic (oxidisable) and residual fractions (Table 1). For Zn, reductions in the percentage present in the exchangeable/adsorbed fraction induced by additions of WT sludge, red mud, and mill mud were accompanied by reductions in the percentages present in the organic fraction and large increases in those present in the residual fraction (Table 2). Where predominantly inorganic materials (BF slag, WT sludge, red mud) were added, increases in the residual fraction were probably as a result of adsorbed metals undergoing slow reactions (i.e. diffusion into adsorbent surfaces and occlusion by precipitation) and becoming less extractable. For the addition of compost and mill mud, the increases in Pb in the residual fraction (Table 1) are probably related to Pb becoming very strongly chelated by stable organic material.

Table 1. Sequential extraction of Pb from a contaminated soil after incubation with five waste materials

Treatments	*Acetic acid extractable (%)*	*Reducible (%)*	*Oxidizable (%)*	*Residual (%)*
CK	30	11	6	53
BF slag	29	11	7	52
WT sludge	25	11	5	59
Red mud	19	14	4	62
Mill mud	2	18	11	69
Compost	14	11	10	66

Table 2. Sequential extraction of Zn from a contaminated soil after incubation with five waste materials

Treatments	*Acetic acid extractable (%)*	*Reducible (%)*	*Oxidizable (%)*	*Residual (%)*
CK	25	13	13	49
BF slag	21	10	12	57
WT sludge	17	13	4	65
Red mud	19	16	5	60
Mill mud	19	14	9	58
Compost	24	13	9	54

Conclusions

Of the waste materials trialled as immobilizing agents, WT sludge, red mud and mill mud seemed most effective for Pb and BF slag, WT sludge and red mud most effective for Zn. However, for immobilization to be an effective remediation strategy bioavailable metals must be reduced in the long-term. For that reason the experiment will be sampled again after one-years reaction time of the amendments with the soil. In addition plant growth/metal uptake and soil microbial activity will be examined at that time.

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