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## **Solute Interactions in Soils in Relation to Bioavailability and Remediation of the Environment**

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Unlike organic contaminants, most metals do not undergo microbial or chemical degradation and the total concentration of these metals in soils persists for a long time after their introduction (Adriano, 2003). With greater public awareness of the implications of contaminated soils on human and animal health there has been increasing interest amongst the scientific community in the development of technologies to remediate contaminated sites. For diffuse distribution of metals (e.g. fertilizer-derived Cd input in pasture soils), remediation options generally include amelioration of soils to minimize the metal bioavailability. Bioavailability can be minimized through chemical and biological immobilisation of metals using a range of inorganic compounds, such as lime and phosphate (P) compounds (e.g. apatite rocks), and organic compounds, such as 'exceptional quality' biosolid (Figure 1; Bolan and Duraisamy, 2003). Reducing metal availability and maximizing plant growth through inactivation may also prove to be an effective method of *in situ* soil remediation on industrial, urban, smelting, and mining sites.

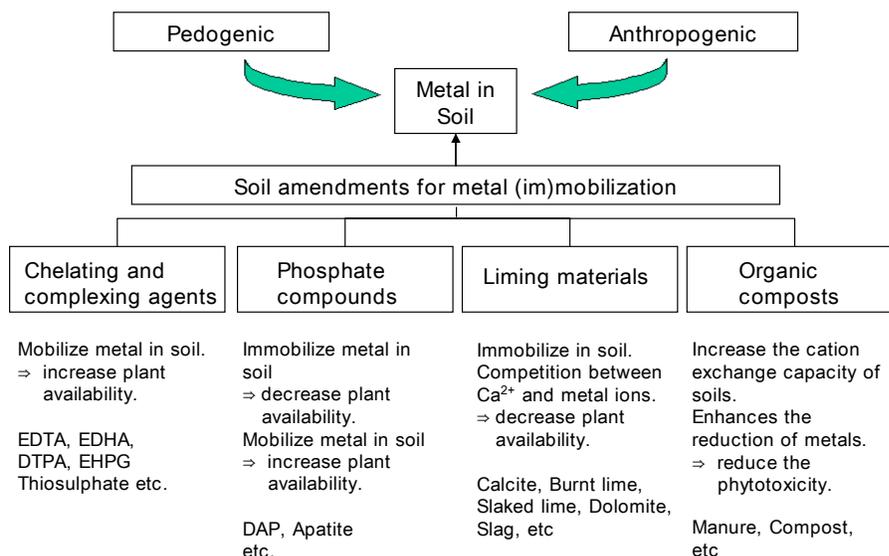
The more localised metal contamination found in urban environments (e.g. Cr contamination in timber treatment plants) is remediated by metal mobilization processes that include bioremediation (including phytoremediation) and chemical washing. Removal of metals through phytoremediation techniques and the subsequent recovery of the metals (i.e. phytomining) or their safe disposal are attracting research and commercial interests. However, when it is not possible to remove the metals from the contaminated sites by phytoremediation, other viable options, such as *in-situ* immobilisation should be considered as an integral part of risk management.

Since bioavailability is a key factor for remediation technologies *in-situ* (im) mobilization using inorganic and organic compounds that are low in heavy metal content may offer a promising option. In this paper, after a brief introduction of sources of metal inputs and their dynamics in soils, the role of various inorganic and organic soil amendments in the (im) mobilization of metals in soils in relation to managing their bioavailability and remediation, will be discussed.

The bioavailability of a chemical in the soil environment has been defined as the fraction of the total contaminant in the interstitial pore water (i.e., soil solution) and soil particles that is available to the receptor organism (Naidu et al., 2008). Bioavailability of metals in soils can be examined using chemical extraction and bioassay tests. Chemical extraction tests include single extraction and sequential fractionation (Ruby *et al.*, 1996; Basta and Gradwohl, 2000). Bioassay involves plants, animals and microorganisms (Yang *et al.*, 1991).



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*In-situ* techniques involving growing of the organisms of interest in the contaminated material and quantifying the uptake of metal into the organism or assessing the toxicological response are being used by many researchers as bioindicators of contamination. Measurements of metal bioavailability and toxicity in soils using soil microorganisms are receiving increasing attention, as microorganisms are more sensitive to heavy-metal stress than plants or soil macrofauna. The methods using microflora and protozoa have the potential to provide a measure of bioavailability of heavy metals in the short-term and even facilitate the measurement of temporal changes. In contrast responses by mesofauna (microarthropods) and macrofauna (enchytridae, invertebrates and earthworms) are cumulative effects.

A number of amendments are used either to mobilise or immobilize heavy metals in soils (Table 1). The basic principle involved in the mobilization technique is to release the metals in to soil solution, which is subsequently removed using higher plants. In contrast, in the case of the immobilization technique the metal concerned is removed from soil solution either through adsorption, complexation and precipitation reactions, thereby rendering the metals unavailable for plant uptake and leaching to groundwater.

Since one of the primary objectives of remediating contaminated sites is to reduce the bioavailability of metals, *in-situ* immobilization using soil amendments that are low in heavy metal content may offer a promising option. However, a major inherent problem associated with immobilisation techniques is that although the heavy metals become less bioavailable, their total concentration in soils remains unchanged. The immobilised heavy metal may become plant available with time through natural weathering process or through breakdown of high molecular weight organic-metal complexes. Although the formation of soluble metal-organic complexes reduces the phytoavailability of metals, the mobility of the metal may be facilitated greatly in soils receiving alkaline-stabilized biosolid because of the reduction of metal adsorption and increased concentration of soluble metal-organic complex in solution.



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**Table 1.** Selected references on the potential value of soil amendments in the (im) mobilization of metals in soils.

Amendments <sup>#</sup>	Metal	Observations	References <sup>\$</sup>
<b>Chelating /complexing agents</b>			
Thiosulphate	Hg	Shoot Hg accumulation in the presence of thiosulphate salt was dependent upon plant species characteristic and humic acid content	Moreno <i>et al.</i> (2004)
EDTA	Cu	Mobilized and increased plant uptake	Thayalakumaran <i>et al.</i> (2003b)
EDTA	Cu, Fe, Mn, Pb, Zn	EDTA had only a limited effect on metal uptake by plants	Walker <i>et al.</i> (2003)
EDTA	Pb	Plant uptake in roots and shoots increased	Chen <i>et al.</i> (2004)
Humic acid	Cd	Plant uptake enhanced significantly	Evangelou <i>et al.</i> (2004)
EDTA	Cd	Mobilized Cd in soil, but did not increase plant total uptake	Jiang <i>et al.</i> (2003)
CCA EDTA	Pb, Zn	CCA improved bioavailability in soil, enhanced shoot content of Pb but not of Zn	Li <i>et al.</i> (2005)
<b>Phosphate compounds</b>			
KH <sub>2</sub> PO <sub>4</sub>	Cd	Enhanced immobilization, decreased plant availability	Bolan <i>et al.</i> (2003c)
Apatate, Zeoilte, Fe-Oxide	Cd, Pb	Reduced the mobility and uptake by plant	Chlopecka <i>et al.</i> (1997)
KH <sub>2</sub> PO <sub>2</sub>	Pb, Zn, Cd	Reduced Pb level but not Zn and Cd in earthworms	Pearson <i>et al.</i> (2000)
Phosphate	As	Increasing phosphate supply decreased As uptake. Increasing As supply decreased the P concentration in the root	Wang <i>et al.</i> (2002)
Phosphate	Pb, As	Increased plant uptake of soil As. No effect on soil Pb phytoavailability	Creger <i>et al.</i> (1994)
<b>Liming materials</b>			
Ca(OH) <sub>2</sub>	Cd	Transformed to less mobile fractions, reduced phytoavailability	Bolan <i>et al.</i> (2003d)
Lime, FBA, Bark	Cr	Reduced the availability for plant uptake and leaching ground water	Bolan <i>et al.</i> (2001)
Lime	Cd	Did not reduce uptake and transfer to the kernels of sunflower	Li <i>et al.</i> (1996)
Lime	Cd	Reduced uptake by lettuce	Lehoczhk <i>et al.</i> (2000)



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Lime	Pb, Cd	Decreased Cd uptake, but little influence Pb uptake by radish	Han <i>et al.</i> (1996)
Ca(OH) <sub>2</sub> , CaCO <sub>3</sub>	Cd	Ca(OH) <sub>2</sub> prevented phytotoxicity, but CaCO <sub>3</sub> was no effective in reducing phytotoxicity	Chaney <i>et al.</i> (1977)
Lime	Cd, Ni, Zn, Cu	Reduced uptake of Cd, Ni, Zn, but did not reduce Cu	Brallier <i>et al.</i> (1993)
<b>Organic matter</b>			
Biosolid	Cd	Reduced the bioavailability	Bolan <i>et al.</i> (2003b)
Biosolid, Manure	Cr	Reduced the phytotoxic effect	Bolan <i>et al.</i> (2003e)
PS, SS	Cd, Zn	Cd uptake increased, but Zn unaffected	Merrington <i>et al.</i> (2000)
Biosolid Manure	Cd Zn, Mn	Reduced plant availability Corn and leaf concentrations of Zn and Mn were enhanced	Brown <i>et al.</i> (1998) Wallingford <i>et al.</i> (2000)
Biosolid	Zn	Decreased plant availability	Shuman <i>et al.</i> (2000)
Biosolid	Cd	Cl-complexation of Cd increased the phytoavailability of Cd in biosolid amended soil	Weggler-Beaton <i>et al.</i> (2000)
Organic matter	Ni, Cd, Zn	Reduced Ni uptake but not Cd, Zn in rice	Kashem <i>et al.</i> (2000)
Compost, Manure	Cr	Reduced the phytotoxicity	Bolan <i>et al.</i> (2003g)

<sup>#</sup>EDTA, ethylene diaminetetra-acetic acid; CCA, coated chelating agent; FBA, Fluidised bed boiler ash; PS, Papermill sludge; SS, Sewage sludge

<sup>§</sup>Adopted from Bolan *et al.* (2008)

A large number of studies have provided conclusive evidence for the potential value of both water-soluble and water-insoluble P compounds to immobilize metals in soils, thereby reducing their bioavailability for plant uptake. However, it should be recognized that, depending on the nature of P compounds and the heavy metal species, application of these materials could cause either mobilization (e.g., As) or immobilization (e.g., Pb) of the metals. While mobilization by certain P compounds enhances the bioavailability of metals, immobilization inhibits their plant uptake and reduces their transport in soils and subsequent ground water contamination. Furthermore, some of these materials contain high levels of metals (e.g., Cd) and can act as an agent of metal introduction to soils. Accordingly, these materials should be scrutinized prior to their large-scale use as immobilizing agent in contaminated sites.

**Keywords:** Phytoremediation; heavy metals; soil remediation



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### **References**

- Adriano, D.C. (2001). Trace Elements in Terrestrial Environments; Biogeochemistry, Bioavailability and Risks of Metals, 2<sup>nd</sup> Ed. *Springer – New York, NY*.
- Basta, N.T. and Gradwohl, R. (2000). *J. Soil. Cont.* 9: 149-164.
- Bolan, N.S. and Duraisamy, D. (2003). *Aust. J. Soil Res.* 41: 533-555.
- Bolan, N.S., Ko, B.J., Anderson, C.W.N., Vogeler, I., Mahimairaja, S. and Naidu, R. (2008). Manipulating bioavailability to manage remediation of metal contaminated soils. In: *Chemical Bioavailability in Terrestrial Environment*. (Eds. Naidu et al). Elsevier, Amsterdam, The Netherlands. ISBN 978-0-444-52. pp 657-678
- Naidu, R., Semple, K.T., Megharaj, M., Juhasz, A.L., Bolan, N.S., Gupta, S., Clothier, B., Schulin, R. and Chaney, R. (2008). Bioavailability, Definition, Assessment and Implications for Risk Assessment. In: *Chemical Bioavailability in Terrestrial Environment*. (Eds. Naidu et al). Elsevier, Amsterdam, The Netherlands. ISBN 978-0-444-52. pp 39-52
- Ruby, M.V., Davis, A., Schoof, R., Eberle, S. and Sellstone, C.M. (1996). *Environ. Sci. Technol.* 30: 420-430.
- Yang, J.E., Skogley, E.O., Georgitis, S.J., and Ferguson, A.H. (1991). *Soil Sci. Soc. Am. J.* 55: 1358-136