BIOTRANSFORMATION OF HEAVY METAL(LOID)S IN RELATION TO BIOAVAILABILITY AND REMEDIATION

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Metal(loid) Input and Dynamics in Soil

Soil represents a major sink for heavy metal(loid)s released into the biosphere through both geogenic (i.e., weathering or pedogenic) and anthropogenic (i.e., human activities) processes. The dynamics of heavy metal(loid)s in soils depend not only on their physico-chemical interactions with soil constituents, but also on biological interactions largely associated with the microbial activities of soil-plant systems (Adriano, 2001). Microorganisms control the transformation (microbial or bio-transformation) of metal(loid)s by various mechanisms that include oxidation, reduction, methylation, demethylation, complex formation, and biosorption (Alexander, 1999; Bolan et al., 2013a). This paper includes case studies covering the various processes involved in the biotransformation of heavy metal(loid)s in relation to bioavailability and remediation.

Biotransformation in Relation to Bioavailability and Remediation

Microbial transformation plays a key role in the behaviour and fate of toxic metal(loid)s, especially As, Cr, Hg, and Se in soils and sediments. Biotransformation processes can influence the solubility and subsequent mobility of these metal(loid)s in soils by altering their speciation and oxidation/reduction state (Gadd, 2010). These processes play a major role in controlling in the bioavailability, mobility, ecotoxicology, and environmental health of these metal(loid)s. For example, microbial reduction/methylation of metal(loid)s and its consequences to human health received attention primarily from a series of widespread poisoning incidents including (i) 'Gasio-gas' poisoning resulted from converting arsenic trioxide in wallpaper glue into volatile poisonous trimethyl arsine or 'Gasio-gas' (Adriano et al., 2004) and (ii) the more recent, As contamination of surface- and ground-waters, mediated through redox reactions of geogenic As (Mahimairaja et al., 2005). Microbial reduction and methylation reactions have also been identified as important mechanisms for detoxifying toxic elements (Zhang and Frakenberger, 2003). These processes are particularly important for elements like As, Hg, and Se that are able to form methyl or metal(loid)-hydride compounds. Thus, a greater understanding of biotransformation processes will help to monitor the fate of metal(loid)s, particularly through the food web, and will help to develop *in situ* bioremediation technologies that are environmentally compatible.

A Case Study on Rhizoreduction of Chromate and Arsenate

Rhizosphere influences the dynamics of nutrients and contaminants through increased microbial activity, release of root exudates, and alteration of pH. The aim of this study was to evaluate the rhizosphere-induced reduction (i.e., rhizoreduction) and redistribution of arsenate [As(V)] and chromate [Cr(VI)] in Australian native vegetation in relation to their bioavailability (Bolan et al., 2013b). The reduction of As(V) and Cr(VI) was examined using rhizosphere soils from a number of Australian native vegetation

(*Acacia pubescens*, *Eucalyptus camaldulensis*, *Enchylaena tomentosa*, *Templetonia retusa*, *Dichantheum sericeum*, and *Austrodanthonia richardsonii*). Field contaminated As and Cr soils were used to examine the effect of *D. sericeum* on the redistribution and bioavailability of As and Cr. Rhizosphere soil contained higher levels of microbial activity, dissolved organic carbon, and organic acid content than the non-rhizosphere soil. The rhizosphere soil caused up to 2.41 and 5.07 fold increases in the reduction rate of As(V) and Cr(VI), respectively. A significant relationship between rhizosphere-induced increases in microbial activity (Δ basal respiration) and As(V) and Cr(VI) reduction (Δ rate of reduction) indicated the role of increased microbial activity in rhizosphere soil on metal(loid) reduction. *D. sericeum* enhanced the reduction of metal(loid)s in the contaminated soils, thereby increasing the bioavailability of As but decreasing that of Cr. Depending on the nature of metal(loid)s present in soil, the rhizosphere-induced reduction has implications to both their bioavailability to higher plants and microorganisms, and remediation of contaminated soils. While rhizoreduction decreases Cr bioavailability it increases that of As.

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