

The application of modified bio-sorbents to heavy metal[loid] contaminated soils

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Combining bio-sorbent materials together in a single soil amendment offers a way to simultaneously reduce the environmental mobility of co-occurring, geochemically dissimilar heavy metal[loid]s.

The risk assessment for contaminants in the environment can be summarised using a source-pathway-receptor model [1]. In the context of heavy metal[loid]s and their potential to cause environmental harm, remediation methods should seek to break the pathway between the source and receptor (see Figure 1). The complex geochemistry of soils means that a high concentration of metal[loid]s may not always be analogous to an increase in the risk to receptors. This is because metal[loid]s can be more or less strongly bound to different constituents of the soil matrix under different environmental conditions. By focusing remediation on those metal[loid]s that are weakly bound to the soil matrix, their mobility in the environment can be substantially reduced, and thus risk minimised [2]. It is possible to modify soils by adding bio-sorbents *in-situ* to ensure stability of the most weakly bound contaminants, reducing potential risk and avoiding the need for the removal and *ex-situ* soil treatments.

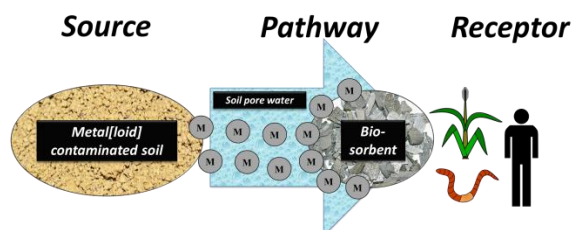


Figure 1: Diagrammatic representation of the role of bio-sorbents in addressing environmental risk posed by elevated metal[loid]s in soil pore water.

Mechanisms of heavy metal influence by bio-sorbents

A wide range of soil amendment materials that act as bio-sorbents have been extensively tested in both laboratory and field trials, including using composts, manures, sludges, digestates, activated and non-activated chars, etc. They may be used at various stages from source material to final product, and exhibit a wide range of physico-chemical compositions.

In general, oxygen containing functional groups at the surfaces of organic bio-sorbents result in a cation-exchange-capacity (CEC) greater than that of the soil they are added to. They act as a sink for metal ions in solution, limiting their leaching and/or uptake in plants. However, bio-sorbents contain compositional artefacts which limit their effectiveness in soils: organic materials often exhibit high concentrations of dissolved-organic-carbon (DOC) leaching; complexes of metals with organic ligands can result in the co-leaching of DOC-associated metals in solution; and many char-based sorbents have high residual ash content, which results in temporary precipitation of metal ions with mineral salts within the porous matrix of the pyrolysed source material until this ash fraction is washed out. This can also result in a reduction in pH, which impacts on metal[loid] mobility during the weathering of the sorbent in soils. Consequently, for a given sorbent material, there will be various mechanisms limiting the longevity of its effectiveness.

The particular problem of arsenic

The metal[loid] arsenic (As) presents contrasting responses when soil amendments are introduced, both because it is present as an anion and because its solubility and mobility generally increase at higher pH. This presents a problem since a high concentrations of As in soils at contaminated sites is often associated with the presence of heavy metals (for example mine sites, old

smelting and metal-working localities). This means that adding soil amendments which increase pH can liberate As into solution.

Iron (Fe) and manganese (Mn) oxide-based sorbents, whose positively charged surfaces attract As oxy-anions, have been successfully deployed to reduce arsenic mobility in soils and waters. Combining these metal oxides with organic-based sorbents has been trialled as a means of applying a ‘one-stop-shop’ sorbent for metal[loid] contaminated soil applications.

Case Studies

Case study 1: Mn-based amendment to a metal[loid] contaminated agricultural soil in UK

A coating of amorphous Mn-oxide on the surface of biochar produces a bio-sorbent with sites for anion and cation binding. This sorbent has been applied to three contaminated agricultural soils where As, Cr, Cu (from contaminated wood-ash application) and Zn (from contaminated sewage-sludge application) were present in high concentrations. In this laboratory pot test, pore water samples and ryegrass samples were analysed for metal[loid]s to determine their mobility and uptake, with and without bio-sorbent addition. Moderate reductions in metal[loid] concentration in pore water and ryegrass were achieved (see Figure 2), but enhanced Mn leaching and uptake was also evident (see Figure 2 inset), illustrating a potential limitation in the useful life of this sorbent in soil.

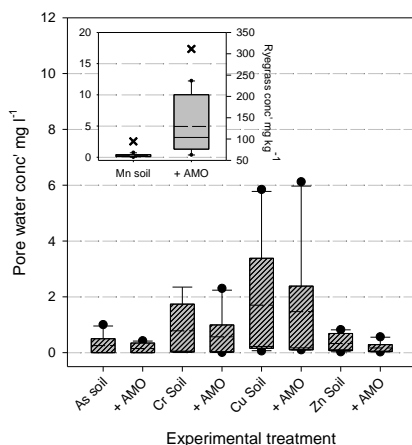


Figure 2: Mean (dashed line) and range of concentrations of metal[loid]s in pore water, as influenced by experimental bio-sorbent application. Inset shows Mn concentrations in pore water (box-plot) and ryegrass (crosses). $n=10$

Case study 2: Fe-based amendments to arsenic contaminated mine soil in Spain

A combination of iron sulphate, lime and organic amendments (biochar and composts) was applied to arsenic and copper contaminated mine soil which was subsequently sown with rye. The hypothesis was that organic matter would improve soil properties and retain metals, whilst a pH around neutrality would precipitate Fe oxides that were able to retain As. The co-applications of the three materials produced better plant growth, decreased metal availability and limited As mobilisation to a greater extent than individual applications (see Figure 3). It proved important to maintain the pH between 6 and 7 because an excess or deficiency of lime caused either arsenic or metal mobilisation respectively [3].

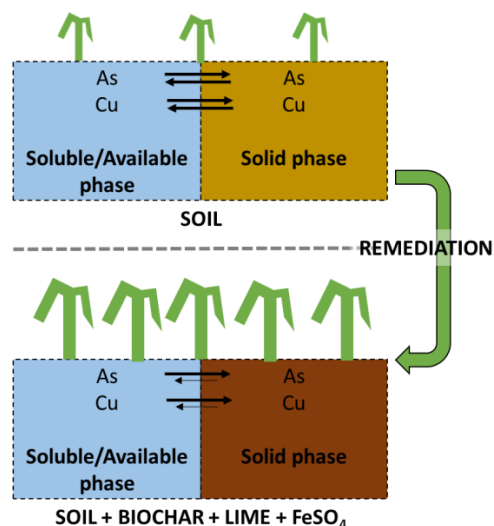


Figure 3: Schematic conceptual model of the effect of co-application of biochar, lime and iron sulphate to remediate a contaminated mine soil.

References

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