VALORISATION OF BY-PRODUCTS AND BIOCHAR TO REDUCE ARSENIC AND COPPER MOBILITY IN CONTAMINATED SOILS

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Introduction

Large amounts of arsenic and metals can be found in the surroundings of the waste piles accumulated during historical metal extraction. One of the strategies to remediate those soils is immobilising contaminants through the incorporation of industrial by-products and organic matter.

Methods

The study site is characterised by the presence of dumping tailings from a former and small arsenopyrite smelter located in an area named "El Verdugal" (Madrid, Spain). A composite sample of soil close to the waste pile (upper 20 cm) was taken, air-dried and sieved to 4 mm. Several amendments were added to soils in 1-L pots: 3% iron-rich cement waste (CEM), 20 % clay-rich material (CL) and 3% de-inking paper sludge+ 3% holm oak-biochar + 1% $FeSO_4$ (PBF). After 9 weeks, a part of soil was kept wet to perform ecotoxicological tests: dehydrogenase activity (Tabatabai, 1994), *Vibrio fischeri's* luminescence (ISO 11348-2, 1998) and screening test for *Phaseolus vulgaris* emergence (ISO 17126, 2005); another part was air-dried to analyse As and Cu (acid digestion and 0.1 M $(NH_4)_2SO_4$-extractable concentration) by fluorescence spectroscopy and atomic absorption spectroscopy respectively.

Results

Total As and Cu concentration were 252±12 and 459±7 $mg \cdot kg^{-1}$ respectively, higher than the reference values (24 and 80 $mg \cdot kg^{-1}$ of As and Cu respectively for Spanish legislation). All the materials have an alkaline pH (cement waste 8.12±0.06, paper sludge 7.63±0.03, biochar 10±0.01 and clay 8.26±0.06). Their effect was reflected in the evolution of soil pH over time. PBF was the only treatment that efficiently diminished As extractability. Increasing pH reduced the positive charge of minerals and arsenate becomes more negatively charged, so CEM and CL promoted a high concentration of extractable arsenic. In PBF, $FeSO_4$ provided the formation of new iron mineral phases and paper sludge buffered the acidity that $FeSO_4$ could have triggered when applied singly. In the literature, biochar was found to mobilise arsenic (Beesley et al., 2011), but its use in this experiment responds to the necessity of providing organic matter to the soil and acted in combination with paper sludge as liming agent. Cu extractability was reduced in every treatment. Both dehydrogenase activity and *V. fischeri* luminescence identified PBF as the best treatment for this type of multi-contaminated soil. A great variability in % of seed emergence did not provide a clear response for soil toxicity.

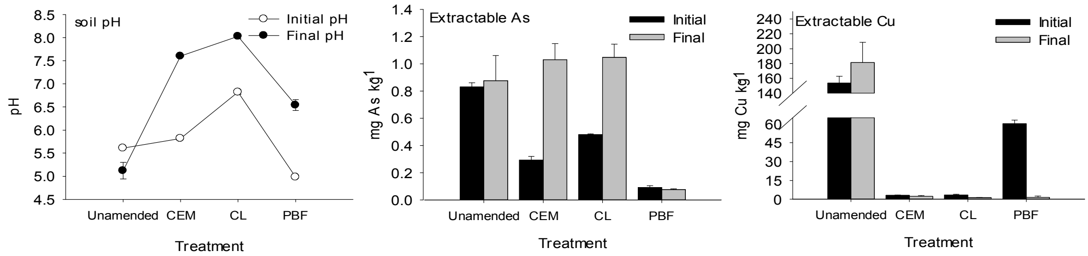

Figure 1. pH, As and Cu extractable concentration at the beginning and at the end of the experiment. Different letters indicate significant differences among treatments ($p<0.05$).

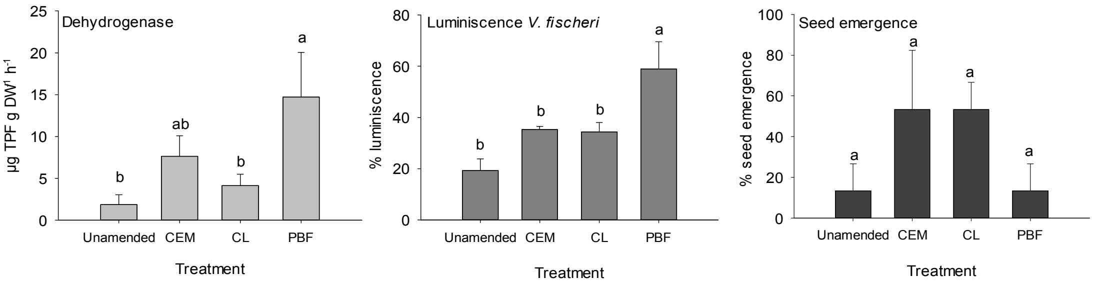

Figure 2. Ecotoxicological parameters at the end of the experiment. Different letters indicate significant differences among treatments ($p<0.05$).

Conclusion

The treatment combining paper sludge, biochar and $FeSO_4$ reduced simultaneously As and Cu extractability and can potentially create favourable conditions to the organisms present in the soil or affected by soil lixiviates.

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