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Assessing the combination of iron sulfate and organic materials as amendment for an arsenic and copper contaminated soil. A chemical and ecotoxicological approach

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HIGHLIGHTS

- The combination of iron sulfate and organic materials efficiently reduced As solubility.
- Organic matter did not interfere with iron oxides capacity to immobilize As.
- Cu mobility was more influenced by pH than by organic matter addition.
- Combining iron sulfate and compost provides a good alternative for the whole remediation process.

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ABSTRACT

The efficiency of combining iron sulfate and organic amendments (paper mill sludge, olive mill waste compost and olive tree pruning biochar) for the remediation of an As- and Cu-contaminated soil was evaluated. Changes in As and Cu fractionation and solubility due to the application of the amendments was explored by leachate analysis, single and sequential extractions. Also, the effects on *Arrhenatherum elatius* growth, germination of *Lactuca sativa* and toxicity to the bacteria *Vibrio fischeri* were assessed. The combination of iron sulfate and the organic amendments efficiently reduced As solubility and availability through the formation of amorphous iron oxides, while organic matter did not seem to mobilize As. At the same time, copper fractionation was strongly affected by soil pH and organic matter addition. The soil pH significantly influenced both As and Cu mobility. Within all the amendments tested, $FeSO_4$ in combination with compost showed to be the most suitable treatment for the overall remediation process, as it reduced As and Cu availability andenhanced soil nutrient concentrations and plant growth. In sipte of contradictory trends between chemical analyses and ecotoxicity tests, we can still conclude that the application of organic amendments in combination with reactive iron salts is a suitable approach for the remediation of soils contaminated by Cu and As.

1. Introduction

Mine-impacted soils generally present high contents of potentially toxic metal/metalloids affecting connected environmental compartments and are usually characterized by poor physico-chemical properties and loss of vegetation (Vangronsveld et al., 1994). To overcome this problem, *gentle* remediation strategies, based on plants and amendments, have been developed not only to act on metal/metalloids mobility but also on the recovery of soil functions (Alvarenga et al., 2009).

Within a soil recovery strategy, the establishment and development of a plant cover is essential, as plants improve soil physical properties and help to mitigate the dispersion of contaminants. For this purpose, the addition of organic amendments provides a suitable substrate for plant growth (Vangronsveld et al., 1995; Wong, 2003).

Iron oxides naturally existing in soils are well known to be important scavengers for As and thus the incorporation of iron oxides to soils has been shown to efficiently immobilize As in short and long time scales. The use of Fe(0) as a precursor of iron oxides results in a reduction in As mobility, but generally the application of

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Fe(II) and Fe(III) salts is proposed as a better alternative for amending As-contaminated soils than iron oxides, as they have shown to immobilize As more efficiently through inducing chemical reactions in soil (*e.g.* co-precipitation) than iron oxides do through adsorption (Hartley et al., 2004; Komárek et al., 2013). Within iron salts, agricultural grade $FeSO_4$ is recommended over $FeCl_3$ due to its lower cost and ease of application) (Cutler et al., 2014).

Olive mill waste or *alperujo* is a semi-solid by-product generated in the two-phase extraction of olive oil. It is rich in organic matter and essential nutrients, although its high content in phenolic compounds limits its direct application to soils as it shows some phytotoxicity that may be reduced by composting (Alburquerque et al., 2004; Alburquerque et al., 2006). Olive mill waste compost has been proved to enhance metals immobilization while alleviating soil toxicity and promoting plant growth (Walker and Bernal, 2008; Clemente et al., 2015). However, its application to As-contaminated soils is less recommended, because it often leads to As mobilization (Moreno-Jiménez et al., 2013; Beesley et al., 2014).

Biochar is a carbonaceous material obtained by the pyrolysis of biomass under limited supply of oxygen. Its application as a soil amendment may bring several benefits such as enhancement of C sequestration, improvement of soil physical properties and, in some cases, recycling of valuable nutrients (Novak et al., 2009). Many studies have shown the efficiency of biochar on heavy metals retention in soils and the reduction in their availability and phytotoxicity (Sneath et al., 2013; Moreno-Jiménez et al., 2016a). But, as it happens with compost, biochar addition to As-contaminated soils may pose a risk due to a potential increase in As solubility (Hartley et al., 2009; Beesley et al., 2013).

Paper mill sludge is a waste product generated in the pulp and paper industry. Its relatively high content of organic matter and carbonates suggests its potential use as an amendment for metal-contaminated soils. It has been proven to rise soil pH and reduce metals availability but it also solubilizes some As (Galende et al., 2014; Manzano et al., 2014b).

The evaluation of a soil remediation process should not only integrate changes in trace elements mobility, but also biological tests that provide comprehensive information on improving soil quality and providing ecosystem functions (Alvarenga et al., 2009a). Additionally, toxicity bioassays may assess potential risks associated not only to the soil, but also to other associated ecosystems such as the groundwater (Alvarenga et al., 2009b; Pardo et al., 2014a).

This work evaluates the co-application of iron sulfate and different organic amendments as a suitable strategy to remediate As- and Cu-contaminated soils. For this purpose, the effects on As and Cu fractionation and mobility as well as the effects on soil quality and ecotoxicological parameters were investigated in a pot experiment using a soil contaminated with As and Cu.

2. Materials and methods

2.1. Soil and amendments characterization

An As and Cu rich material mainly composed of arsenopyrite-scorodite masses (Recio-Vazquez et al., 2010) was collected from the spoil heaps of El Verdugal ancient smelting factory located in the North of Madrid (Spain). Soil was collected from the surroundings of this area and was not directly affected by the contaminated spoil heaps. The soil was air-dried, sieved (<4 mm) and gently mixed with the contaminated material (<2 mm, air dried) in a ratio 90:10 (w:w).

The following materials were selected as amendments. Iron sulfate ($FeSO_4 \cdot 7H_2O$) and calcium carbonate ($CaCO_3$) were obtained from Panreac (Barcelona, Spain). Paper mill sludge (PS) was provided by Holmen Paper (Madrid, Spain). Olive tree pruning biochar (BC) was obtained by slow pyrolysis at 450 °C in the University of Leon (Spain) (Brennan et al., 2014b). Compost was prepared from solid olive mill waste (*alperujo*) and cow manure (OMWC) at CEBAS-CSIC (Murcia, Spain). The main characteristics of the soil and the amendments are shown in Table 1. All the amendments were air-dried, homogenized and sieved (<2 mm) before mixing with the soil.

2.2. Experimental design

The following mixtures were applied as amendments in a dry soil weight basis: in all of them $FeSO_4$ (1%) was combined with (1) $CaCO_3$, 1% (Fe+lime); (2) Paper mill sludge, 1% (Fe+PS); (3) olive mill waste compost, 3% (Fe+OMWC); (4) Biochar, 3% (Fe+BC). A control consisting of the non-amended contaminated soil was also included. The soil and the amendments were individually manually mixed and 600 g of each treatment were placed in methacrylate cylinders, which were used as pots, over a 2 cm layer of sand; the bottom of the pots was covered with a cloth to prevent soil loss. Four replicates were established for each treatment. The mixtures were moistened to achieve ~70% of the soil water holding capacity (WHC) and were incubated for 15 days in a growth chamber under controlled conditions (day/night: 13/11 h; 25/20 °C; 40/60% of humidity and a photon flux of 520 $\mu mol\ m^{-2}\ s^{-1}$). Soil humidity was maintained at ~70% of the WHC by weighing and adding water losses every two days.

After 15 days of incubation, a soil sample was taken from each pot (D15) and four one- week-old seedlings of *Arrhenatherum elatius*, previously germinated in peat, were transplanted to each pot. Pots were watered slightly over the WHC to collect leachates once a week. The volume of the leachates was recorded and pH and EC were immediately measured. The leachate samples were filtered through 0.45 μm filters and stored at 4 °C until their analysis.

After 45 days of soil incubation, shoots of *A. elatius* were cut above the soil surface, washed, dried with tissue paper and weighed. The plant material was oven-dried for 3 day at 60 °C and weighed again for dry weights recording and As and Cu analysis. Soils from each pot were homogenized and part of sample was air-dried, sieved (<2 mm) and stored for further analysis (D45).

2.3. Toxicity bioassays

Fresh and dry weights of *A. elatius* were recorded to evaluate the shoot growth response to the treatments. Arsenic and Cu concentrations in *A. elatius* shoots were used to evaluate risk of transfer to plant shoots.

A germination test was performed using *Lactuca sativa* (lettuce) seeds. Ten grams of dried soil from each pot (D45) were placed in petri dishes and hydrated to ~80% of their WHC. Then, 25 lettuce seeds were placed in each petri dish and kept for two days in the darkness (25/25 °C, 40/60% RH) and for three more days with a photoperiod of 13/11 h (day/night). Germination success was calculated as the percentage of seeds germinated from those placed in each petri dish.

The effect of soil extracts on the bioluminescence of the bacteria *Vibrio fischeri* was tested according to the standardized method ISO 11348-2. Soils were mixed with water in a ratio 1:10 (w:v) and shaken for 24 h at 140 rpm and room temperature. The extracts were diluted with NaCl 2% (w:v) to achieve concentrations of 0, 6.25, 12.5, 25, 50 and 100% (v/v). The luminescence of the bacteria was measured using a luminometer (Optocom I, MGM Instruments) after the diluted extracts were in contact with a suspension of the bacteria for 30 min at 15 °C. All the measurements