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Efficiency of organic and mineral based amendments to reduce metal[loid]mobility and uptake (*Lolium perenne*) from a pyrite-waste contaminated soil

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ABSTRACT

High concentrations of heavy metal[loid]s in soils, spoils, vegetation and waters in the proximity of former metalliferous mining areas may pose a risk to the environment if dispersed. Several amendments were compared for their abilities to reduce the phyto-toxicity of a contaminated mine spoil (≤10,000 mg kg^{-1} As, Bi, Cd, Cu, Hg, Pb and Zn). Iron and phosphorus based amendments or compost were mixed into mine soil [spoil] and ryegrass was germinated on the mixtures in a 90-day pot trial. Metal[loid] concentrations in pore waters and ryegrass tissues were measured to compare the effects of each amendment on 1) metal[loid]s in solution, 2) their uptake to plant tissue and 3) plant biomass production. The data were evaluated in terms of environmental risk and practical application to mine site remediation.

Iron based amendments significantly reduced As, Cd and Cu concentrations in pore water >2 fold compared to the untreated mine spoil. Compost and Fe(II) + $CaCO_3$ resulted in the lowest concentrations of metal[loid]s in ryegrass tissue and a significant increase in biomass, matching that achieved in a control, non-contaminated soil. Phosphorus based amendments generally had no significant impact on, or increased metal[loid]s in pore water whilst also failing to improve ryegrass biomass yields significantly, suggesting that factors other than nutrient deficiency, for example phyto-toxicity, hindered vegetation growth. Given that compost induced the particularly displeasing effect of considerable solubilisation of As (>300 μg l^{-1} in pore water) when added to the mine soil [spoil], Fe based amendments can be adjudged as the most suitable to deploy for the remediation of metal[loid] affected areas at this mine site. This is especially the case for Fe(II) + $CaCO_3$ due to its more favourable effects on pH and ryegrass yield than Fe oxide alone.

1. Introduction

Among other anthropogenic activities that release heavy metal[loid]s into the environment are metallic mining processes (Adriano 2001), the spoil from which can contain phyto-toxic concentrations of metal[loid]s. A combination of poor structure and low nutrient capital generally inhibits the establishment of vegetation cover on such mine spoils, leaving them bare (Ernst 2005) and thus subject to erosion, whereby contaminants can be released to the wider proximity. Various methods exist to remediate mine areas including total removal or burial of spoils under imported topsoil, partial soil removal and capping of spoils with inert substrates. Environmentally harmonious measures to improve conditions for revegetation, thereafter stabilising the spoil *in situ*, are increasingly favoured, especially if they also involve the re-use of locally derived wastes materials as soil conditioners. Given that direct seeding of mine spoils is likely to be infrequently successful, remediation involving plants can be assisted after soils have been treated with amendments to reduce phyto-toxicity and contaminant leaching (Alvarenga et al., 2009; Vangronsveld et al., 2009) and/or improve soil structure and nutrient status. Among such amendments, four inorganic (iron oxide and phosphorus based amendments) and an organic (compost) amendment were selected for the present study because: 1) iron based amendments are especially suitable in arsenic enriched environments as iron oxides (the most stable species of Fe in aerated soils) can reduce metal[loid] solubility. Many mine affected soils have a poor nutritional status, so 2) the application of P or NPK supplements may improve plant establishment, but P will adjust metal[loid] chemistry and could enhance As leaching. Finally 3) compost is often a default choice for contaminated land remediation because it can retain some inorganic contaminants in relatively stable organo-mineral complexes, improves soil structure and provides some nutrients. It is also usually available in abundance as a result of municipal recycling initiatives.

The aim of the present study was to test the efficiency of Fe and P based amendments for reducing phyto-toxicity of a metal[loid]

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contaminated mine spoil, by assessing metal[loid] mobility and uptake to ryegrass. The Fe and P based amendments were compared to mine spoil treated with compost and spoil without treatment.

2. Methods

2.1. Soil and mine spoil selection

Soil and mine spoil were collected from sporadically vegetated areas of La Mina Monica mine site, close to the village of Bustarviejo (Madrid, Spain; Fig. 1). The studied site extends across approx. 20 Ha within the La Mina valley (40º 52′07.06″N; 3º 43′48.87″ W) and has been previously studied in relation to heavy metal[loid] mobility and uptake to native vegetation (Moreno-Jiménez et al., 2009; Moreno-Jiménez et al., 2010). Mine spoil samples were collected from the surface 20 cm, bulked, air dried (25 °C) and sieved to 2 mm. Control soil (C), which was not contaminated, was collected from the vicinity of the mine by the same method as above. Soil and mine spoil were mixed in a proportion 60:40 (w:w) to produce a contaminated soil (T0), referred to hereafter as soil rather than spoil. This was done because the spoil was known to be highly contaminated and plant establishment would be unlikely without mixing with soil; in real conditions mine spoils frequently mix naturally with adjacent soils over time resulting in weakly formed soils with poor structure, abrupt textural variability and inconsistent chemical properties.

2.2. Soil amendments

The amendments (hereafter denoted as T1–T5) were chosen due to their availability, likely efficiency to influence metal[loid] geochemistry and/or benefits to soil fertility and plant growth. The dose of commercial Fe oxide (T1) was selected as a maximum realistic dose comparable to the dose of Fe applied as $FeSO_4$ (T2), *i.e.* 0.4% Fe in both cases, although in the second case (T2) calcium carbonate was added to promote Fe oxide formation and provide liming. Fertiliser doses were adjusted to the recommendations of P input for *L. perenne* in turf, either as solely P (T3) or NPK (T4). Finally, commercial green waste compost was applied at 5% (w:w) equivalent to a maximum practicable application rate in the field (T5). The compost was of green waste origin and obtained from Carrefour supermarket and is recommended for soil application and horticultural cultivation, with a circumneutral pH (6–7).

Mixing of soil and spoil, plus the treatments above was done mechanically using the end-over-end method in a sealed drum for 2 h. Mixtures were subsequently placed into triplicated pots with a dish underneath each pot to collect leachate, which was returned to the pot by capillarity action through a cotton wick. The substrates were left to equilibrate for 3 weeks, the moisture content maintained at 75% of their field capacity, watering them every 2 days to maintain mass. Rhizon samplers (Eijkelkamp Agrisearch equipment, Netherlands) were placed horizontally in the middle of the pot (Fig. 1) and after a further equilibration period of 36 h, pots were re-watered and 1 g of seeds of *Lolium perenne* L. var. Cadix were placed on the top of each pot. Each pot was covered with film plastic for 3 days to maintain humidity in the seeding zone. Pots were then uncovered to allow plant development and watered daily to maintain 75% of field capacity during the cultivation (5 weeks). Throughout the experiment pots were maintained in a greenhouse at 18–22 °C with natural light (photo-period approx. 15 h). Exactly the same procedure was carried out on the control soil pots (C).

A summary is provided below of soil and treatments (per pot):

- C: soil (S, 1.8 kg).
- T0: S 60% (1.08 kg) + mine spoil 40% (MS, 0.72 kg).
- T1: S + MS + 18 g E33P (iron oxide commonly used in water treatment, BAYERN®).
- T2: S + MS + 44 g $FeSO_4$ + 16 g $CaCO_3$.

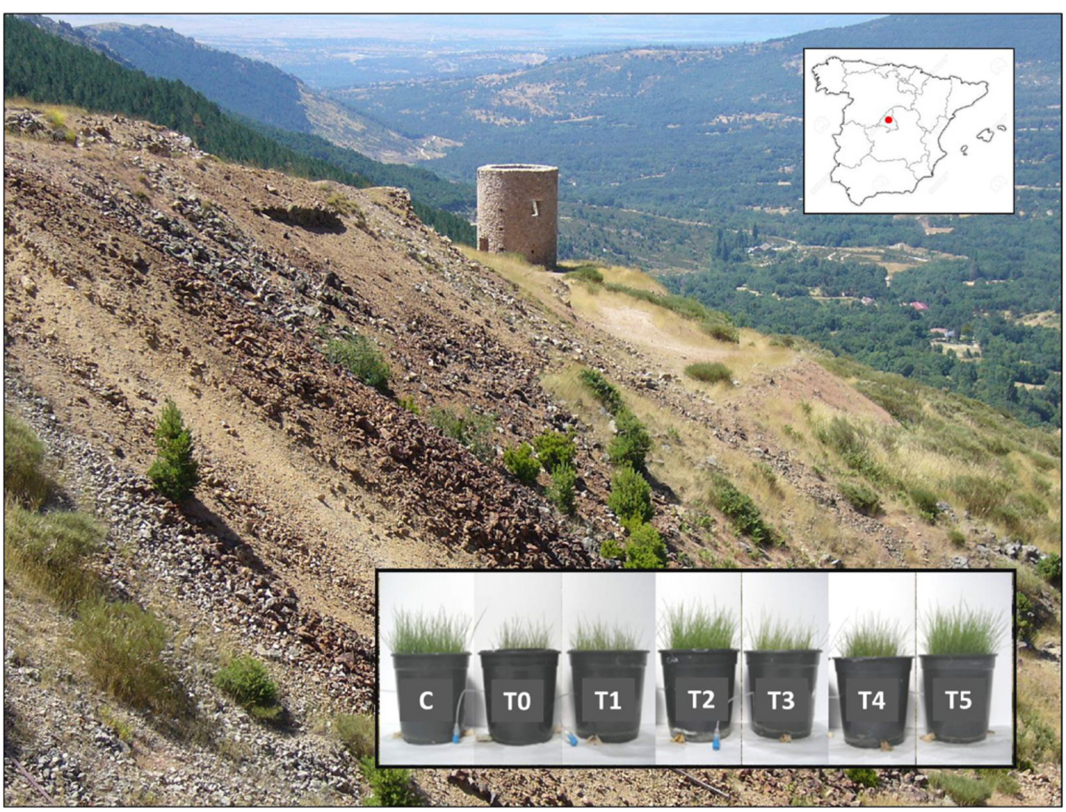

Fig. 1. La Mina Monica mine site (Madrid, Spain; map inset top), showing hillside location of unvegetated soils [spoils]. Inset bottom shows experimental pot set-up, placement of rhizon samplers and ryegrass growth in progress; note that T2 and T5 display greater biomass growth compared to T0, T1 and T3.