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Assessment of native shrubs for stabilisation of a trace elements-polluted soil as the final phase of a restoration process

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ABSTRACT

Re-vegetation is the main aim of ecological restoration projects, where the use of native plants is recommended over exogenous species, which may result in an undesirable modification of the ecosystem. A 10-year phytoremediation programme was carried out in a site affected by the toxic spill of pyritic (iron sulphide) residue at Aznalcóllar (Spain) in 1998, contaminated with heavy metals (Cd, Cu, Pb and Zn) and arsenic. The success of the re-vegetation of the area with native species after a large (6 years) active phytoremediation intervention was evaluated during 4 years as the final step of the ecological restoration process. Mediterranean native shrubs (*Retama sphaerocarpa*, *Tamarix gallica*, *Rosmarinus officinalis* and *Myrtus communis*) were selected and their potential for restoration of the soils affected by the pyritic residue was assessed. Plant survival was negatively affected by soil acidity, which was the main factor controlling trace elements (TEs) solubility and soil microbial biomass, and therefore, soil quality. Nevertheless, the surviving plants were well developed and reached a large size at the end of the experiment (except *M. communis*). Trace element transfer from soil to harvestable parts was low for all species, and some species have been able to decrease TEs availability in the soil. The results suggest that *R. sphaerocarpa* was the most adequate plant species for the restoration of these soils, as it showed the highest survival rate, elevated tolerance to strong soil acidity and low TEs transfer factors.

1. Introduction

Mining activities generally involve the contamination of large areas with potentially toxic elements, such as trace elements (TEs), whose dispersion may suppose a serious threat to nearby communities and ecosystems (Alloway, 2013). In mine affected sites, unvegetated areas and tailings piles exposed to wind and water erosion and lixiviation are the main sources of contamination (Clemente et al., 2007; Zornoza et al., 2012). In addition, catastrophic tailing dam failures such as those that occurred in China, Romania, Sweden, USA, Spain, and Hungary are another possible contamination source associated to mining activities (Macklin et al., 2003). These accidents frequently result in huge amounts of highly polluted sludge being rapidly discharged into the ecosystem, covering land surface, destroying plant and wildlife, and the soil matrix becoming saturated with contaminant particles (Alloway, 2013).

In the last decades, phytoremediation has moved forward from a conceptual methodology to a practical and commercially-viable technology for environmental clean-up for both organic and some inorganic contaminants, such TEs (Dickinson et al., 2009). The primary aim of phytostabilisation is the reduction of contaminants' mobility and of the effects of pollutants on humans and ecosystems (Domínguez et al., 2008). Therefore, re-vegetation is the main goal of ecological restoration projects as the soil surface must be stabilised so that wind and water erosion are minimised and there is a reduced risk for humans and animals (Vangronsveld et al., 2009). The success of phytoremediation of TEs-contaminated sites requires a thorough understanding of the physico-chemical and biological constraints upon plant growth, as well as the combination of suitable soil amendments and well-chosen plant species that tolerate particular local conditions, including the elevated concentrations of TEs (Mench et al., 2009).

The Aznalcóllar mining district (Seville, SW Spain) includes several deposits of sulphide ore, from which Ag, Cu, Pb and Zn sulphides used to be separated by flotation from unwanted sulphides such as pyrite (López-Pamo et al., 1999). On April 1998, an accident at the Aznalcóllar mine provoked a toxic spill consisting of approximately 4 million m^3 of acid water and 2

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million m^3 of mining sludge, which were released through a breach that opened in the dam of the mine's tailings pond (Grimalt et al., 1999). Since then, different phytoremediation experiments have been carried out at the Aznalcóllar site (Clemente et al., 2006; Domínguez et al., 2008; Moreno-Jiménez et al., 2011), where elevated concentrations of toxic TEs remained in the soil after the removal of the pyritic sludge (Taggart et al., 2004; Vázquez et al., 2011). Long term reclamation of these soils requires the establishment of stable nutrient cycles for plant growth and microbial processes (Kavamura and Esposito, 2010; Lone et al., 2008; Singh et al., 2002). However, the success of remediation projects frequently remains unevaluated.

Restoration of the vegetation cover can fulfil the objectives of stabilisation, pollution control, visual improvement and removal of threats to human beings (Singh et al., 2002; Wong, 2003). The re-vegetation must be carried out with plant species selected on the basis of their ability to survive and regenerate in the local environment. In this sense, the use of native Mediterranean shrubs in phytoremediation is of special interest (Lepp and Dickinson, 1998), as they are well adapted to this specific environment, and avoids introduction of non-native and potentially invasive species, stimulating at the same time natural ecological succession (Mendez and Maier, 2008; Pardo et al., 2014a). The extensive canopy of this type of plants and their deep root network could effectively reduce leaching and wind erosion of contaminant particles, minimising the dissemination of the contamination while improving soil ecosystem functions (Pardo et al., 2014b).

In this study we sought to assess the success of re-vegetation with selected native shrubs (*Retama sphaerocarpa*, *Tamarix gallica*, *Rosmarinus officinalis* and *Myrtus communis*) as the final step of the restoration process of soils affected by residual contamination from the Aznalcóllar spill that had undergone an active phytoremediation intervention. The evolution of the main soil physico-chemical properties including TEs availability, plant survival, TEs accumulation by plants, and transfer factors were assessed during three years, once plants were well stabilised in the soil (one year after transplanting). At the end of the experiment, a soil quality index based on soil microbial biomass and soil physico-chemical properties was determined to assess the efficacy of the recovery process and to identify the most-interesting species for phytostabilisation.

2. Materials and methods

2.1. Experimental site

The experiment was performed in the experimental site "El Vicario", which is located on the right bank of the Guadiamar river (37°26′21″N; 06°13′00″W), 10 km downstream from the Aznalcóllar mine, and was affected by pyritic sludge contamination from the mine accident that occurred in 1998. This site was previously subjected to two different intervention steps: (i) a two year (2000–2001) active phytoremediation experiment, with the addition of organic amendments (compost and cow manure) and lime to the soil, and the growth of two successive crops of *Brassica juncea* (L.) Czern. as a metal-accumulator species; and (ii) a natural attenuation phase, without external intervention (2002–2005) (Clemente et al., 2003, 2006). The present experiment is framed in a third phase that sought the restoration of the site using native plant species (2006–2010). For this final phase, any possible remaining effects of the addition of amendments in the initial phase were disregarded, because of both the long period of time that had passed since the application of the amendments and the fact that the top 20 cm of the soil were tilled before the establishment of the new experiment. This soil presented a wide range of pH (from 2 to 7), low contents of organic matter (12–16 mg of TOC kg^{-1}) and carbonates (5%), and a loam texture. Total concentrations of TEs in these soils varied widely due to the patches of sludge that remained in the area: Zn (457–1617 mg kg^{-1}), Cu (126–305 mg kg^{-1}), Pb (172–839 mg kg^{-1}), As (135–634 mg kg^{-1}) and Cd (0.6–5.5 mg kg^{-1}), which also provoked high levels of DTPA-extractable Zn (up to 965 mg kg^{-1}), Cu (up to 109 mg kg^{-1}), Pb (up to 11 mg kg^{-1}) and Cd (up to 3.3 mg kg^{-1}) in the soil (Clemente et al., 2003, 2005, 2006).

2.2. Experimental design

The experimental area (18 × 24 m) was divided into 12 plots (8 × 4 m, distributed in two rows separated by a corridor of 1 m) for the development of the two previous intervention phases. Each plot was further divided into 6 subplots of approximately 2.6 × 2 m for the present experiment, resulting in a total of 72 subplots (Fig. 1).

Four native species were selected amongst those used for the Green Corridor of the Guadiamar river restoration project (Domínguez et al., 2008): *R. sphaerocarpa* L., *T. gallica* L., *R. officinalis* L. and *M. communis* L. These species had been previously studied to understand their interaction with TEs (Moreno-Jiménez et al., 2011, 2012). Seedlings of similar size (around 20 cm height), provided by the Red de Viveros (native plants nursery) of the Junta de Andalucía, were transplanted to the soil in December 2005. In each subplot, one plant of two of the selected species was grown combining large-sized and low-sized species in a random distribution, i.e. *R. sphaerocarpa* or *T. gallica* with *M. communis* or *R. officinalis* (Fig. 1). Three plants of each species were planted per plot; thus, a total of 36 plants of each species was grown in the experimental area. Plants were grown under natural conditions (average annual rainfall and temperature around 500 mm and 18–20 °C, respectively) without any agricultural practice or irrigation system.

Soil and plants were sampled at three different dates once plants were stabilised in soil (one year after transplanting): June 2007, June 2008 and May 2010. Soil sampling consisted of extracting three subsamples from the surface soil (<20 cm depth) in each subplot that were mixed to form a composite sample. Soil pH, electrical conductivity (EC), total (in the first sampling) and soluble and exchangeable ($CaCl_2$-extractable) concentrations of heavy metals (Cd, Cu, Fe, Mn and Zn) and As ($NaHCO_3$-extractable) were measured. Soil microbial biomass C and N were determined only in the last sampling as soil quality indicators, as these parameters are sensitive to trace element pollution (McGrath, 1994). Aerial plant material, consisting in young and fully-grown leaves from the middle part of the plants, was also collected at the three sampling times. Survival percentage of each plant species was monitored every 6 months after transplanting during the first year, and then annually until the end of the experiment.

2.3. Analytical methods

The soil samples were air-dried and sieved to <2 mm prior to analysis. Soil pH was measured for saturated pastes and EC was determined in 1:5 (soil:water) extracts. Soil pseudo-total heavy metals were determined after nitric–perchloric acid (2:1) digestion. Soluble and exchangeable metals were extracted with 0.1 M $CaCl_2$ (1:10 w/v) for 12 h. Available As concentrations in soil samples were measured after extraction (1:10 w/v) with 0.5 M $NaHCO_3$ (Clemente et al., 2006). Heavy metals were measured by flame atomic absorption spectrometry (FAAS, UNICAM 969, Thermo Elemental), and As concentrations were determined using electro-thermal atomic absorption spectrometry (ETAAS, PerkinElmer Analyst 800) or atomic fluorescence spectrometry (AFS, PS Analytical Millennium Excalibur System).