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Phytostabilisation of severely contaminated mine tailings using halophytes and field addition of organic and inorganic amendments

T. Pardo [1], M.P. Bernal, R. Clemente [*]

Department of Soil and Water Conservation and Organic Waste Management, CEBAS-CSIC, PO Box 164, 30100, Murcia, Spain

HIGHLIGHTS

- Trace elements solubility in a mine tailings soil was lowered by amendments addition.
- Speciation of soluble metals changed to hydroxides and/or organo-metallic forms.
- Arsenic extractability and thallium solubility increased in red mud treated soils.
- The different treatments allowed plant growth and limited TEs accumulation in shoots.
- Combination of red mud, compost and halophyte species succeed as remediation option.

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ABSTRACT

Phytostabilisation strategies have proven to be an efficient remediation option for mine tailings, but the adequate plant species and amendments have to be carefully selected. A remediation experiment was carried out at the semi-field level in tailings (pH 3.2, ≈1100, 4700 and 5000 mg kg^{-1} of As, Pb and Zn, respectively) from the mining district of La Unión-Cartagena (SE Spain). A red mud derivative (Fe/Al oxides), its combination with compost, and hydrated lime (Ca hydroxide) were applied in field plots of 0.25 m^2. After four months of field stabilisation, tailings were transferred unaltered to a plant growth facility, and *Atriplex halimus* and *Zygophyllum fabago* (halophytes) were sown. Three months later, trace element (TE) solubility, plant accumulation and chemical speciation in the tailings pore water were studied. In unamended tailings, soluble TEs concentrations were very high (e.g., 40 mg Zn l^{-1}), the dominant species being free ions and SO_4^{2-}- complexes (>70%). The addition of amendments increased tailings pH (6.7–7), reduced TEs solubility and extractability (>80–99%) and changed the dominant species of soluble Al, Cu, Pb and Zn to hydroxides and/or organo-metallic complexes, but increased slightly the extractable As and soluble Tl concentrations. Plants were able to grow only in amended tailings, and both species presented low levels of Al, As, Cd and Zn. Therefore, the use of combined red mud derivative and compost and halophytes was shown to be a good phytostabilisation strategy, although the dose applied must be carefully chosen in order to avoid possible solubilisation of As and Tl.

1. Introduction

Tailings formed from mine spoil accumulation are considered one of the most relevant sources of contamination associated with mining activities as they contain large amounts of trace elements (TEs), usually in highly available chemical forms (Bes et al., 2014; Candeias et al., 2015). This contamination is usually of special concern when mining has been carried out for long periods of time with little environmental regulation (Alloway, 2013). A clear example is the mining district of La Unión-Cartagena (SE Spain), where the extraction of minerals has been carried out for centuries and numerous (>80) currently abandoned former tailing-accumulation ponds, which contain very high levels of As and heavy metals, can be found (Robles-Arenas et al., 2006; Conesa et al., 2006; Navarro Flores and Martínez Sola, 2010). Trace element mobility and toxicity in these tailings represent a threat to the surrounding ecosystem and require remediation to reduce the environmental risk they pose (Bes et al., 2014; Navarro et al., 2008).

* Corresponding author.
E-mail address: rclemente@cebas.csic.es (R. Clemente).
[1] Present address: Department of Soil Biochemistry, IIAG-CSIC, Av. de Vigo s/n, 15780, Santiago de Compostela, Spain.

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As a consequence, this area has been the subject of a number of scientific papers published in the last decade regarding soil contamination (Conesa et al., 2006, 2008) and possible strategies for the remediation or the alleviation of the TE toxicity of these soils (Clemente et al., 2012; Pardo et al., 2014b, 2016; Zornoza et al., 2012a). Phytostabilisation has been shown to be a suitable remediation option for the soils of this site (Párraga-Aguado et al., 2014; Pardo et al., 2016). However, mine tailings present particularly unfavourable conditions for plant growth (extreme pH values, elevated salinity, low content of organic matter (OM) and nutrients, etc.) and the selection of the adequate combination of amendments is a critical step for the success of the remediation procedure. The addition of inorganic and organic soil amendments is a common procedure in phytostabilisation processes, to facilitate plant establishment and improve soil fertility (Clemente et al., 2015). But, any modification of the tailings' physico-chemical and biological properties caused by the addition of amendments will have an influence on TEs mobility and bioavailability and, therefore, on their potential dispersion and transfer to living organisms (Pardo et al., 2016). In this sense, the evaluation of the effects of the amendments on parameters related to both the mobility and availability of TEs, like their solubility, speciation or accumulation in the plants, will help to optimise the remediation procedure and minimise any potential undesired environmental impact.

The use of plant species tolerant of poor soil conditions, seasonal drought and high temperatures is normally required for the phytostabilisation of TEs contaminated (semi-arid sites; Clemente et al., 2012). In this sense, halophytic native plant species have clear advantages as they usually possess high tolerance of extreme soil conditions and show lower TEs accumulation in their tissues than non-halophytes (Párraga-Aguado et al., 2014). Certain physiological mechanisms related to their salt tolerance (e.g., ions compartmentalisation and/or restriction of entry into the transpiration stream) are thought to be involved in the adaptation of these species to TEs stresses (Lefèvre et al., 2009; Van Oosten and Maggio, 2015). Species of the genus *Atriplex* (Amaranthaceae) - in particular, halophytic shrubs like *Atriplex halimus* - have been reported as promising candidates for phytostabilisation due to their fast growth and low water requirement (Walker et al., 2014), and their ability to develop a sustainable vegetative cover and stimulate the ecological functions of the soil (Clemente et al., 2012; Pardo et al., 2014b). The Syrian beancaper (*Zygophyllum fabago*) is a succulent perennial species that forms a compact multi-branched shrub, is adapted to harsh environments such as arid and saline areas (Lefèvre et al., 2005) and is able to grow on sites that have been severely disturbed, like mining areas (Lefèvre et al., 2014; Kabas et al., 2014). Interestingly, *Z. fabago* is one of the pioneer species observed in several mine sites in South East Spain (Conesa et al., 2006, 2007; Martínez-Sánchez et al., 2012), and several studies have evidenced that this species can tolerate high concentrations of Cd and Zn in its growing environment (up to 10 μM Cd and 100 μM Zn in nutrient solution; Lefèvre et al., 2005, 2010).

Red mud derivatives are known to be able to increase soil pH and immobilise TEs in soil (Hua et al., 2017). Indeed, their combination with compost (that results in the addition of plant nutrients) has been shown to be effective for the phytostabilisation of severely contaminated mine tailings under controlled conditions (Pardo et al., 2016), reducing TE availability and allowing plant growth, which was otherwise inhibited. However, the success of these materials under real or semi-real field conditions has not yet been confirmed. Hydrated lime and other liming materials also have been used satisfactorily in the remediation of mine tailings - mainly due to their metal immobilisation capacity, associated with an increase in soil pH (Clemente et al., 2012; Zornoza et al., 2012b).

The aim of the present study was to assess, at the field level, the use of lime, a red mud derivative and its combination with compost in the phytostabilisation of a highly acidic TEs-contaminated mine tailing, using *A. halimus* and *Z. fabago* as soil-stabilising, TEs-tolerant plant species. The use of native halophytic species in mine tailings phytostabilisation has to be further studied under field conditions, to realistically evaluate the effectiveness of the remediation procedure in reducing the potential environmental risk that mine tailings pose. This will substantially facilitate possible future reclamation processes. With that aim, TEs solubility and plant accumulation were studied and the chemical speciation of TEs in the soil solution was modelled.

2. Materials and methods

2.1. Tailings and amendments description

A remediation experiment was carried out using tailings from a mine pond situated in an area known as “El Descargador”, within the mining district of La Unión-Cartagena (37°37′04.4″N 0°51′49.6″W; SE Spain) where Pb and Zn minerals had been mined previously. These tailings are characterised by an extremely acidic pH (<3.3), high concentrations of TEs (especially As, Pb and Zn) and elevated electrical conductivity (EC) (3–9 dS m^{-1}; Table 1).

As amendments, a commercial product derived from red mud (R, 20 t ha^{-1}), its combination with a mature compost prepared from solid olive-mill waste (R-CM, 20 t ha^{-1} and 30 t ha^{-1}, respectively) and hydrated lime (HL, 20 t ha^{-1}) were used. The R derivative (commercialised as ViroBind™) was provided by the company Sinergias S.L. (Cartagena (Murcia), Spain), and is mainly composed of Fe and Al oxides and Ca and Mg minerals. The hydrated lime ($Ca(OH)_2$) was used as acquired commercially (Cales Pascual S.L.). The main characteristics of these materials are shown in Table 1.

2.2. Experimental design

2.2.1. Phase I: addition and stabilisation of the amendments in the field

An initial assessment of the distribution of the pH in the mine pond surface layer (0–20 cm) was carried out in order to avoid extremely acid (<3) spots within the experimental area (data not shown). Then, the amendments R, R-CM and HL were applied (incorporated into the tailings) in field plots of 0.25 m^2, in patches that showed similar pH values (3–3.5); unamended control (CT) plots were also established at this mine pond. In the middle of each plot a PVC cylinder, 20 cm in diameter and 7 cm high, was carefully inserted, avoiding any further disruption in the tailings. The four treatments were distributed in a fully-randomised design with five replicates per treatment, and were kept without any intervention for four months, for the stabilisation of the amendments. According

Table 1
Chemical properties of the tailings and amendments. R: red mud derivative.

	Tailings	R	Compost
pH	3.2	10.9	8.8
EC (dS m^{-1})	2.97	0.14	6.1
TOC (g kg^{-1})	0.20	7.2	439
Total-N (g kg^{-1})	0.04	0.15	31.7
As (mg kg^{-1})	1128	4.68	4.9
Cd (mg kg^{-1})	8.2	0.27	<0.01
Cu (mg kg^{-1})	671	55.7	48
Fe (g kg^{-1})	264	90.2	1.62
Mn (mg kg^{-1})	925	901	92
Pb (mg kg^{-1})	4692	41.2	36
Zn (mg kg^{-1})	5085	10.7	141