Ecological Engineering 109 (2017) 25–34

Contents lists available at ScienceDirect

Ecological Engineering

journal homepage: www.elsevier.com/locate/ecoleng

Nutritional status and its interaction with soil properties and trace elements in six Mediterranean shrub species grown in reclaimed pyritic tailings

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ARTICLE INFO

Keywords:
Nutrient uptake
Pig manure
Calcium carbonate
Tailings
Mediterranean shrubs

ABSTRACT

For phytostabilization to successfully reclaim mine tailings, an adequate soil nutrient level should be provided to promote the growth of healthy plants and plant succession. In this study, six Mediterranean shrub species (*Lavandula dentata, Rosmarinus officinalis*, *Thymus vulgaris*, *Nerium oleander, Cistus albidus* and *Pistacia lentiscus*) were grown in mine tailings, unamended and amended with calcium carbonate and pig manure, and in a reference unpolluted substrate as positive control. We aimed to assess if amendments enhanced plant growth and nutritional status and to study the relationships between soil properties, soil metal(loid) contents and nutrients and plant growth and nutritional status. These data are necessary to infer how soil characteristics influence plant health in tailings for proper management. The experiment was conducted in pots for 120 d. The results showed that at the end of the experiment the addition of amendments had increased soil pH from ~4.5 to ~7.7, exchangeable Ca, K and P and had decreased exchangeable Mn and Fe, with no effect on N and Mg. In general, unamended tailings supported plants with high accumulation of Cd, Zn, Mn and B in their tissues, related to high availability of metals and low pH. Amended tailings supported plants with better root development and higher levels of N, K, Ca, Mg, Fe and Cu in all parts, with regard to unamended tailings. Thus, the reclamation strategy improved the nutritional status of plants and root development, mainly related to increases in soil $CaCO_3$ and pH. However, reclamation led to enhanced accumulation of As and Pb (below toxicity limits), related to increases in pH and soluble organic compounds, respectively. Amendment addition did not favor P accumulation by the plants, despite its increase in the soil. Among species, *L. dentata* and *C. albidus* were the species with the highest improvement in nutrient content with the addition of the amendments, while *T. vulgaris* was the species least affected by soil conditions.

1. Introduction

Intensive mining and industrial activities have produced a high amount of hazardous waste materials around the world. As a consequence, five of the ten most polluted places in the world are related to the mining activity (Choi, 2011). Mine tailings from either inactive or abandoned mine sites are prevalent in arid and semiarid regions throughout the world. Major areas include Northern Mexico and the Western United States, the Pacific coast of South America (Chile and Peru), Southern Spain, Western India, South Africa, and Australia (Mendez and Maier, 2008; Munshower, 1994; Tordoff et al., 2000). Many of these areas with tailings and overburdens are currently abandoned, with high contents of acid generating sulfide minerals, and potentially toxic metals and metalloids which can be transported by leaching, runoff and wind. Some of the metal(loid)s extracted during the mining processes, such as Zn, Cu, Pb, Cd, As or Hg, have serious effects on terrestrial and aquatic ecosystems, which increase the physiological health risks if dumped in the environment and not correctly managed (Bardin et al., 2005; Pandey, 2012; Ubalua et al., 2007). Therefore, remediation of mining lands is necessary in order to protect the environment from the toxic effects of metal(loid)s from tailings and overburdens, and to conserve the environment for future generations (Glick, 2010; Ullah et al., 2015). Coelho et al. (2011) performed a review on the health problems derived from exposure to these metal(loid) s. Cancer or neurological problems are the major health problems described after long-term exposure to them in high concentrations. Furthermore, the reconstruction of a native vegetation community in these denuded environments is a priority in order to maintain a sustainable system which in time will stabilize the toxic metal(loid)s and reduce their transfer to the surroundings (Nussbaumer et al., 2016).

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http://dx.doi.org/10.1016/j.ecoleng.2017.08.027
Received 17 April 2017; Received in revised form 20 July 2017; Accepted 23 August 2017

Many proposals have been established to reclaim lands covered by mine tailings, although not all of them are technically and economically feasible (Anawar, 2015). Such a situation highlights the need for studies focusing on reclamation of tailings from the standpoint of feasibility and long-term sustainability, in which tailings can be used as a medium for native plant growth and, consequently, for forest ecosystems re-establishment (Araujo and Costa, 2013). Phytostabilization can be chosen as one of the most suitable options for reclaiming tailings. The mobility of contaminants is reduced by their accumulation in plant roots, absorption onto roots, or precipitation within the root zone (Kamran et al., 2014; Ullah et al., 2015; Yang et al., 2014). Phytostabilization can also contribute to preventing soil erosion and the dispersion of contaminants (Mendez and Maier, 2008); improve soil conditions to enhance plant succession (support a diversity of native plants close to the natural vegetation of the area) (de-Bashan et al., 2012); and create a beneficial habitat for wildlife (Tordoff et al., 2000).

For the success of phytostabilization, an adequate soil nutrient level should be provided in order to promote plant growth and succession. To overcome soil nutrient deficiencies, inorganic fertilizers are usually applied to increase plant density, percentage vegetation cover, and species richness (Bell, 2001; Daws et al., 2013; Nusbaumer et al., 2015). Depending on the underlying substrate properties, ions released from inorganic fertilizer can be rapidly leached (Wilden et al., 2001) or tightly bound making them unavailable to plants, linked to a not economically sustainable alternative. Thus, the incorporation of organic residues as amendments into tailings and mine soils has been proposed as a feasible, inexpensive, and environmentally sound disposal practice as such residues can improve the soil physical and chemical properties, and contain nutrients which are beneficial to microorganisms and plants (Parra et al., 2016; Zornoza et al., 2013). The reclamation strategy must promote the development of a soil which is of a high quality and is fertile, thus providing the nutrients and adequate conditions for plant uptake and microbial growth, so that vegetation is able to grow and survive in an adverse environment. The success of land reclamation strategies depends on the addition of amendments (Salmi, 2008), but the proper choice of plant species that will grow in the area also deserves attention (Goel and Behl, 2004) so that the vegetation community is self-sustaining (Araujo et al., 2013). Although there has been abundant research on the reclamation of mine soils and tailings, little information is available about the nutritional status of potential candidates for phytostabilization and its interaction with soil properties and metal(loid)s mobility.

In the present study, six native Mediterranean shrub species were grown in mine tailings, unamended and amended with calcium carbonate and pig manure as reclamation strategy, and in a reference unpolluted substrate used as positive control. Soil properties, plant growth, carbon content, nutrient uptakes and their interrelationships were studied. The objectives of this experiment were to: i) assess if the reclamation strategy proposed for tailings enhanced plant growth and plant nutritional status so that phytostabilization can be effective with development of healthy plants; ii) assess if metal(loid) availability in soils affects nutrient uptake by plants; and iii) study the relationships between soil properties and nutrients and plant growth and nutritional status so we can infer how soil characteristics influence plant health and development in reclaimed tailings for proper management. We hypothesized that the addition of calcium carbonate to ameliorate pH and provide exchangeable Ca, and pig manure to provide organic matter and nutrients should overcome the nutrient deficiencies and high availability of toxic elements in the tailings and to thus promote the development of a soil with high fertility to provide the nutrients and suitable conditions for plant uptake, while decreasing the uptake of metal(loid)s. This experiment needs to be conducted so that the tested plant species can be proposed to land managers as potential candidates for phytostabilization of mine tailings, since the assessment of the nutritional status of plants and its interaction with soil properties and metal(loid)s mobility is essential to ensure true landscape reclamation by self-sustaining vegetation communities.

Table 1
Main properties and total concentration of metals and metalloids for tailings, substrate of peat moss, Coconut fiber and perlite (positive control) and amendments used.

Property	Pyritic tailings	Positive control	Pig manure	Marble waste
pH	3.5	7.2	9.1	8.0
Electrical conductivity (dS m^{-1})	2.3	1.6	10.2	2.2
$CaCO_3$ (%)	< d.l.	< d.l.	n.d.	99.0
Total organic carbon (g kg^{-1})	1.78	172.92	170.81	n.d.
Total N (g kg^{-1})	0.21	3.91	13.6	n.d.
C/N	8	44	13	n.d.
Available P (g kg^{-1})	< d.l.	224	9.64	< d.l.
Exchangeable Ca (g kg^{-1})	8.97	4.14	0.85	2.19
Exchangeable Mg (mg kg^{-1})	321	568	802	347
Exchangeable Na (mg kg^{-1})	174.22	919.90	4.24	0.06
Exchangeable K (mg kg^{-1})	36.04	2935.92	15.66	0.05
As (mg kg^{-1})	177.91	2.23	6.35	< d.l.
Cd (mg kg^{-1})	13.28	0.29	0.08	0.05
Cu (mg kg^{-1})	42.31	8.97	157	0.36
Pb (mg kg^{-1})	1141	6.22	7.99	< d.l.
Zn (mg kg^{-1})	3877	2091	732	0.26
Mn (mg kg^{-1})	542.81	36.06	6.65	35.25
Fe (mg kg^{-1})	133730	169	26	979

n.d.: not determined.
< d.l.: below detection limit ($CaCO_3$: 0.07%; P: 60 μg kg^{-1}; As: 7 μg kg^{-1}; Pb: 30 μg kg^{-1}).

2. Materials and methods

2.1. Soil, amendments and plant material

Pyritic tailings were collected from a tailings pond at the Mining District of Cartagena-La Unión (SE Spain) (37°35‘38″ N, 0°53′11” W). It was characterized by the absence of vegetation, high acidity and metal concentrations, extremely low organic matter content, and erosion by wind and water. The climate of the area is semiarid Mediterranean, with a mean annual temperature of 18 °C and mean annual rainfall of 275 mm. Tailings were collected from the top 20 cm, air-dried for 7 d, and sieved < 2 mm. We used two different amendments (pig manure and marble waste ($CaCO_3$)) for reclamation purposes, in order to increase organic matter and nutrients, decrease heavy metals availability, ameliorate soil structure and neutralize acidity. The pig manure came from a pig farm in Pozo Estrecho (SE Spain) and the marble waste was collected from quarries in Cehegín (SE Spain). Tailings, substrate and amendments characteristics are shown in Table 1.

The experiments were performed with three different substrates: unamended tailings (TS), amended tailings (ATS) and substrate of peat moss, Coconut fiber and perlite (2:2:1 volume) were used as unpolluted positive control (CT). For ATS, marble waste was added at a rate of 10 g kg^{-1}. This rate was calculated using the method proposed by Sobek et al. (1978), which provides an indication of the quantity of $CaCO_3$ required to neutralize all the potential acid according to the percentage of sulfides present in the tailings, to reach a final pH of 7–8, which is the pH value in the native shrubland soils of the area (Martínez-Martínez et al., 2013). Pig manure was added at 23 g kg^{-1}. This dose was calculated on the basis of its organic carbon content to increase soil organic carbon by 10 g kg^{-1}, corresponding to the organic C content in the native shrubland soils of the area (Martínez-Martínez et al., 2013). This solid manure was obtained after separation of the solid phase of the raw pig slurry from the liquid phase using a physical phase separator. The solid fraction was outdoor air-dried under environmental conditions for one month. Final moisture was 10%. The experiment was conducted at “Tomás Ferro” Experimental Agro-Food Station, Universidad Politécnica de Cartagena (UPCT; 37°41′ N; 0°57′ W).