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Improvement of chemical and biological properties of *gossan* mine wastes following application of amendments and growth of *Cistus ladanifer* L.

E.S. Santos [a,b], M.M. Abreu [b,*], F. Macías [c], A. de Varennes [d]

[a] Universidade de Lisboa, Instituto Superior de Agronomia, Unidade de Investigação de Química Ambiental, Tapada da Ajuda, 1349-017 Lisboa, Portugal
[b] Centro de Investigação em Ciências do Ambiente e Empresariais, Instituto Superior Dom Afonso III, Convento Espírito Santo, 8100-641 Loulé, Portugal
[c] Departamento de Edafología y Química Agrícola, Facultad de Biología, Universidad de Santiago de Compostela, Campus Universitario Sur, 15782 Santiago de Compostela, Spain
[d] Universidade de Lisboa, Instituto Superior de Agronomia, Centro de Engenharia dos Biossistemas, Tapada da Ajuda, 1349-017 Lisboa, Portugal

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ABSTRACT

Gossan wastes represent one of the most hazardous mine wastes in several mining areas from the Iberian Pyrite Belt. Phytostabilisation of mine wastes with *Cistus ladanifer* L. could be a good option, but its growth and germination are impaired by substrata conditions. To overcome these limitations, application of organic and inorganic amendments may speed up the growth of *C. ladanifer* while improving the mine wastes. This study evaluated the simultaneous influence of different application rates of amendments and growth of *C. ladanifer* on chemical and biological properties of *gossan* wastes.

Amendments used were mixtures (30, 75, 150 Mg/ha, 1:1:1) of rockwool, agriculture wastes and wastes from liquor distillation of *Arbutus unedo* L. fruits. A microcosm assay with four treatments was carried out (control and three amended treatments) under controlled conditions in a greenhouse during 505 days. *Cistus ladanifer* was sown in half of the pots from each treatment while the remainder was left bare.

Gossan wastes had large total concentrations of several elements (g/kg; Al: 24.8, As: 3.03, Cu: 0.23, Pb; 9.21) whereas the available concentrations of these elements were small (<5.7 % of total). The amendments applied (in particular at 75 and 150 Mg/ha) improved the structure and increased the water-holding capacity, pH and nutrient concentrations in the available fraction of the *gossan* materials. They also led to increases in dehydrogenase and β-glucosidase activities and in plant growth (plant cover, plant height, length of young leaves, fresh biomass). In addition, plants from amended treatments presented lower concentrations of hazardous elements in shoots than plants from unamended control. The presence of the plant did not increase the available concentrations of hazardous elements in wastes, except for As when 150 Mg/ha of amendments was applied.

Phytostabilisation with *C. ladanifer* using a Technosol, resulting from the application of the studied amendments at 75 and 150 Mg/ha to *gossan* materials, seems a promising solution for rehabilitation of this type of mine wastes.

1. Introduction

One of the major global environmental concerns in abandoned mining areas, namely in the Iberian Pyrite Belt (IPB), is related to the large volume of dispersed tailings, composed of different mine wastes (Abreu et al., 2010a; Matos and Martins, 2006; Tordoff et al., 2000). Mine wastes from Portuguese IPB have high total concentrations of several chemical elements and usually also acid-generating solid phases in some wastes (e.g. smelting ashes, milled pyrite) that can intensify their environmental impact, due to enhanced availability of chemical elements that can be transported by surface runoff to adjacent areas and/or leaching, and delay natural attenuation of mine wastes (Abreu et al., 2010a; Matos and Martins, 2006). Nevertheless, these mine tailings usually have sparse vegetation with slow natural colonization and scarce biodiversity.

The São Domingos mine (SE Portugal, Portuguese IPB) was exploited from the pre-roman period until 1960 decade, both in the *gossan* and volcanogenic massive sulfide ore deposits. Nowadays, this mine is abandoned and has large amounts of different mining wastes sparsely dispersed, which reach a total volume of 10.8×10^6 m^3, with high total concentrations of hazardous chemical elements (Álvarez-Valero et al., 2008; Matos and Martins, 2006). Considering the metal mobility, mass/volume and the bioavailable fraction of the potential contaminants, the *gossan* wastes represent the fourth most hazardous mine waste in São Domingos mine (modern slag > leaching tanks > country rocks > *gossan* wastes; Pérez-López et al., 2008), with approximately 1.7×10^6 m^3 of this material/residue (Álvarez-Valero et al., 2008).

* Corresponding author at: Universidade de Lisboa, Instituto Superior de Agronomia, Tapada da Ajuda, 1349-017 Lisboa, Portugal.
E-mail address: manuelaabreu@isa.utl.pt (M.M. Abreu).

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Phytostabilisation is considered an in situ green technology appropriate for the rehabilitation of mine wastes and multi-elemental contaminated soils in the Mediterranean basin (Abreu and Magalhães, 2009; EPA, 2000; Mendez and Maier, 2008; Tordoff et al., 2000). According to these authors, the importance of a plant cover is related to the improvement of the physical (e.g. structure), chemical (e.g. increase of organic matter and nutrients, immobilization of contaminants, decreased leaching) and biological (e.g. increase of microbial activity and diversity) characteristics of soil or wastes (Abreu and Magalhães, 2009 and references therein). Plants also restore ecosystem functions and lead to ecological succession, without requiring further disposal of the resulting biomass (EPA, 2000).

Cistus ladanifer L. is considered a good option for phytostabilisation of mine wastes and soils developed on mine wastes as it is already present in several mining areas from the Portuguese IPB (Alvarenga et al., 2004; Batista et al., 2009; Freitas et al., 2004; Santos et al., 2009, 2012, 2014). However, this species grows slowly and has a small germination rate, due to the conditions of the mine substrata and Mediterranean climate (e.g. nutritional constraints, drought, intense irradiance, high total concentrations of trace elements), which are disadvantages for the success of phytostabilisation.

Application of amendments can speed up the phytostabilisation of the mine wastes (Abreu and Magalhães, 2009; Adriano et al., 2004; EPA, 2000; Macías, 2004; Macías et al., 2011). Several organic and inorganic wastes that can be used as amendments would otherwise end up in landfills (Macías, 2004; Macías et al., 2011). In general, the amendments improve substrata structure and increase the nutrients and organic matter contents and water-holding capacity, essential characteristics in the rehabilitation of Mediterranean mining areas, and can also immobilize hazardous elements by several chemical processes (Adriano et al., 2004; Kumpiene et al., 2008; Tordoff et al., 2000), although some of these effects may not last long (Macías, 2004; Macías et al., 2011). In addition, mixtures of amendments should be adjusted to the conditions of each mine waste in order to produce a specific Technosol that promotes and maintains biogeochemical processes and reduces availability of contaminants to plants (Macías, 2004; Macías et al., 2011; Yao et al., 2009).

This study aimed to: evaluate the influence of combined use of different application rates of amendments and *C. ladanifer* growth on the improvement of chemical and biological properties of *gossan* wastes from the São Domingos mine; and assess the growth and accumulation of chemical elements of *C. ladanifer* during a phytostabilisation process.

2. Materials and methods

2.1. Experimental set-up

Composite samples (0–20 cm deep, nine subsamples, a total of approximately 90 kg) of mining wastes, which are composed of *gossan* materials mixed with host rocks (hereinafter named as *gossan* wastes — GW), and seeds from *C. ladanifer* (50 plants), were collected near of the open pit of São Domingos mine in 2009. This waste material was chosen due to the large amounts of trace elements, the corresponding potential environmental risk they pose (Álvarez-Valero et al., 2008; Pérez-López et al., 2008) and the fact that the area is already naturally colonized by autochthones plants.

The amendment applied was a mixture (1:1:1) of used rockwool from strawberry production in hydroponics, plant remains from several berries and substrate used in strawberry crops at 2:3 m/m, and wastes from liquor distillation of *Arbutus unedo* L. fruits (regional liquor). The proportion and type of organic and inorganic wastes used were chosen because of their physical and chemical properties and large quantities available near the mine at almost “zero cost”. These wastes are usually deposited in various locations without any treatment or legal permission.

The GW and amendment were air-dried before use. A microcosm assay was set up with four treatments (unamended control and application of the amendment at 30, 75 and 150 Mg/ha, each with six replicates) in pots containing about 2 kg of GW (fraction < 10 mm) mixed manually with the organic/inorganic wastes.

After 15 days of incubation at 70 % of the maximum water-holding capacity, *C. ladanifer* was sown (0.5 g seeds per pot) in half of the pots from each treatment ($n = 3$), while the other three pots remained bare. The seeds were pre-treated for optimal germination (heating at 100 °C for 30 min; Corral et al., 1990). All pots (with and without plants) were kept at 70 % of the maximum water-holding capacity in a greenhouse for 505 days.

Plants were thinned to 60 and 35 plants per pot 50 and 167 days after sowing, respectively, to minimize plant competition. Nitrogen was applied 280 days after sowing as an aqueous solution corresponding to 50 mg N/kg per pot in the form of calcium nitrate.

2.2. Experimental monitoring and analytical methods

The initial materials (fraction < 2 mm of GW and total fraction of organic and inorganic wastes) were characterised for pH and electrical conductivity (EC) in water suspension (1:2.5 m/V), organic C (Tinsley method), extractable P and K (Egner–Riehm method), total N (Kjeldahl method) and multi-elemental concentrations, which were analysed by atomic emission spectrometry with induced plasma and instrumental neutron activation analysis after acid digestion with $HClO_4 + HNO_3 + HCl + HF$ (Actlabs, ISO/IEC 17025, Activation Laboratories, 2014). In GW (fraction < 2 mm), Fe from iron oxides (de Endredy, 1963) and Mn from manganese oxides (Chao, 1972) were also determined. Particle size distribution of GW (total fraction) was determined by sieving and sedimentation, with the clay fraction (<2 μm) separated from coarser materials (<2 mm) after water dispersion and sedimentation following Stokes law.

At the beginning (after 15 days of incubation and before sowing) and end of the experiment (505 days after sowing), composite samples of the materials from each pot were collected (0–15 cm of depth). These samples were homogenised and sieved (<2 mm). A part of these samples were kept fresh (4 °C) for soil enzymatic analysis and determination of multi-elemental concentration in the available fraction while the remaining subsamples were air-dried for analysis of pH, EC, organic C, total N and extractable P and K, by the same methodologies referred above.

To determine the available fraction, elements were extracted from GW by the rhizosphere-based method, which uses a 10 mM mixture of organic acids (acetic acid + lactic acid + citric acid + malic acid + formic acid; Feng et al., 2005).

Several enzymatic activities were analysed as biological parameters to evaluate the rehabilitation process, namely: dehydrogenase (Tabatabai, 1994), β-glucosidase (EC 3.2.1.21; Eivazi and Tabatabai, 1988), acid phosphomonoesterase (acid phosphatase EC 3.1.3.2; Eivazi and Tabatabai, 1977) and urease (EC 3.5.1.5; Kandeler and Gerber, 1988). Dehydrogenase was used as an index of overall microbial activity while other enzymatic activities are related to C, P and N cycling.

The percentage of vegetation cover was determined 25 and 50 days after sowing (Qu and de Varennes, 2010) and plant growth was analysed at each thinning (dominant plant height and length of young leaves and fresh biomass). At the end of the experiment, roots and shoots (composed of leaves and twigs) of *C. ladanifer* plants were collected. Plant samples were washed with tap water and then with distilled water. After washing, the roots were sonicated in distilled water for 30 min. Plant samples were dried (40 °C), homogenised and finely ground. Elements (except N) were extracted from samples with ultrapure concentrated nitric acid (69 %) under pressure in a microwave digester during 2 min at 85 °C + 5 min at 145 °C + 5 min at 200 °C + 18 min at 200 °C. Total concentration of N was analysed by combustion with a Leco analyser. Certified reference samples of bush branches and