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Chemical and ecotoxicological effects of the use of drinking-water treatment residuals for the remediation of soils degraded by mining activities

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ABSTRACT

The aim of this study was to evaluate the use of drinking-water treatment residuals (DWTR) in the amendment of a soil affected by mining activities (Aljustrel mine, Portuguese sector of the Iberian Pyrite Belt), considering the effects on its chemical, biochemical and ecotoxicological characteristics. The DWTR had neutral characteristics (pH 6.7) and an organic matter (OM) content of 575 g kg^{-1} dry matter (DM), which makes them a potential amendment for the remediation of mine degraded soils, as they may correct soil acidity and reduce the extractable metal fraction. An incubation assay, with soil and DWTR, with or without lime, was carried out to test the doses to be used in the assisted-phytostabilization experiment. Based on the results obtained, the doses of DWTR used were the equivalent to 48, 96, and 144 t DM ha^{-1}, with and without lime application ($CaCO_3$ 11 t DM ha^{-1}). *Agrostis tenuis* Sibth was used as the test plant. Some amendments doses were able to improve soil characteristics (pH and OM content), to decrease metal extractability by 0.01 M $CaCl_2$ (especially for Cu and Zn), and to allow plant growth, that did not occur in the non-amended soil. Copper, Pb and Zn concentrations in the plant material were lower than the maximum tolerable level for cattle feed, used as an indicator of risk of entry of those metals into the human food chain. The simultaneous application of DWTR (96 and 144 t ha^{-1}), with lime, allowed a reduction in the mine soil ecotoxicity, as evaluated by some lethal and sub-lethal bioassays, including luminescence inhibition of *Vibrio fischeri*, *Daphnia magna* acute immobilization test, mortality of *Thamnocephalus platyurus*, and 72-h growth inhibition of the green microalgae *Pseudokirchneriella subcapitata*. However, DWTR were unable to increase soil microbial activity, evaluated by dehydrogenase activity, an important soil-health indicator. Also, OM content and $N_{Kjeldahl}$, concentrations increased slightly but remained low or very low (P and K extractable concentrations were not affected). In general, the bioassays highlighted a decrease in soil ecotoxicity with the presence of lime and DWTR (144 t DM ha^{-1}). In conclusion, DWTR are recommended to amend acidic soils, with high concentrations of trace elements, but an additional application of organic or mineral fertilizers should be considered.

1. Introduction

In Portugal, mining exploration is ancient, at least since the Roman occupation of the peninsula (Alvarenga et al., 2004). Generally, the ore extraction and processing led to the production of large volumes of waste rocks and tailings, which were deposited in the surroundings of the mine (Matos and Martins, 2006). Nowadays, many of these mines are abandoned, but the erosion of these soils, by wind and water, contributes to the progressive enlargement of the contaminated area (Alvarenga et al., 2004; Matos and Martins, 2006). In Portugal, thousands of hectares of abandoned mine lands, affected by low pH, poor nutritional conditions, and high concentrations of potentially toxic trace elements, need reclamation (Alvarenga et al., 2012; 2103; Matos and Martins, 2006; Abreu et al., 2010; Silva et al., 2009).

The most conventional option for the rehabilitation of areas affected by mining activities consists in digging out the polluted soil and its confinement, without treatment, in a controlled landfill, followed by surface capping using unpolluted material, excavated from elsewhere. This option is often expensive and can have a huge environmental impact in both sites, the one to be recovered and the one where the soil was deposited (Sarkar et al., 2007; Volchko et al., 2014; Söderqvist et al., 2015). Therefore, it is very important to develop strategies that

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can treat and stabilize contaminants *in situ*, in an efficient and cost-effective manner (Sarkar et al., 2007; Volchko et al., 2014; Söderqvist et al., 2015; Peña et al., 2015). *In situ* chemical immobilization, where land applied amendments are used to retain contaminants *via* adsorption and/or precipitation reactions, is an effective and cost-effective option (Adriano et al., 2004). Even more promising, is to combine the *in-situ* immobilization of metals with phytoremediation, in a strategy that can be called "aided phytostabilization". The latter could be a realistic, environmentally sound, and cost-effective alternative, especially for vast industrial sites, like abandoned mine areas, because not only the potentially toxic trace elements are immobilized, but also because the soil is protected from erosion by the establishment of a plant cover (Vangronsveld et al., 1995; Tordoff et al., 2000; Mench et al., 2003; Wong, 2003; Adriano et al., 2004; Pérez-de-Mora et al., 2006; Alvarenga et al., 2009a, 2009b; Pardo et al., 2011; Galende et al., 2014; Peña et al., 2015). In a phytostabilization strategy, it is very important to improve the soil capacity to sustain a plant cover, which can be achieved by properly amending the soil, for instance with organic and inorganic amendments, like those obtained in the valorisation of wastes (Alvarenga et al., 2008a, 2009a, 2014; Pardo et al., 2011; Galende et al., 2014; Peña et al., 2015). The soil amendment can promote the re-establishment of a vegetative cover on these soils by: adding essential nutrients for plant growth, increasing the organic matter content, raising the pH, increasing the water-holding capacity, and by rendering the metals less mobile/bioavailable by shifting them from "plant-available" forms, extractable with water or solutions of neutral salts, to fractions associated with organic matter, carbonates or metal oxides (Alvarenga et al., 2008a, 2009a, 2014; Peña et al., 2015). Numerous inorganic (*e.g.* clays, red mud, Al/Fe/Mn oxides and hydroxides; Lombi et al., 2004; Sarkar et al., 2007; Rodríguez-Jordá et al., 2010a; Rodríguez-Jordá et al., 2010b; Castaldi et al., 2014; Garau et al., 2014) and/or organic amendments (*e.g.* sewage sludge, municipal solid waste compost, green waste compost, biochar; Beesley et al., 2010; Pérez-de-Mora et al., 2011; Pardo et al., 2011; Galende et al., 2014) have been land-applied with success, reducing trace elements mobility.

Polyelectrolytes, like Fe and Al salts (*e.g.* $FeCl_3$, $Fe_2(SO_4)_3$, Al_2O_3), are often used to remove particulate and dissolved constituents from water supplies, acting as coagulant agents, in the production of potable drinking water (Ippolito et al., 2011). Besides the desired treated water, a waste sludge is produced, called drinking-water treatment residuals (DWTR), which are rich in Fe/Al (hydr)oxides. Elliott and Dempsey (1991), reported one of the first studies of the agronomic effects of land application of these sludges, emphasizing the need for their useful use, as opposed to the large costs for their landfill disposal. However, they alerted for the fact that DWTR should be mostly used as a soil conditioner, for their liming and water-holding capacities, and not because of their organic matter or nutrient content (Elliott and Dempsey, 1991). That liming capacity, associated with the potential ability of Fe/Al (hydr)oxides to bind As in soils (Lombi et al., 2004; Sarkar et al., 2007; Castaldi et al., 2014; Garau et al., 2014), may turn these residual materials into interesting conditioners in trace elements contaminated soils. Several authors have evaluated the capacity of DWTR to immobilize As and other metalloids in contaminated soils, because it is known that the adsorption of As in soils is primarily controlled by Fe/Al (hydr)oxides (Sarkar et al., 2007; Garau et al., 2014; Castaldi et al., 2014). In fact, Fe/Al (hydr)oxides can be very effective in decreasing metalloids bioavailability in soils due to their high specific surface area and reactive surficial functional groups (Sarkar et al., 2007; Garau et al., 2014). Other authors have studied the capacity of DWTR, in combination with diammonium phosphate, composted biosolids, or lime-stabilized biosolids, to act as metal adsorbents in tailings contaminated with Pb, Zn and Cd, and found promising results with one of the combinations, which allowed the revegetation of the tailing (Ippolito et al., 2011; Brown et al., 2007).

The improvement in soil quality, because of its remediation, can be assessed by general physicochemical properties, which are related to soil fertility status, and using chemical extraction procedures, as surrogate measures of trace elements immobilization (Rao et al., 2008; Alvarenga et al., 2009a, 2013; Davidson, 2013). However, chemical data should be complemented with results from biochemical and ecotoxicological tests, which allow an integrated evaluation of the toxic effects of pollutants on organisms and the interactions between contaminants, matrix and biota (ISO 17402, 2008; Leitgib et al., 2007; Alvarenga et al., 2009b; Epelde et al., 2009; Epelde et al., 2014). Ecotoxicological tests using aqueous soil extracts can be used to assess soil toxicity, not only because chemical compounds present in the soil aqueous phase affect soil organisms, but also because they evaluate the impact of soil composition on ground water and runoff to surrounding receiving waters (*i.e.* soil retention function) (van Gestel et al., 2001; Loureiro et al., 2005; Leitgib et al., 2007; Antunes et al., 2008; Alvarenga et al., 2008b, 2009b, 2016).

Another important indicator of soil fertility and ecological status are soil enzymatic activities. Dehydrogenase is an intracellular oxidoreductase, related to the oxidative phosphorylation process, which, because of that, can be used as an overall indicator of microbial activity in a soil (Tabatabai, 1994; Gil-Sotres et al., 2005; Izquierdo et al., 2005; Tejada et al., 2006). That is why the measurement of its activity has been used by several authors as an early and sensitive indicator of soil health recovery in remediation processes (Pérez-de-Mora et al., 2005, 2006; Tejada et al., 2006; Hinojosa et al., 2008).

Taking all these facts into account, the aim of this study was to evaluate the effectiveness of DWTR, from the Roxo water treatment plant (Alentejo – Portugal), as the amendment of a soil affected by mining activities (Aljustrel mine, Iberian Pyrite Belt), in order to assess: (i) the effects of the amendments in soil chemical properties, (ii) the capacity of the soil to establish a plant cover using *Agrostis tenuis* Sibth., (iii) the capacity of DWTR to immobilize metals in the soil, avoiding their transference to the plant, and (iv) the effects of the amendments in the soil ecotoxicological and biochemical properties.

2. Materials and methods

2.1. Characterization of the drinking water treatment residuals

Drinking water treatment residuals were obtained from a water treatment plant (WTP) which is located at the Roxo dam in Alentejo (Portugal). The water is captured in the dam and submitted to a sequence of processes and operations to produce a safe drinking water. First, the water passes through a screen to remove coarse material, and then to a pre-chlorination, by the injection of ClO_2, for algae control and arresting biological growth. The addition of a polyelectrolyte, Al_2O_3, promotes the coagulation and flocculation steps, which neutralizes the negative charge of the suspended colloids, promoting coagulation and the formation of thicker flocs, which settle during the sedimentation. The clear water obtained on top, after the settlement, will pass through sand and activated carbon filters, to remove dissolved particles, and, afterwards it is submitted to a final disinfection, again with ClO_2, which has a strong oxidizing potential and will not only kill any remaining microorganism, but also allow the elimination of iron and manganese.

Drinking water treatment residuals are produced during the sedimentation and filtration stages and are submitted to thickening to increase their solid content. First, an organic flocculant is added (Superfloc C-496®), which will promote the liquid-solid separation, and then they are mechanical dewatered in a belt-filter press. At the time of this experiment, all DWTR produced at Roxo WTP were sent to a municipal landfill.

The characterization of the DWTR was performed in accordance with the Decree-Law No. 276/2009, which regulates the use of sewage sludge, and similar sludges, in agricultural practices (Table 1), with techniques described elsewhere (Alvarenga et al., 2015). The DWTR have neutral characteristics (pH 6.7), which may contribute to the