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Improving the mining soil quality for a vegetation cover after addition of sewage sludges: Inorganic ions and low-molecular-weight organic acids in the soil solution

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ABSTRACT

We assessed the effects of applying stabilized sewage sludge (SSL) and composted sewage sludge (CLV), at 5 and 10% to an acid mining soil. Limed soil (NC_L) amended or not with SSL and CLV was incubated for 47 days. We studied the cations and organic and inorganic anions in the soil solution by means of ion chromatography. Liming led to big increases in Ca^{2+} and SO_4^{2-} and to significant decreases in K^+, Mg^{2+}, NH_4^+ and NO_3^-. Addition of both organic amendments increased some cations (NH_4^+, K^+, Mg^{2+}, Na^+) and anions (Cl^-, NO_3^- only with CLV and PO_4^{3-} only with SSL) and provided a greater amount of low-molecular-weight organic acids (LMWOAs) (SSL more than CLV). Incubation led to decreases in all cations, particularly remarkable for Ca^{2+} and Mg^{2+} in SSL-10. A decrease in NH_4^+ was associated with variations in NO_2^- and NO_3^- resulting from nitrification reactions. During incubation the LMWOAs content tended to decrease similarly to the cations, especially in SSL-10. Chemometric tools revealed a clear discrimination between SSL, CLV and NC_L. Furthermore, treatment effects depended upon dose, mainly in SSL. Amendment nature and dose affect the quality of a mining soil and improve conditions for plant establishment.

1. Introduction

Mining areas constitute degraded ecosystems resulting from mineral extraction for over long periods of time giving rise to large areas of derelict land. Intensification of mining causes a ecological impact at local and regional scales. Mining wastes can be stabilised by revegetation policies (Clemente et al., 2007). Establishment of a vegetation cover calls for a water-soil system capable of supporting the nutrient and water requirements of plants. In acid mine tailings, revegetation must primarily overcome extreme acidity by addition of a liming agent, and then correct nutrient deficiencies by application of fertilizers.

In Andalusia (Southern Spain) mining activities date from pre-Roman times. Intensive deforestation have led to degraded and abandoned land incapable of sustaining commercial agriculture, as well as destruction of the natural vegetation. In the Riotinto mining area, located in the Iberian Pyrite Belt, acidification of soils occurred due to oxidation of the metallic sulphides (pyrite) transported by acidic mine drainage and to atmospheric deposition of wind-blown dust (Rodríguez-Liébana et al., 2013). These soils present high levels of toxic elements and low levels of plant nutrients; so, application of organic residues has become a popular strategy due to the agronomic benefits involved. In addition, although the total levels of toxic elements is high, concentrations of soluble and exchangeable chemical forms of metals depend on their bio-accessibility properties and speciation, being those levels usually lower than total concentrations (Ciarkowska et al., 2014). For instance Martínez-Sánchez et al. (2013) demonstrated that arsenic bio-

Abbreviations: CA, Cluster Analysis; CLV, Compost of sewage sludge with vegetal remains; DOC, Dissolved organic carbon; LMWOAs, Low-molecular-weight organic acids; LOD, Limit of detection; LOQ, Limit of quantitation; NC, Native soil; NC_L, Limed soil, with $CaCO_3$ (Carbocal); PCA, Principal Component Analysis; PCs, Principal components; RSD, Relative standard deviation; SSL, Stabilized sewage sludge; $t_{1/2\downarrow}$, Time for the disappearance of half of the initial ion concentration; $t_{1/2\uparrow}$, Time for the increase to 50% the initial ion concentration.

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accessibility to humans in mine soils was really low regarding the high total concentrations. Besides, speciation studies next to mine soils have shown that there was no risk to humans by soluble lead and zinc levels in arable and pasture lands (Rodríguez et al., 2009). However, the possible negative effects in plants depend on the metal studied; this way, Struckhoff et al. (2013) showed that high concentrations of lead caused adverse native floristic quality, although no other human disturbance was evident.

Urban sewage sludge constitutes an economical alternative and contributes to solving the problem of waste disposal. Furthermore, composted residues have become an attractive option, because degradation–transformation reactions during the composting process turn the organic matter into a more stable humus-like product (Senesi, 1989). Organic amendments improve soil quality but, at the same time, supply the soil solution with organic and inorganic ions (Kayikcioglu, 2012). Bioremediation of soils with biochars, where carbon mineralization is lower and slow, constitutes another alternative to the conventional amendments (Wu et al., 2014; Sun et al., 2014).

Although the benefits of lime and organic residues addition are initially evident, the incubation process leads to changes in soil solution composition, with possible implications for retention or availability of nutrients or other compounds (Rodríguez-Liébana et al., 2011). Not only the inorganic composition of soil solution will evolve with waste addition, but also the content in low-molecular-weight organic acids (LMWOAs) (Drever and Stillings, 1997). LMWOAs have been reported to play key roles in many soil and plant processes, relying on their ability to complex metal cations (Jones et al., 2003; Strobel, 2001) or to interfere in sorption-desorption processes of hydrophobic organic pollutants (González et al., 2010). Concentrations in non-amended soil solution of aliphatic mono-, di- and tri-carboxylic acids are an order of magnitude lower than those of inorganic solutes. Furthermore, application of organic amendments implies the introduction of large amounts of dissolved organic matter, with carbon in LMWOAs comprising less than 10% of total dissolved organic carbon (DOC) in most soil solutions (Strobel et al., 1999).

We therefore attempted to evaluate the changes in the soil-solution composition of an acidic mine soil amended with organic residues from urban sewage sludge. An understanding of the chemistry of the soil-water-plant interface is important with regard to optimising revegetation strategies (Mingorance et al., 2014). A vegetation cover improves soil quality by reducing soil erosion, both eolian and water erosion, by improving soil structure and natural soil fertility and by favoring microbial activity. In addition, the application of a vegetative cover helps to avoid the natural dispersion of pollutants along the time (Rodríguez et al., 2009; Vázquez et al., 2011). Although this study was not focused directly on vegetation cover, it takes part of a more wide study aiming at improving soil quality with a view to revegetating mine soils (Rodríguez-Liébana et al., 2013; Mingorance et al., 2014; Peña et al., 2014).

2. Experimental methods

2.1. Site description. Soil and amendment properties

We collected the soil (NC) from an abandoned mine in the Riotinto mining zone, in the vicinity of the village of Nerva, Huelva province (SW Spain) (Fig. 1), located in the Iberian Pyrite Belt. Soil collection and characterization was done as in Mingorance et al. (2014). In brief, the sandy-loam soil (55% sand, 14% clay) is extremely acidic (pH_{H2O} 2.4), presents high electrical conductivity (1.3 dS m^{-1}) (both at 1:2.5 ratio) and low organic carbon content (1.4%). The content of some potentially hazardous metals and non-metals usually present in mining areas (As, 3951; Cd, 13; Cu, 694; Pb, 3976 in mg kg^{-1}) is above local guidelines for total concentrations (Aguilar et al., 1999).

We employed two organic amendments from wastewater treatment plants: stabilized sewage sludge (SSL) and composted sewage sludge with remains from olive pruning (CLV). Both SSL and CLV share, respectively, a neutral pH (6.9 and 7.0), have a humification index (HIX) of 0.43 and 2.16, as well as high OC content (35.5 and 16.0%) and electrical conductivity (2.8 and 4.2 dS m^{-1}) (1:10 ratio). Humic acid content was 1.6 and 8.2% and fulvic acid content, 0.47 and 7%, respectively, for SSL and CLV. The potential toxic metal loads of SSL at the 5% dose and CLV at any dose were lower than those corresponding to European guidelines concerning external application to soil (European Commission, 1986).

2.2. Incubation procedure

Prior to addition of amendments, soil was first limed (NC_L) with Carbocal (Azucarera Ebro), a residue rich in $CaCO_3$ (83.4% and an OC

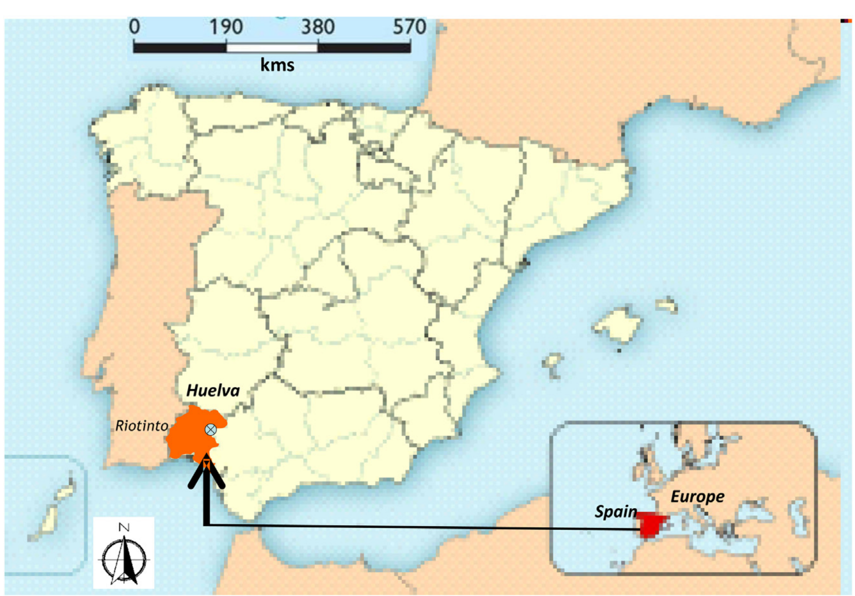

Fig. 1. Location of the Nerva mine in the Riotinto area, Huelva (SW Spain, UTM: 29S 715131 4175471).