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Technosols designed for rehabilitation of mining activities using mine spoils and biosolids. Ion mobility and correlations using percolation columns

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ABSTRACT

The restoration technologies in areas degraded by extractive activities are more efficient under the use of their own spoils. Reducing deficiencies in physical properties, organic matter, and nutrients with a contribution of treated sewage sludge is proposed. This experiment was based on a controlled study using columns. The work was done with two limestone quarry spoils, both very rich in calcite. Two biosolid doses were undertaken (30,000 and 90,000 kg/ha of sewage sludge) in addition to different quarry spoils used as substrates. The water contribution was provided by a device simulating short duration rain. The leached water was collected 24 h after the last application. Nitrate, ammonium, phosphate, sulfate, and chloride ions were determined, as well as Ca, Mg, Na and K, the pH and electrical conductivity. The electrical conductivity limit value is <1000 μS/cm. These values will be met from the fourth irrigation application onward, while the values up to that point were far superior. Significant nitrate concentrations appeared that may pose an environmental contamination risk. A comparison between the concentrations of the chemical elements obtained in the leachates from our experiment and the established limit values for water of the third quality group has been performed. The electrical conductivity correlated well with the cations, with the exception of potassium. For sulfates, significant correlations were obtained with the Mg^{2+}, Ca^{2+}, and K^{+} cations. The chlorides showed excellent correlation with the sodium. The good correlations obtained for some physical–chemical parameters can help to establish indicators of environmental quality of leachates over time.

1. Introduction

The restoration of extensive areas degraded by mining activities requires the use or their own waste materials (Jordán et al., 1998, 2006; Tedesco et al., 1999; Ram et al., 2006; Almendro-Candel et al., 2014; Galán et al., 2014). These materials do not possess the necessary fertility to ensure a successful process of restoration (implementation of adequate plant cover). Therefore, it requires the addition of organic amendments to achieve efficient substrate (Jordán et al., 2008). The obligation to restore abandoned quarries and the correct application of biosolids is guaranteed by the legislation on waste management, biosolids and soil conservation (Jordán et al., 2008). Technosols are one of the latest additions to the World Reference Base for Soil Resources (FAO, 2006). This new reference soil group contains a large range of artifacts and materials of natural and anthropic origin. They include a variety of refuse-based soil-like quarry spoils, landfills, ashes, or sludges, whose properties and pedogenesis are dominated by their technical origin (FAO, 2006). An adequate Technosol selection, based on its nature and intrinsic properties, can constitute a valuable and cost-effective solution for soil remediation and waste management (Novo et al., 2013). Sewage sludge application in restoration has demonstrated its efficiency in previous studies using percolation columns (Clapp et al., 1986; Albiach et al., 2001; Pond et al., 2005; Jordán et al., 2008; Soriano-Disla et al., 2014). The use of treated sewage sludge can be a guarantee of success in the restoration of areas affected by mining activities, but it is important to preserve the conservation of the environment with less risk of contamination of surface and groundwater. Many physical and chemical properties in soils amended with sludge, such as water retention capacity, aggregate stability, contribution of N, P, and other nutrients to crop growth, depend, to some extent, upon the quantity of organic matter in the sludge that is added (Roldán et al., 1994). Knowledge about the quantity of organic matter in the sludge can be used to estimate the quantities that must be applied to the soil (Giovannini et al., 1985). Use of sewage sludge and quarry spoils to construct Technosols represents an innovative strategy of waste management, whose application

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allowed the species to grow and develop (Novo et al., 2013). The materials resulting from the acquisition of arid particles produced from crushed limestone present very limited results in restoration because of their chemical and mineralogical characteristics. The materials resulting from limestone extraction, with elevated soil stoniness and low fertility, are usually used in restoration, and the efficiency depends upon the organic corrections (Jordán et al., 2008).

The studied area, Sierra de Callosa has an area of 8 km^2 and a maximum altitude of 566 masl (Jordán et al., 2008). Geologically, it is found to be primarily comprised of carbonated rocks. Limestones have been worked for many thousands of years, initially for building stone and agricultural lime and more recently for a wide range of construction and industrial uses. In former days, limestone quarries were small operations with limited production due to the labor-intensive nature of the business and restricted markets for stone. Stone quarries can answer the demand of aggregates for concrete applications (Jordán et al., 2008).

The main objective is to evaluate the ion mobility and correlations in columns packed with quarry spoils from a limestone quarry amended with biosolids. Similar experiments based in columns have been developed with columns of the same material (Emmerich et al., 1982) but with 10 cm internal diameters in order to evaluate the potential movement of metals in soils where sewage sludge was applied on the soil surface. Esaki et al. (1993) employed glass columns to analyze the composition of organic materials in leachates, while Smith et al. (1995) used this same type of column to study water flow in soil.

2. Materials and methods

2.1. Substratum

The experiment was carried out using two different limestone quarry spoils, both very rich in calcium carbonate (450–750 g/kg). The first, of poor quality, originates from the crushed limestone (Z). It is composed of coarse materials (up to 75% by weight) and sand. The other tested waste material comes from the extraction of limestone. This waste was formed by the levels of interspersed non-limestone materials and remains of stripped soils (D). This usually presents more balanced textures but with elevated heterometry soil stoniness (up to 60% by weight), and is richer in clays (approx. 25% by weight). Analytical parameters were determined in accordance with ISRIC (1993). Organic matter was quantified by wet oxidation, using the method of Walkley and Black (1974), total nitrogen by the Kjeldahl method, pH in a 1:2.5 soil/water suspension, the $CaCO_3$ equivalent with a Bernard calcimeter, by atomic absorption (Ca, Mg, Fe, Cu, Mn, Zn) and flame atomic emission spectroscopy (Na, K). Particle size distribution was determined by the pipette method.

The characteristics of the mineral substrata employed appear in Table 1. Both these materials were amended with the biosolid according to Alcañiz et al. (1997) quarry restoration methodology.

2.2. Sewage sludge

The biosolid used in this experiment comes from a wastewater treatment plant located near Aspe (Alicante). Prior to the composting process, the sludge needs to be mixed with a bulking agent, a supporting structure that favors aeration, absorbs humidity, and furthermore contributes with organic matter. Chopped hay and sawdust are used as bulking agents, and silos exist for their storage. Hay favors aeration, sawdust absorbs humidity, and both materials constitute sources for carbon. The composition by volume of the sludge-bulking agent mixture is 50% sludge, while the remaining 50% is 1/4 hay and 3/4 sawdust. This sludge-bulking agent mixture progresses through the composting tunnel and is simultaneously homogenized by a tumbler, which in addition to permitting the progress and homogenization of the mixture, promotes its aeration. During the first weeks, the mixture is placed upon a porous base connected to an air injection system using fans or blowers, which maintains discontinuous forced aeration. Afterwards, the aeration is passive and natural (Clapp et al., 1986; Hernández-Fernández et al., 1986).

Table 1
Characteristics of the substrata used in the experiment (Jordán et al., 2008).

Parameter	Z	D
Clay < 2 μ (g/kg)	150	210
Silt 2 – 50 μ (g/kg)	160	260
Sand 50 μ − 2 mm(g/kg)	690	530
pH	8.25	8.92
EC μS/cm (25 °C)	257.20	56.32
OM (g/kg)	5.3	2.7
P (mg/kg DM)	2.04	2.07
Ca (g/kg DM)	3.37	3.26
Mg (mg/kg DM)	134.13	337.57
Na (mg/kg DM)	222.15	63.27
K (mg/kg DM)	34.66	64.31
Fe (mg/kg DM)	2.25	1.48
Cu (mg/kg DM)	0.29	0.18
Mn (mg/kg DM)	2.08	1.07
Zn (mg/kg DM)	0.73	0.36
N (g/kg)	0.3	0.2
$CaCO_3$ (g/kg)	450–750	550–700
Active $CaCO_3$ (g/kg)	180	150

Total concentrations.
Z: Limestone spoils; D: Stripped soil; DM: Dry matter.

For the biosolid analysis, total content of metals was determined following microwave digestion using HNO_3 and analyzed by inductively coupled plasma mass spectrometry. In the solution thus obtained, the solubilized elements except for nitrogen were assessed. This was determined by the Kjeldahl method, which quantifies the organic nitrogen and ammonium contents within the sample. The easily oxidizable organic carbon was estimated by sulfochromic digestion and subsequent assessment with Mohr's salt, while the easily oxidizable organic matter was calculated by multiplying the organic carbon by 1.72. The total organic matter was obtained by calcination in a muffle furnace at 500 °C for 2–4 h. Table 2 shows sewage sludge composition.

2.3. Columns

The experiment was based on a controlled study using columns. Fifteen columns, each 30 cm tall (Fig. 1), were constructed from 10.5 cm internal diameter PVC pipe that was cut into two 15 cm lengths. Each column was divided into two different 15 cm sections, the first one from 0 to 15 cm and the second from 15 to 30 cm. For each treatment three replicates were done (Table 3).

Table 2
Sewage sludge composition (dry matter, DM) from the Aspe wastewater treatment plant.

Parameter	Value
Organic C (g/kg)	430.4
Kjeldahl N (g/kg)	30.8
P (g/kg DM)	3.2
Na (g/kg DM)	2.9
K (g/kg DM)	1.8
Ca (g/kg DM)	1.0
Mg (g/kg DM)	0.7
Fe (g/kg DM)	5.58
Cu (mg/kg DM)	279
Cd (mg/kg DM)	0.98
Ni (mg/kg DM)	19
Pb (mg/kg DM)	123
Zn (mg/kg DM)	778
Hg (mg/kg DM)	1.26
Cr (mg/kg DM)	22

Total concentrations.