Trabajo Seleccionado del XV Congreso Internacional en Ciencias Agrícolas. Instituto de Ciencias Agrícolas, Universidad Autónoma de Baja California. Responsable del Comité Científico del XV CICA: Dra. Silvia Mónica Avilés Marín

MARBLE WASTE AND PIG SLURRY INCREMENT SOIL QUALITY AND REDUCE METAL AVAILABILITY IN A TAILING POND

El Uso de Residuo de Mármol y Purines Porcinos Incrementa la Calidad del Suelo y Disminuye la Disponibilidad de Metales Pesados en un Depósito Minero

Raúl Zornoza[1‡], Ángel Faz[1], Silvia Martínez-Martínez[1], José Alberto Acosta[1], María Dolores Gómez-López[1] y Silvia Mónica Avilés-Marín[2]

SUMMARY

Tailing ponds pose environmental hazards, such as toxic metals reaching water sources through wind and water erosion and leaching. These abandoned mine sites contain materials with high contents of Fe-oxyhydroxides, sulfides, and heavy metals. As a consequence, soils have null vegetation and low soil organic matter. In this study, various physicochemical properties, together with microbial biomass carbon and available metals, were measured before and six months after application of marble waste (6.7 kg m^{-2}), raw pig slurry (4.3 L m^{-2}), and solid phase pig slurry (7 kg m^{-2}) as reclamation strategy in a tailing pond in southeastern Spain, to reduce hazards for the environment and human health. Results showed that aggregate stability, pH, organic carbon, total nitrogen, cation exchange capacity, available phosphorus, exchangeable potassium and microbial biomass carbon increased with the application of the amendments, while available metals and metalloid (As, Cd, Pb and Zn) drastically decreased (90-99%). This study confirms the high effectiveness of initial applications of marble wastes together with pig slurry to initialize the recovery of ecosystems in bare mine soils under Mediterranean semiarid conditions.

Index words: *contamination, heavy metals, tailing pond, amendments.*

[1] Grupo de Investigación, Gestión, Aprovechamiento y Recuperación de Suelos y Aguas. Universidad Politécnica de Cartagena. Paseo Alfonso 12, 52. 30230 Cartagena, Murcia, España.
‡ Autor responsable (raul.zornoza@upct.es)
[2] Instituto de Ciencias Agrícolas. Universidad Autónoma de Baja California. Carretera a Delta s/n, Ejido Nuevo León. 21705 Baja California, México.

Recibido: febrero de 2013. Aceptado: mayo de 2013.
Publicado en Terra Latinoamericana 31: 105-114.

RESUMEN

Los depósitos de acumulación de residuos procedentes de la minería llevan asociados grandes riesgos ambientales, como la transferencia de metales tóxicos que pueden contaminar aguas y suelos por transporte aéreo, escorrentía y lixiviación. Estos depósitos contienen minerales ricos en óxidos de hierro, sulfuros y elevadas concentraciones de metales pesados y metaloides. Como consecuencia, el desarrollo de la vegetación está muy limitado, siendo la cubierta vegetal casi inexistente y el contenido de materia orgánica del suelo muy bajo. En este estudio se han analizado diferentes propiedades físico-químicas, junto con el carbono de la biomasa microbiana y la fracción disponible de varios metales y un metaloide antes y seis meses después de la aplicación de residuo de mármol (6.7 kg m^{-2}), purín porcino bruto (4.3 L m^{-2}) y la fase sólida de purín porcino (7 kg m^{-2}) como estrategia de rehabilitación de un depósito de residuos mineros ubicado en el sureste de España, con el objetivo de reducir los riesgos para el medio ambiente y la salud pública. Los resultados obtenidos mostraron que la estabilidad de agregados, el pH, el carbono orgánico, el nitrógeno total, la capacidad de intercambio catiónico, el fósforo disponible, el potasio intercambiable y el carbono de la biomasa microbiana se incrementaron tras la aplicación de las enmiendas. La fracción disponible de los metales y metaloide medidos (As, Cd, Pb y Zn) descendió drásticamente (90-99%). Por tanto, este estudio confirma la alta efectividad de la aplicación inicial de residuo de mármol y purines porcinos para iniciar la recuperación del ecosistema en suelo mineros desnudos bajo condiciones Mediterráneas semiáridas.

Palabras clave: *contaminación, metales pesados, depósito minero, enmiendas.*

INTRODUCTION

In the Region of Murcia (southeastern Spain) past mining activities have generated large amounts of unconfined wastes accumulated in tailing ponds due to intensive mining activities that occurred during the last century, especially in the Mining District of Cartagena-La Unión. Although mining activity was abandoned in 1991, tailing ponds still remain in the area. These tailing ponds contain materials rich in Fe-oxyhydroxides, sulfides, sulfates, and heavy metals (mainly Cd, Pb, Cu and Zn), as a consequence, these soils remain bare and have low soil organic matter content (Conesa *et al.*, 2006). High incidences of wind and water erosion events negatively effect soil, water, vegetation, fauna, and human populations in the surrounding areas (Zanuzzi *et al.*, 2009). Revegetation is needed to reinforce the topsoil and reduce soil erosion and runoff velocity. However, owing to metal toxicity and extremely low organic matter content and nutrients, the establishment of vegetation is compromised (Zornoza *et al.*, 2011). As a consequence, the reclamation of abandoned mine sites relies on achieving optimum conditions for plant growth by improving the soil physical and chemical characteristics by using different amendments (Bradshaw and Johnson, 1992; Acosta *et al.*, 2011). Conventional remedial approaches to metal-contaminated soils usually involve removal and replacement of soil with clean materials (Brown *et al.*, 2005), although it is not considered the most economically or environmentally sound solution available (Alvarenga *et al.*, 2008). Organic wastes such as sewage sludge or animal manure can be used as nutrient sources which stimulate the formation of aggregates (Zanuzzi *et al.*, 2009). The management of organic wastes coming from the pig industry represents a serious environmental problem because of their huge volume and poor recovery. One of the main concerns is how to treat them in an environmentally sound way. Concretely, the Region of Murcia has more than 8% of the pig production of Spain, with almost 2 000 000 pigs. This quantity of pigs generates an annual production of 6.5 Hm^3 of wastes. This large volume of pig slurry continuously increases with high demands for pork, and consequently, it creates disposal problems for many pig producers. Using pig slurries as soil amendment addresses two environmental problems: disposal of industrial wastes from pig production and reclamation of mine soils. As a consequence, the raw slurry, or the solid organic phase after physical separation, can be reused to reclaim polluted and degraded soils, always applied in correct doses, to avoid the excess of salinity and nitrates, which are highly mobile in water.

The transformation of metals into less bioavailable forms is a possible solution for the remediation of a mining area. Alkaline materials, such as marble wastes, are commonly used as an amendment for ameliorating the acidic conditions of many acid-generating mine wastes. Correction of acidity not only enables a wide range of plants to establish but it also mitigates metal toxicity and increases availability of plant nutrients such as potassium, calcium, magnesium, molybdenum and phosphorus, which are more mobile at pH above 6 (Barker, 1997). Organic residues are also normally used as amendments because the addition of organic matter can significantly improve the physical characteristics and nutrient status, stimulate microbial populations, and possibly reduce the availability of toxic metals through complexation (Ye *et al.*, 2002). The use of organic amendments and materials rich in carbonates has been successfully used to reduce the bioavailability of contaminants and restore the ecological function of soils contaminated with heavy metals (Pérez de Mora *et al.*, 2005, 2006; Alvarenga *et al.*, 2008; Zornoza *et al.*, 2011).

The objective of this study was to assess the effectiveness of the reclamation strategy followed in a tailing pond (Southeastern Spain), consisting of application of marble waste and pig slurry to increase soil quality and pH, and reduce heavy metal availability.

MATERIALS AND METHODS

Study Site

The selected tailing pond is called Santa Antonieta and is located in Cartagena-La Unión Mining District (Murcia Region, SE Spain), where great mining activities had been carried out for more than 2500 years (37° 35’ 38” N, 0º 53’ 11” W). The climate of the area is semiarid Mediterranean with mean annual temperature of 18 ºC and mean annual precipitation is 275 mm, with rainfall events occurring mostly in autumn and spring. The potential evapotranspiration rate surpasses 900 mm $year^{-1}$. Soil is classified as a Spolic Technosol (Toxic) (IUSS, 2007), with sandy loam texture. The range of concentrations of total heavy metals was 1246-2048 mg kg^{-1} for Pb, 829-5899 mg kg^{-1} for Zn, 0.73-6.65 mg kg^{-1} for Cd, 187-606 mg kg^{-1} for As. Mine soil from Santa Antonieta tailing pond was mechanically, physically, chemically and biologically deficient, characterized by instability and limited cohesion, with low contents of nutrients and organic matter and high levels of heavy metals.

Experimental Design and Soil Sampling

We used two different amendments (pig slurry and marble waste ($CaCO_3$)) for reclamation purposes, in order to increase soil organic matter and soil nutrients, decrease availability of heavy metals, ameliorate soil structure, neutralize potential acidity generated by sulfides, and facilitate vegetation colonization. The characteristics of soil amendments are given in Table 1.

To achieve correct application of amendments, the topsoil of the tailing pond was levelled and a drainage system was created to avoid the formation of flooded areas that could compromise real reclamation of the tailing pond. In addition, amelioration of access roads was needed to permit passage of trucks and agricultural machinery. The first application of pig slurries was carried out in July 2011 and subsequent applications in September and November 2011. We applied the organic amendment in three different episodes to favor suitable assimilation and stabilization of organic matter and nutrients in soil before introduction of vegetation. Marble waste application was carried out in July 2011. Amendments were applied mechanically.

After application of amendments, all materials were mixed to a depth of 0-50 cm to incorporate the amendments into the soil. Marble was applied at a rate of 6.7 kg m^{-2}. This rate was calculated using the method proposed by Sobek *et al.* (1978), which provides an indication of the quantity of lime required to neutralize all the potential acid according to the percentage of sulfides present in the mine soil. Total sulfide content in each tailing pond was determined by oxidation with H_2O_2 to establish the highest production of potential acid in soil as a consequence of the reaction of sulfide (mainly as pyrite, FeS_2) with the atmospheric oxygen, a normal process taking place in tailing ponds rich in sulfides:

$$4FeS_{2\,(s)} + 30\ H_2O_{2\,(aq)} = 4\ Fe(OH)_{3\,(s)} + 8\ SO_4^{2-}{}_{(aq)} + 16\ H^+_{(aq)} + 16\ H_2O_{(aq)} \quad (1)$$

Average sulfide content in Santa Antonieta was 0.22. Using the following Equation (2):

$$\text{mol H}^+ \text{t}^{-1} = \%\text{S} * \frac{1\ \text{mol S}}{32.066\ \text{g S}} * \frac{2\ \text{mol H}^+}{1\ \text{mol S}} * \frac{1000\text{g}}{1\text{kg}} * \frac{1000\text{kg}}{1\ \text{t}} = \%\ \text{S} * 627.7 \quad (2)$$

Table 1. Main characteristics of the raw pig slurry (RPS), solid phase of the pig slurry (SPPS) and marble waste (MW) used.

Parameters	RPS	MW	SPPS
pH	7.8	8.0	9.1
Electrical conductivity (dS m^{-1})	39.1	2.2	10.2
$CaCO_3$ (%)	-	99	-
Moisture (%)	96	1	10
Total organic carbon (g L^{-1} g^{-1} kg^{-1})	17.8	-	170.8
Total N (g L^{-1} g^{-1} kg^{-1})	5.1	-	13.6
C/N	3.5	-	12.5
Cu (mg L^{-1} mg^{-1} kg^{-1})	19.3	0.36	157.35
Zn (mg L^{-1} mg^{-1} kg^{-1})	28	0.26	732.05
Available phosphorus (mg L^{-1} mg^{-1} kg^{-1})	623	<d.l.	9.64
Calcium (mg L^{-1} mg^{-1} kg^{-1})	249	2190	855
Magnesium (mg L^{-1} mg^{-1} kg^{-1})	14.4	347	802
Sodium (mg L^{-1} mg^{-1} kg^{-1})	459	69	4283
Potassium (mg L^{-1} mg^{-1} kg^{-1})	1059	59	15662

< d.l.: below detection limit.

the quantity of H^+ generated by oxidation of sulfides was calculated. To determine the quantity of marble waste needed to neutralize the potential acidity, we used the reaction of acid solution with calcium carbonate, which shows that each mol of $CaCO_3$ neutralizes 2 mols of H^+ (equation 3):

$$CaCO_3 + 2H^+ = Ca^{2+} + H_2O + CO_2 \quad (3)$$

Thus, the calculation is developed as follows (Equation 4):

$$\text{kg CaCO}_3\ t^{-1} = \text{mol H}^+ t^{-1} * \frac{1\ \text{mol CaCO}_3}{2\ \text{mol H}^+} * \frac{100.087\ \text{g CaCO}_3}{1\ \text{mol CaCO}_3} * \frac{1\ \text{kg}}{1000\ \text{g}} = \text{mol H}^+\ t^{-1} * 0.05 \quad (4)$$

After all these calculations, and taking into account that marble waste purity is 99% carbonates, and the bulk density of the tailing pond material is 1300 kg m^{-3}, the quantity of marble waste applied in the Santa Antonieta tailing pond was 6.7 kg m^{-2}. We applied 1.7 L raw pig slurry m^{-2} in July, 2.6 L raw pig slurry m^{-2} in September and 7 kg of solid phase pig slurry m^{-2} in November 2011. We applied raw pig slurry as a source of nutrients according to the agronomic rate established by Spanish legislation RD 261/1996 (framed within the European Directive 91/676/CEE), to avoid contamination of groundwater by nitrates. The dose of solid phase pig slurry was calculated on the basis of its organic carbon content to increase soil organic carbon > 5 g kg^{-1}. 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 air-dried outdoors under environmental conditions for one month.

The topsoil of the tailing pond was divided using a square grid of 35 × 35 m and samples were taken in the nodes of this grid giving a total of 11 points. This sampling grid was used to carry out an initial characterization of the tailing pond before application of amendments (October 2011) and to monitor the evolution of soil properties six months after the application of the amendments (January 2012). In each soil point of the tailing pond a topsoil sample (0-15 cm) and a subsoil sample (15-30 cm) were taken. Samples were carried to the lab, air-dried for 7 days, passed through a 2-mm sieve and stored at room temperature prior to laboratory analyses.

Analytical Methods

Soil pH and electrical conductivity (EC) were measured in de-ionized water (1:2.5 and 1:5 w/v, respectively); the texture was determined using the Robinson pipette method combined with sieving; aggregate stability was determined by the method proposed by USDA (1999); total organic carbon (TOC) and total nitrogen (Nt) were determined by an elemental analyzer CNHS-O (EA-1108, Carlo Erba); cation exchange capacity (CEC) by the method of Chapman (1965); available phosphorus was measured by the Olsen method (Watanabe and Olsen, 1965); exchangeable potassium was measured by atomic absorption spectrophotometer (AAnalyst 800, Perkin Elmer) in the $BaCl_2$ extract from CEC measurement (Chapman, 1965); microbial biomass carbon (MBC) was determined using the fumigation-extraction procedure (Vance *et al.*, 1987); total heavy metals (As, Cd, Pb and Zn) were determined using $HNO_3/HClO_4$ digestion at 210 ºC for 1.5 h (Risser and Baker, 1990), the available metal fractions were determined using 0.01 M $CaCl_2$ (1:10 soil-extractant ratio) (Pueyo *et al.*, 2004). Metal concentrations were measured using ICP-MS (Agilent 7500CE). The standards concentrations of the calibration curve for all metals measured were 0, 2, 5, 10, 25, 50, 100, 200, 500 and 1000 µg L^{-1}. When the sample concentration was higher than the highest standard, a corresponding suitable dilution was made. The detection limits of the equipment were 0.07 µg L^{-1} for As, 0.02 µg L^{-1} for Cd, 0.35 µg L^{-1} for Pb and 0.96 µg L^{-1} for Zn. The methodology for total metal concentration was referenced using the Certified Reference Material BAM-U110 (Federal Institute for Materials Research and Testing, Germany). The reference sample was analyzed in triplicate. The overall recovery ratios were 93-104% for As, 96-126 % for Cd, 95-106% for Pb and 82-98% for Zn. Certified internal standard solutions of Ga, Rh and Tl (1000 mg L^{-1} High Purity Standards, Charleston, USA) were used as quality control for each sample measured in the ICP-MS, with overall recovery ratios of 97-108% for Ga, 94-115% for Rh and 99-117% for Tl. In addition, every 10 samples run in the equipment was measured against the calibration standard of 50 µg L^{-1} to assess that values were within the range of

±10%. Should some value be outside this range, the calibration was remade.

Statistical Analysis

Data fit to a normal distribution for all properties measured was checked with the Kolmogorov-Smirnov test. The data were submitted to a one-way ANOVA to assess the differences found before and after application of amendments and between depths. The separation of means was made according to Tukey's verified significant difference at $P < 0.05$. These analyses were performed with the software IBM SPSS for Windows, Version 19.

RESULTS AND DISCUSSION

Aggregate stability was very similar in topsoil and subsoil samples, with significant increments with the application of amendments (Figure 1a). In topsoil samples, aggregate stability increased from 7.8 % before application of amendments to 14.9% after applications of amendments, while in subsoil samples it increased from 7.2% before application of amendments to 14.5% after application of amendments. Aggregate stability can serve as an indicator of the resistance of soils to water erosion, topsoil seal or crust formation, compaction leading to decreased infiltration and subsoil aeration, and as a general soil quality indicator, constituting a pathway of organic carbon stabilization and long term sequestration (Six *et al.*, 2004). Thus, the incorporation of organic matter and calcium carbonate contributes to forming new aggregates, which will help to increase porosity, water holding capacity, root establishment and development, microbial community growth, animal movement and to reduce erosion and compactness. Soil pH increased after application of amendments (Figure 1b). In topsoil samples, pH significantly increased

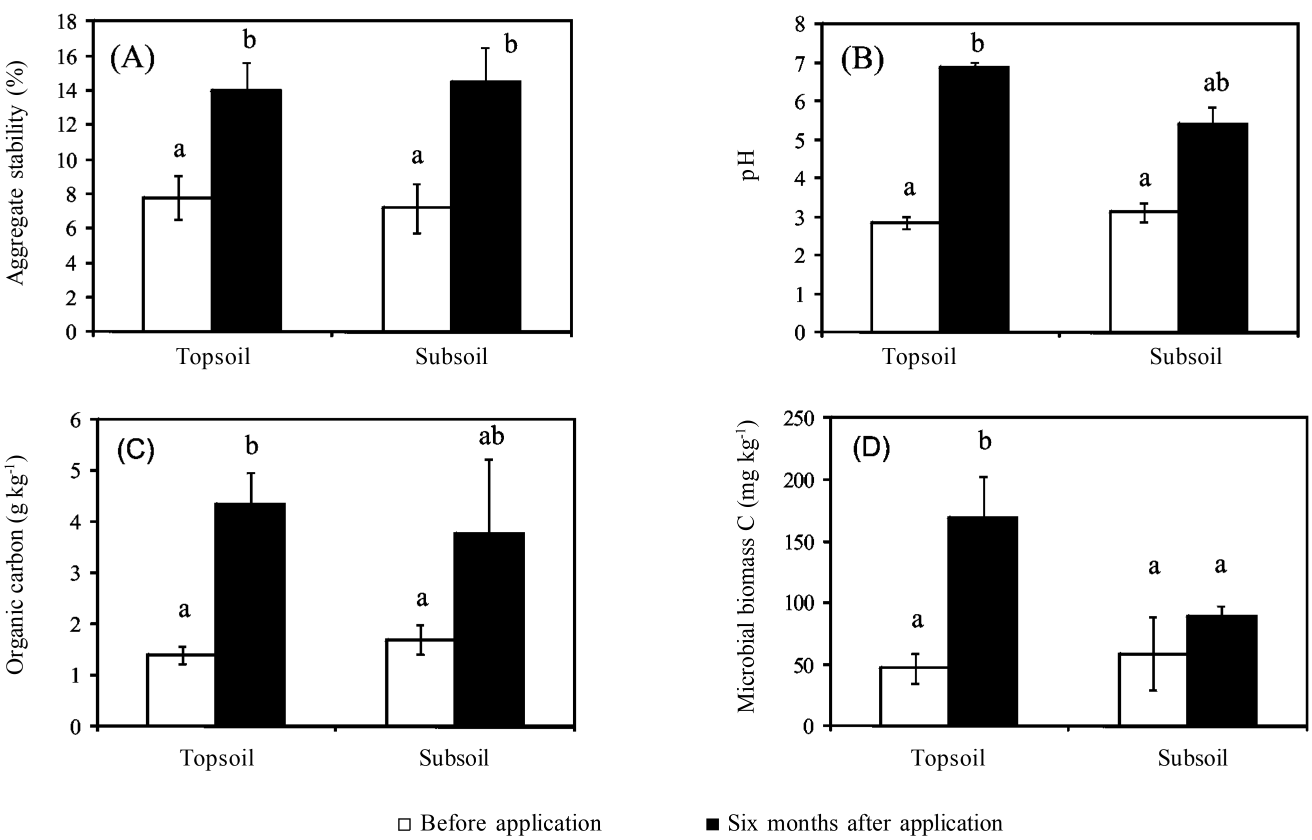

Figure 1. Aggregate stability (A), pH (B), organic carbon (C) and microbial biomass carbon (D) in soil samples collected before and six months after the application of the amendments. Error bars denote standard error. Different letters indicate significant differences according to Tukey's test. Bars with the same letter are statistically alike, while bars with different letters are statistically different at $P < 0.05$.

from 2.89 before application of amendments to 6.89 after application of amendments, while in subsoil samples it increased from 3.12 before application of amendments to 5.42 after application of amendments, indicating good evolution of this parameter with application of amendments. These increments in pH are due to the presence of carbonates in soils, which react with acidity making soil pH close to neutrality. CE showed no significant difference with the application of amendments, with values ranging from 2.70 to 3.99 dS m^{-1}. TOC was slightly higher in topsoil samples than in subsoil samples after the application of amendments (Figure 1c), since application was on topsoil and the incorporation procedure to homogenize the content of pig slurry and marble residue in the first 50 cm was not as efficient as expected. In topsoil samples, TOC increased from 1.40 before application of amendments to 4.35 g kg^{-1} after application of amendments, while in subsoil samples it increased from 1.71 before application of amendments to 3.78 g kg^{-1} after application of amendments. This initial incorporation of organic matter to the soil should improvement soil structure, stimulate microbial populations, and release nutrients (Zanuzzi *et al.*, 2009; Zornoza *et al.*, 2013).

MBC increased after application of amendments, although it was only significant in topsoil samples (Figure 1d). These increments were due to improvement of physical soil properties by tillage and application of amendments, increments in pH and increments in organic matter and nutrients such as nitrogen, phosphorus, calcium and potassium. In topsoil samples, microbial biomass carbon increased from 47.15 before application of amendments to 169.40 mg kg^{-1} after application of amendments, while in subsoil samples it increased from 58.97 mg kg^{-1} before application of amendments to 89.67 mg kg^{-1} after application of amendments. Lower increments of this property in the subsoil may likely be due to lower contents of organic carbon (Figure 1), since both parameters are highly correlated (R = 0.74; $P < 0.01$). Microbial size increased after the application of the organic amendment due to increments in organic carbon. A greater availability of carbon should increase the possibility of microorganism growth (Pérez de Mora *et al.*, 2005). Moreover, pig slurry also contains microbial biomass which can be incorporated into the soil. Nonetheless, this trend is common in all soils, with decreases in organic matter and microbial biomass with depth. The MBC values and enzyme activities were lower than those generally reported in literature for contaminated soils amended with different organic residues (e.g. Pérez de Mora *et al.*, 2005, Clemente *et al.*, 2007, Alvarenga *et al.*, 2008). This could be due to different organic matter quality added with the amendment, and higher contents of heavy metals in our study.

Even though before the application of amendments total nitrogen was similar in topsoil and subsoil samples, it is slightly higher in topsoil samples after the addition of amendments (Figure 2a), since topsoil application and the incorporation procedure to homogenize the content of pig slurry and marble residue within the first 50 cm were not as efficient as expected. In topsoil samples, total nitrogen significantly increased from 0.35 g kg^{-1} before application of amendments to 0.75 g kg^{-1} after application, while in subsoil samples it increased from 0.36 g kg^{-1} before application of amendments to 0.59 g kg^{-1} after application. These results are very positive, indicating significant increment in macronutrients such as N, essential for the development of microbial communities and vegetation. Thus, soil fertility increases, promoting the growth of native vegetation by spontaneous colonization of plants from the surrounding environment. Around the tailing pond there is a high biodiversity of vegetation including mainly *Brachypodium retusum* (Pers.) Beauv., *Stipa tecnacissima* L., *Calicotome intermedia* C. Presl, *Dorycnium pentaphyllum* Scop., *Thymus hyemalis* Lange, *Lavandula dentata* L., *Tamarix canariensis* Willd., *Chamaerops humilis* L., *Pinus halepensis* Mill. and *Tetraclinis articulata* (Vahl) Mast. (Kabas *et al.*, 2012). CEC was very similar in topsoil and subsoil samples, in topsoil samples, CEC increased from 5.79 $cmol_+$ kg^{-1} before application of amendments to 10.75 $cmol_+$ kg^{-1} after application of amendments, while in subsoil samples it increased from 6.62 $cmol_+$ kg^{-1} before application of amendments to 9.55 $cmol_+$ kg^{-1} after application of amendments (Figure 2b). The application of pig slurry positively contributed to improvement in the indicator CEC of soil fertility, owing to increments in organic compounds with higher exchange positions. Available P content was significantly higher in topsoil than in subsoil samples, with significant increments after the application of amendments (Figure 2c). In topsoil samples, available P increased from 0.50 mg kg^{-1} before application of amendments to 12.06 mg kg^{-1} after application of amendments, while in subsoil samples it increased from 0.03 mg kg^{-1} before application of

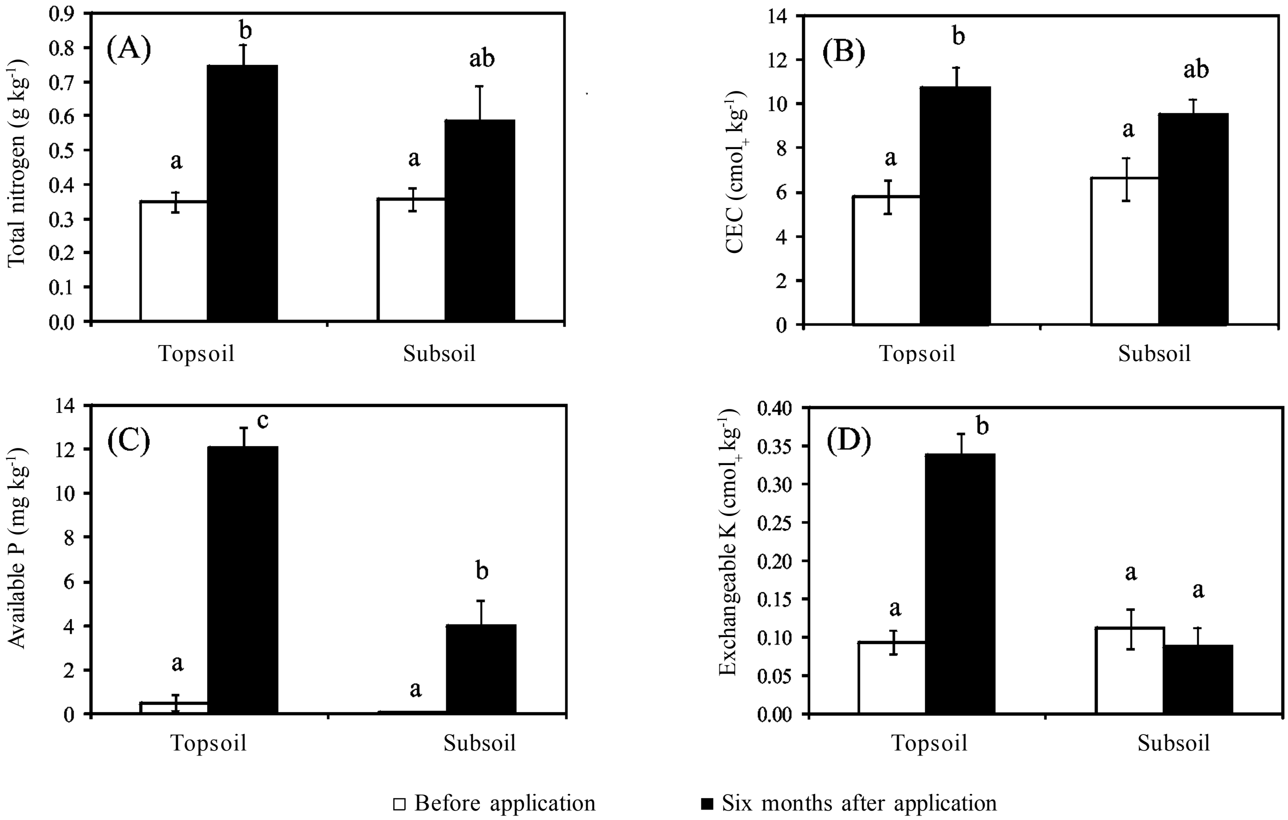

Figure 2. Changes in cation exchange capacity, total nitrogen, available phosphorus and exchangeable potassium in soil samples collected before and six months after the application of the amendments. Error bars denote standard error. Different letters indicate significant differences according to Tukey's test. Bars with the same letter are statistically alike, while bars with different letters are statistically different at $P < 0.05$.

amendments to 3.99 mg kg^{-1} after application. Exchangeable K content was significantly higher in topsoil than in subsoil samples after the application of amendments (Figure 2d). In topsoil samples, exchangeable K increased from 0.093 $cmol_+$ kg^{-1} before application of amendments to 0.338 $cmol_+$ kg^{-1} after application of amendments, while in subsoil samples it remained without significant changes with values around 0.100 $cmol_+$ kg^{-1}. That there were no significant increments of exchangeable K in subsoil samples after the application of amendments may likely be due to a lack of perfect homogenization of soil within the first 50 cm. Nonetheless, we do not consider this is a negative effect for the development of vegetation, since plants are able to obtain K from the topsoil mainly the first months after planting since the root system is shallow. Thus, the application of pig slurry positively contributed to the improvement in both of these soil fertility indicators; this amendment is a source of nutrients essential for vegetation such as P and K.

All available heavy metals decreased with the application of amendments (Figure 3). This is due to different reasons such as direct increments in pH, formation of chelates with organic matter, formation of metal carbonates (provided by marble) and formation of metal phosphates (provided by pig slurry) (Alvarenga *et al.*, 2008; Liu *et al.*, 2009; Zornoza *et al.*, 2013). Zornoza *et al.* (2013), reported that organic complexation and precipitation as phosphate was very effective for Cd immobilization, while immobilization by carbonates was needed to reduce the availability of Pb and Zn. In topsoil samples, Pb decreased from 2.02 mg kg^{-1} before application of amendments to 0.05 mg kg^{-1} after application of amendments (a reduction of 97%), while in subsoil samples it decreased from 4.63 mg kg^{-1} before application of amendments to 0.07 mg kg^{-1} after application of amendments (a reduction of 98%). In topsoil samples, Zn decreased from 107.28 mg kg^{-1} before application of amendments to 0.99 mg kg^{-1} after application of amendments (a reduction of 99%), while

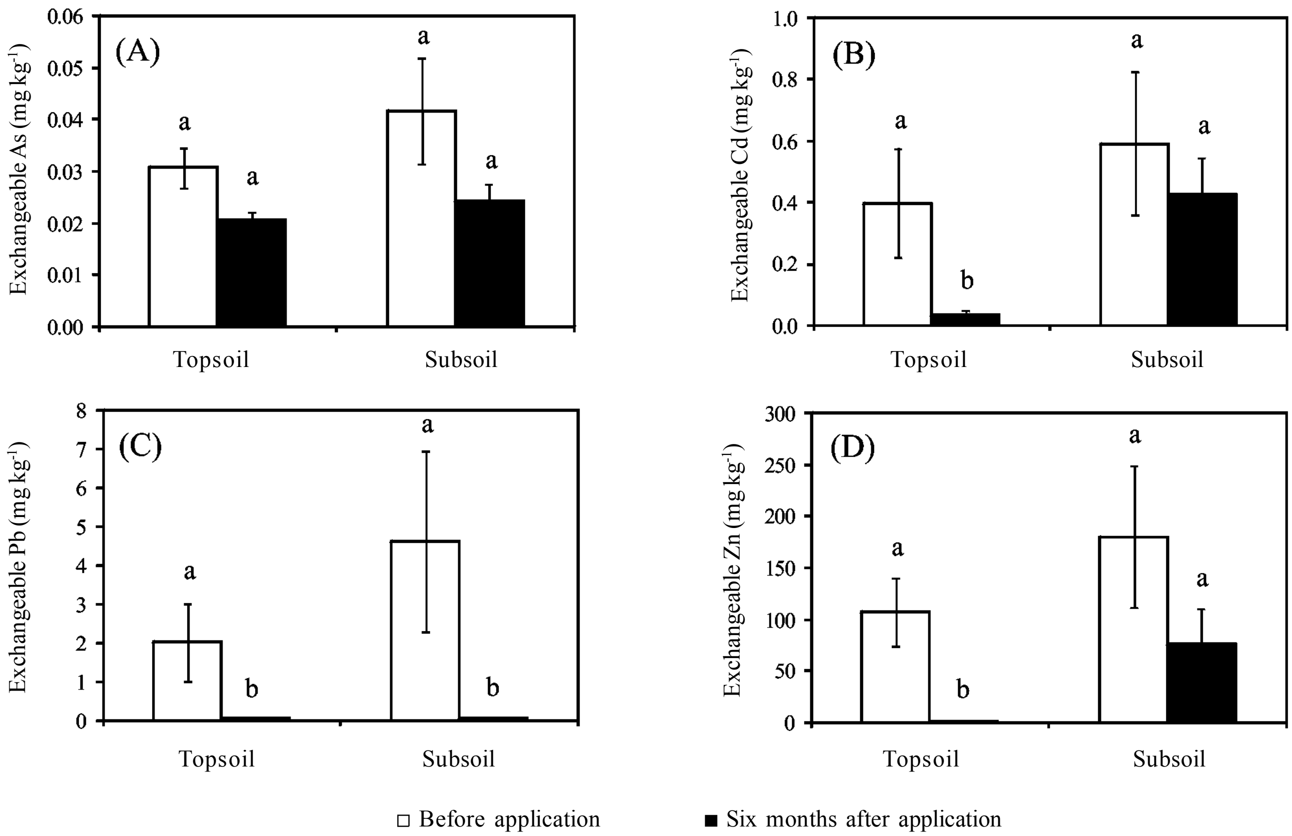

Figure 3. Available metals in soil samples collected before and six months after the application of the amendments. Error bars denote standard error. Different letters indicate significant differences according to Tukey's test. Bars with the same letter are statistically alike, while bars with different letters are statistically different at $P < 0.05$.

in subsoil samples it decreased from 180.28 mg kg^{-1} before application of amendments to 76.76 mg kg^{-1} after application of amendments (a reduction of 60%). Cd decreased from 0.39 mg kg^{-1} before application of amendments to 0.03 mg kg^{-1} after application of amendments (a reduction of 90%), while in subsoil samples it decreased from 0.59 mg kg^{-1} before application of amendments to 0.42 mg kg^{-1} after application of amendments (a reduction of 30%). In topsoil samples, As decreased from 0.031 mg kg^{-1} before application of amendments to 0.021 mg kg^{-1} after application of amendments (a reduction of 30%), while in subsoil samples it decreased from 0.042 mg kg^{-1} before application of amendments to 0.024 mg kg^{-1} after application of amendments (a reduction of 40%). Lower pH and lower content of carbonates and phosphates in subsoil samples may have to lower decreases in available metals in subsoil.

Owing to the semiarid climate of the area, water content in soils is very low, averaging 5%. Only after the very few rainfall events, are soils wet for a few days. Furthermore, high evaporation rates during summer months result in the seasonal formation of thick crusts of salt efflorescence on the top. Groundwater piezometric levels are between 70 and 150 m. In addition, the tailing pond is formed by cementing agents such as oxides and hydroxides of iron, which provoke the formation of very hard crusting, "hardpans", forming a strongly cemented coherent mass, which causes difficulties for water infiltration. Thus, water infiltration and leaching into groundwater is minimal. The main problem of this area is runoff after intense rainfall events. However, levelling the tailing topsoil, ploughing soil and incorporating amendments into the soil has reduced overflows into areas outside the tailing. With the reduction of sediment runoff from the pond, risk of groundwater contamination via leaching from streams has also been reduced.

The results showed here confirm that pig slurry is a good fertilizer providing high quantity of nutrients needed to promote vegetation growth. Thus, the use of this waste to reclaim degraded lands is of increasing interest, although some procedures, such as liming, should be carried out to minimise organic matter mineralization from this type of waste (Zornoza *et al*., 2013). Pardo *et al.* (2011), also concluded that the use of pig slurry has positive effects on reclamation strategies improving soil properties and seed germination. This is of special interest in regions where the management of pig industry represents a serious environmental problem because of the huge volume of wastes and their poor recovery. One of the main concerns is how to treat them in an environmental sound way.

CONCLUSIONS

In order to bring about functional and sustainable land use in a highly contaminated mine tailing, it is foremost to reduce or eliminate environmental risks through suitable reclamation activities. The strategy followed here based on the application of marble waste to increase pH and immobilize metals as carbonates, and pig slurry as a source of organic matter and nutrients, had positive results in decreasing the availability of heavy metals up to 90-99% and in improving soil quality and fertility. This is promising in areas with quarries of carbonate material (limestone, dolomite, marble) and extra production of organic residues such as pig slurries, since these residues can be used as amendments to reclaim bare main soils with no cost but for transportation. The valorization of residues is essential for sustainable development, since landfilling must be reduced to a minimum to avoid undesirable negative environmental impacts. Once the soil quality of mine tailings is improved, the development of vegetation is favored, promoting the reclamation of the area. The content of water in the soil is crucial to ensure activation of biogeochemical cycles for true reclamation. Owing to the semiarid climatic conditions of the area, the water content in soil is generally very low. The application of raw pig slurry provided extra water for the reaction of calcium carbonate with soil protons to neutralize acidity and form soil aggregates.

ACKNOWLEDGEMENTS

This work was funded by the European Union LIFE+ project MIPOLARE (LIFE09 ENV/ES/000439). J.A. Acosta acknowledges a “Saavedra Fajardo” contract from Comunidad Autónoma de Murcia (Spain).

REFERENCES

Acosta, J. A., A. Faz, S. Martínez-Martínez, R. Zornoza, D. M. Carmona, and S. Kabas. 2011. Multivariate statistical and GIS-based approach to evaluate heavy metals behavior in mine sites for future reclamation. J. Geochem. Explorat. 109: 8-17.

Alvarenga, P., P. Palma, A. P. Gonçalves, N. Baião, R. M. Fernandes, A. de Varennes, G. Vallini, E. Duarte, and A. C. Cunha-Queda. 2008. Assessment of chemical, biochemical and ecotoxicological aspects in a mine soil amended with sludge of either urban or industrial origin. Chemosphere 72: 1774-1781.

Barker, A. V. 1997. Composition and uses of compost. pp. 140-162. *In:* J. E. Rechcigl and H. C. Mackinnon (eds.). Agricultural uses of by-products and wastes. ACS Symposium Series vol. 668. American Chemical Society. Washington, DC, USA.

Bradshaw, A. D. and M. Johnson. 1992. Revegetation of metalliferous mine waste: The range of practical techniques used in western Europe. Elsevier. Manchester, UK.

Brown, S., M., Sprenger, A. Maxemchuk, and H. Compton. 2005. Ecosystem function in alluvial tailings after biosolids and lime application. J. Environ. Qual. 34: 139-148.

Chapman, H. D. 1965. Cation exchange capacity. pp. 891-900. *In:* C. A. Black (ed.). Methods of soil analysis. American Society of Agronomy. Madison, WI, USA.

Clemente, R., C. de la Fuente, R. Moral and M. P. Bernal. 2007. Changes in microbial biomass parameters of a heavy metal-contaminated calcareous soil during a field remediation experiment. J. Environ. Qual. 36: 1137-1144.

Conesa, H. M., A. Faz, and R. Arnaldos. 2006. Heavy metal accumulation and tolerance in plants from mine tailings of the semiarid Cartagena-La Union mining district (SE Spain). Sci. Total Environ. 366: 1-11.

IUSS (International Union of Soil Sciences). 2007. World reference base for soil resources 2006, first update 2007. World Soil Resources Reports No. 103. FAO, Rome.

Kabas, S., A. Faz, J. A. Acosta, R. Zornoza, S. Martínez-Martíenz, D. M. Carmona, and J. Bech. 2012. Effect of marble waste and pig slurry on the growth of native vegetation and heavy metal mobility in a mine tailing pond. J. Geochem. Explorat. 123: 69-76.

Liu, L., H. Chen, P. Cai, W. Liang, and Q. Huang. 2009. Immobilization and phytotoxicity of Cd in contaminated soil amended with chicken manure compost. J. Hazard. Mater. 163: 563-567.

Pardo, T., R. Clemente, and M. P. Bernal. 2011. Effects of compost, pig slurry and lime on trace element solubility and toxicity in two soils differently affected by mining activities. Chemosphere 54: 642-650.

Pérez de Mora, A., J. J. Ortega-Calvo, F. Cabrera, and E. Madejón. 2005. Changes in enzyme activities and microbial biomass after “in situ” remediation of a heavy metal-contaminated soil. Appl. Soil Ecol. 28: 125-137.

Pérez de Mora, A., P. Burgos, E. Madejón, F. Cabrera, P. Jaeckel, and M. Schloter. 2006. Microbial community structure and function in a soil contaminated by heavy metals: effects of plant growth and different amendments. Soil Biol. Biochem. 38: 327-341.

Pueyo, M., J. F. López-Sanchez, and G. Rauret. 2004. Assessment of $CaCl_2$, $NaNO_3$ and NH_4NO_3 extraction procedures for the study of Cd, Cu, Pb and Zn extractability in contaminated soils. Anal. Chim. Acta 504: 217-226.

Risser, J. A. and D. E. Baker. 1990. Testing soils for toxic metals. pp. 275-298. *In:* R. L. Westerman (ed.). Soil testing and plant analysis. Soil Sci. Soc. of Am. Spec. Publ. 3. Madison, WI, USA.

Six, J., H. Bossuyt, S. Degryze, and K. Denef. 2004. A history of research on the link between (micro) aggregates, soil biota, and soil organic matter dynamics. Soil Tillage Res. 79: 7-31.

Sobek, A. A., W. A. Schuller, J. R. Freeman, and R. M. Smith. 1978. Field and laboratory methods applicable to overburdens and mine soils. EPA-600/2-78-054.

USDA (United States Department of Agriculture). 1999. Soil quality test kit guide. United Stated Department of Agriculture, Washington, DC, USA.

Vance, E. D., P. C. Brookes, and D. S. Jenkinson. 1987. An extraction method for measuring soil microbial biomass C. Soil Biol. Biochem. 19: 703-707.

Watanabe, F. S. and S. R. Olsen. 1965. Test of an ascorbic acid method for determining phosphorus in water and $NaHCO_3$ extracts from soil. Soil Sci. Soc. Am. J. 29: 677- 678.

Ye, Z. H., W. S. Shu, Z. Q. Zhang, C. Y. Lan, and M. H. Wong. 2002. Evaluation of major constraint to revegetation of lead/zinc mine tailings using bioassy techniques. Chemosphere 47: 1103-1111.

Zanuzzi, A., J. M. Arocena, J. M. van Mourik, and A. Faz Cano. 2009. Amendments with organic and industrial wastes stimulate soil formation in mine tailings as revealed by micromorphology. Geoderma 154: 69-75.

Zornoza, R., D. M. Carmona, J. A. Acosta, S. Martínez-Martínez, N. Weiss, and A. Faz. 2011. The effect of former mining activities on contamination dynamics in sediments, surface water and vegetation in El Avenque stream, SE Spain. Water Air Soil Pollut. 223: 519-532.

Zornoza, R., A. Faz, M. Carmona, J. A. Acosta, S. Martínez-Martínez, and A. de Vreng. 2013. Carbon mineralization, microbial activity and metal dynamics in tailing ponds amended with pig slurry and marble waste. Chemosphere 90: 2606-2613.