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Carbon mineralization, microbial activity and metal dynamics in tailing ponds amended with pig slurry and marble waste

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HIGHLIGHTS

- ▶ Pig slurry and marble waste led to a rapid decrease of exchangeable Cd, Pb and Zn.
- ▶ Respiration rates were affected by heavy metals, carbonates and texture.
- ▶ The application of marble reduced the degradability of the organic amendment.
- ▶ Enzyme activities increased after the application of the organic amendment.
- ▶ Arylesterase maintained high activity in pig slurry + marble waste treatment.

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ABSTRACT

A field experiment was set up in Cartagena-La Unión Mining District, SE Spain, aimed at evaluating the short-term effects of pig slurry (PS) amendment alone and together with marble waste (MW) on organic matter mineralization, microbial activity and stabilization of heavy metals in two tailing ponds. These structures pose environmental risk owing to high metals contents, low organic matter and nutrients, and null vegetation. Carbon mineralization, exchangeable metals and microbiological properties were monitored during 67 d. The application of amendments led to a rapid decrease of exchangeable metals concentrations, except for Cu, with decreases up to 98%, 75% and 97% for Cd, Pb and Zn, respectively. The combined addition of MW + PS was the treatment with greater reduction in metals concentrations. The addition of PS caused a significant increase in respiration rates, although in MW + PS plots respiration was lower than in PS plots. The mineralized C from the pig slurry was low, approximately 25–30% and 4–12% for PS and MW + PS treatments, respectively. Soluble carbon (Csol), microbial biomass carbon (MBC) and β-galactosidase and β-glucosidase activities increased after the application of the organic amendment. However, after 3 d these parameters started a decreasing trend reaching similar values than control from approximately day 25 for Csol and MBC. The PS treatment promoted highest values in enzyme activities, which remained high upon time. Arylesterase activity increased in the MW + PS treatment. Thus, the remediation techniques used improved soil microbiological status and reduced metal availability. The combined application of PS + MW reduced the degradability of the organic compounds.

1. Introduction

In the Region of Murcia (SE Spain) past mining activities during more than 2000 years have generated large amounts of unconfined wastes accumulated in tailing ponds due to intensive mining activities, especially in the Mining District of Cartagena-La Unión. Although mining activity was abandoned in 1991, tailing ponds still remain in the area. The environmental impacts of such structures generally result from their low pH, high metal content, low organic matter and null vegetation (Conesa et al., 2006). High incidence of wind and water erosion events negatively affects soil, water, vegetation, fauna, and human populations in the surrounding areas (Zanuzzi et al., 2009).

Revegetation is needed to reinforce the topsoil, reducing 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

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consequence, the reclamation of abandoned mine sites relies on achieving optimal conditions for plant growth by improving the soil physical, chemical and biological characteristics by using different amendments (Bradshaw and Johnson, 1992; Acosta et al., 2011). Alkaline materials are commonly used as an amendment for ameliorating the acidic conditions of many acid-generating mine wastes and for immobilizing metals such as carbonates, mitigating metal toxicity (Barker, 1997). Organic residues are also normally used as amendments because the addition of organic matter can significantly improve the physical characteristics, the nutrient status, stimulate microbial populations and possibly reduce the availability of toxic metals through complexation (Ye et al., 2002).

Soil organic matter is universally recognized to be among the most important factors responsible for soil fertility and land protection from contamination, degradation, erosion and desertification, especially in semiarid areas (Senesi et al., 2007). Soil organic matter plays a major role in maintaining soil quality, supplying plant nutrients, reducing soil erosion, improving soil structure and water quality, and increasing biomass and vegetal productivity (Stevenson, 1994; Lal and Kimble, 1999). A correct management of the application of amendments in soil reclamation relies mainly on two aspects: efficient increase of the soil organic matter and adequate match of the release of mineral nutrients to vegetation demand. Applying organic wastes to soil could represent a useful tool in maintaining and increasing amounts of organic matter (Mondini et al., 2007). Effective recycling of organic residues in soil requires the optimization of the organic waste management in order to minimize CO_2 emissions and optimize soil C sequestration efficiency. Therefore, the knowledge of carbon mineralization dynamics in amended soils is of intrinsic interest. Since the main objective after application of organic amendments is the permanent increment of organic matter, a thorough study on organic carbon stability and mineralization is crucial. Efforts have to be made to use amendments that release nutrients but do not mineralize so fast that organic matter disappears before an adequate development of vegetation cover. In addition, the improvement of soil health will act as indicator of the effectiveness of the reclamation procedures (Epelde et al., 2009). In this sense, biochemical properties are considered as potentially sensitive, early and effective indicators of soil health in contaminated soils (Clemente et al., 2007).

In the current study, the short-term effects of pig slurry amendment alone and together with marble waste on organic matter mineralization, microbial activity and stabilization of heavy metals in two tailing ponds were investigated in a field remediation experiment.

2. Materials and methods

2.1. Study sites and experimental setup

The study was conducted in the Cartagena-La Unión Mining District (Region of Murcia, SE Spain). The climate is semiarid Mediterranean, with mean annual temperature of 18 °C and mean annual rainfall of 275 mm. Two tailing ponds were selected, Gorguel (37°35′N, 0°52′W; 7470 m^2), and Lirio (37°36′N, 0°49′W; 14 600 m^2), characterized by absence of vegetation, high metal concentrations, low organic carbon content and affection by wind and water erosion.

Both tailing ponds were divided in four field-scale plots with a surface of 25% of the total area. Thus, plots in Gorguel had a surface of ~1868 m^2, while plots in Lirio had a surface of ~3650 m^2. Soil characteristics of the plots in each tailing pond are shown in Table 1. 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 heavy metals availability, ameliorate soil structure, neutralize potential acidity generated by sulfides, and facilitate vegetation colonization. Each plot in both tailing ponds received a different treatment. The treatments were: marble waste (MW), pig slurry (PS), marble waste + pig slurry (MW + PS), and control (CT), the latter receiving no amendment. The pig slurry came from a pig farm in Pozo Estrecho (SE of Murcia), while marble waste (formed by particles of 5–10 μm diam.) was collected from quarries at NE of Murcia. The characteristics of soil amendments are given in Table 2. The first activity consisted of tilling the first 50 cm of the surface soil in order to prepare it for the application of the amendments (control plot was also tilled). Amendments were mechanically applied. In the MW + PS plots, we first added the MW followed by the application of the PS. Afterwards, all materials were mixed to a depth of 0–30 cm. Application of amendments was carried out on 10 September 2010 in Lirio, and on 4 October 2010 in Gorguel.

These doses of marble waste were calculated using the method proposed by Sobek et al. (1978), which provides an indication of the quantity of lime required to neutralise all the acid according to the sulfides present in the soil. Total sulfides 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:

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

Average sulfide contents in Gorguel and Lirio were 0.62 ± 0.16% and 0.25 ± 0.06%, respectively. According to the following equation:

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

the quantity of H^+ generated by oxidation of sulfides is provided. To determine the quantity of marble waste needed to neutralize the potential acidity we use the reaction of acid solution of calcium carbonate, which shows that each mol of $CaCO_3$ neutralizes 2 mols of H^+:

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

Thus, calculation is developed as follows:

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

After all these calculations, and taking into account that marble waste purity is 98% carbonates, and the bulk density of the tailing pond material is 1300 kg m^{-3}, the quantities of marble waste applied in Gorguel and Lirio were 4 kg marble m^{-2} and 1.4 kg marble m^{-2}, respectively. Thus, even though Lirio presents higher actual acidity than Gorguel, the latter has higher quantity of sulfides which can generate higher potential acidity by oxidation.

Doses for pig slurry were established by thresholds imposed by legislation regarding the addition of N to soil to avoid contamination by nitrates (Council Directive 91/676/EEC, 1991). We applied 3 L pig slurry m^{-2}, corresponding to 60 g C m^{-2}.

2.2. C mineralization monitoring

Soil carbon mineralization was determined using a static chamber method with alkali absorption (Zibilske, 1994). Soil respiration was determined using white plastic cylinders (25 cm diam., 30 cm