Monitoring soil properties and heavy metals concentrations in reclaimed mine soils from SE Spain by application of different amendments

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Abstract
Mine soils stabilization is an in situ remediation method that uses inexpensive amendments to reduce heavy metals availability and increase soil organic matter, nutrients and water retention in polluted soils. We tested the long-term effects of several amendments (pig manure, sewage sludge and marble mud) on the immobilization of heavy metals and improvement in soil physico-chemical properties in abandoned tailing ponds from SE Spain affected by former mining activities. Results showed that an initial increase in pH close to neutrality occurred and remained practically stable with time. However, soil organic matter decreased owing to mineralization and leaching. Total contents of heavy metals remained stable for a long time, but bioavailable metals decreased in the amended plots. However, increments in Pb and Zn in El Lirio, and in Cd and Zn in Brunita in the amended plots after 5 years of monitoring were observed. The main reasons could be slight decreases in pH, water and wind erosion of surface particles that provokes shifts in bioavailable metals, decrease in soil organic matter, which initially immobilized metals, and release of root exudates by colonizer plants in amended plots, which tend to mobilize nutrients and as a consequence metals.

Key Words
Metal pollution, in situ remediation, pig slurry, swage sludge, marble waste, long-term effects.

Introduction
In SE Spain, there are many mining tailing ponds due to intensive mining activities. Although mining activity was abandoned decades ago, those ponds with high amount of heavy metals still remain in the area.. As a consequence, these mine soils have scarce or null vegetation due to very poor properties, including extremely low soil organic matter. Since a long time those mine residues has been transported downstream during periods of high flow, erosion is evident in these areas, causing migration of pollutants into surface and ground water. Thus, efforts are needed for long-term reclamation of these contaminated areas to stabilise soil metals, create a structured soil and avoid health risks in the ecosystems. The transformation of metals into harmless species or their removal in a suitable recycled mineral form such as carbonates using marble wastes or lime (Geebelen *et al.* 2003) is a possible solution for the remediation of a mining area. In addition, incorporation of organic amendments into contaminated mine soils has been proposed as feasible, inexpensive and environmentally sound disposal practice leadind to an improvement of soil characteristics needed for microorganisms and plants development (Barker 1997). Thus, the objective of this study is to monitor the evolution of some physico-chemical properties and availability of heavy metals during five years to assess the capacity of several amendments for long-term immobilization of heavy metals and recover soil properties to guarantee true landscape rehabilitation.

Methods
The study was conducted in the province of Murcia (SE Spain), in the Cartagena-La Unión Mining District. The climate of the area is semiarid Mediterranean with mean annual temperature of 18ºC and mean annual rainfall of 275 mm. Two tailing ponds generated by mining activities were selected: El Lirio (L) and Brunita (B), representative of the rest of existent ponds in Cartagena-La Unión Mining District. The field trial was established in 2004. Plots (2 m x 2 m) were randomised replicated 3 times. Two different organic amendments were used to reclaim the soils, pig manure (P) and sewage sludge (S). In addition, 3 different doses per amendment were applied. Thus, the treatments were: Untreated contaminated soil (C), soil treated with pig manure at dose 1 (P1), dose 2 (P2) and dose 3 (P3); and soil treated with sewage sludge at dose 1 (S1), dose 2 (S2) and dose 3 (S3). For pig manure, doses were 2.5, 5 and 10 kg per plot, respectively. For sewage sludge, doses were 1.99, 3.98 and 7.97 kg per plot, respectively. With the purpose of increasing soil pH to immobilise metals marble mud was applied in all plots except for control, at the rate of 22 kg/ plot.

The soil samplings were carried out previous to the application of amendments (time 0), and at 6 months, 1, 2 and 5 years after application of amendments. One sample (0-15 cm depth) was collected for each plot, taken to the lab, air-dried, passed through a 2-mm sieve and stored at room temperature. Soil pH and electrical conductivity (EC) were measured in deionised water (1:2.5 and 1:5 w/v, respectively). Soil organic carbon (SOC) and total nitrogen (N_t) were determined according to Duchaufour (1970). For the quantification of the total metals an acid digestion was used and bioavailable metals were extracted with DTPA. Metals were measured using atomic absorption spectrophotometer (AAnalyst 800, Perkin Elmer).

Results and discussion

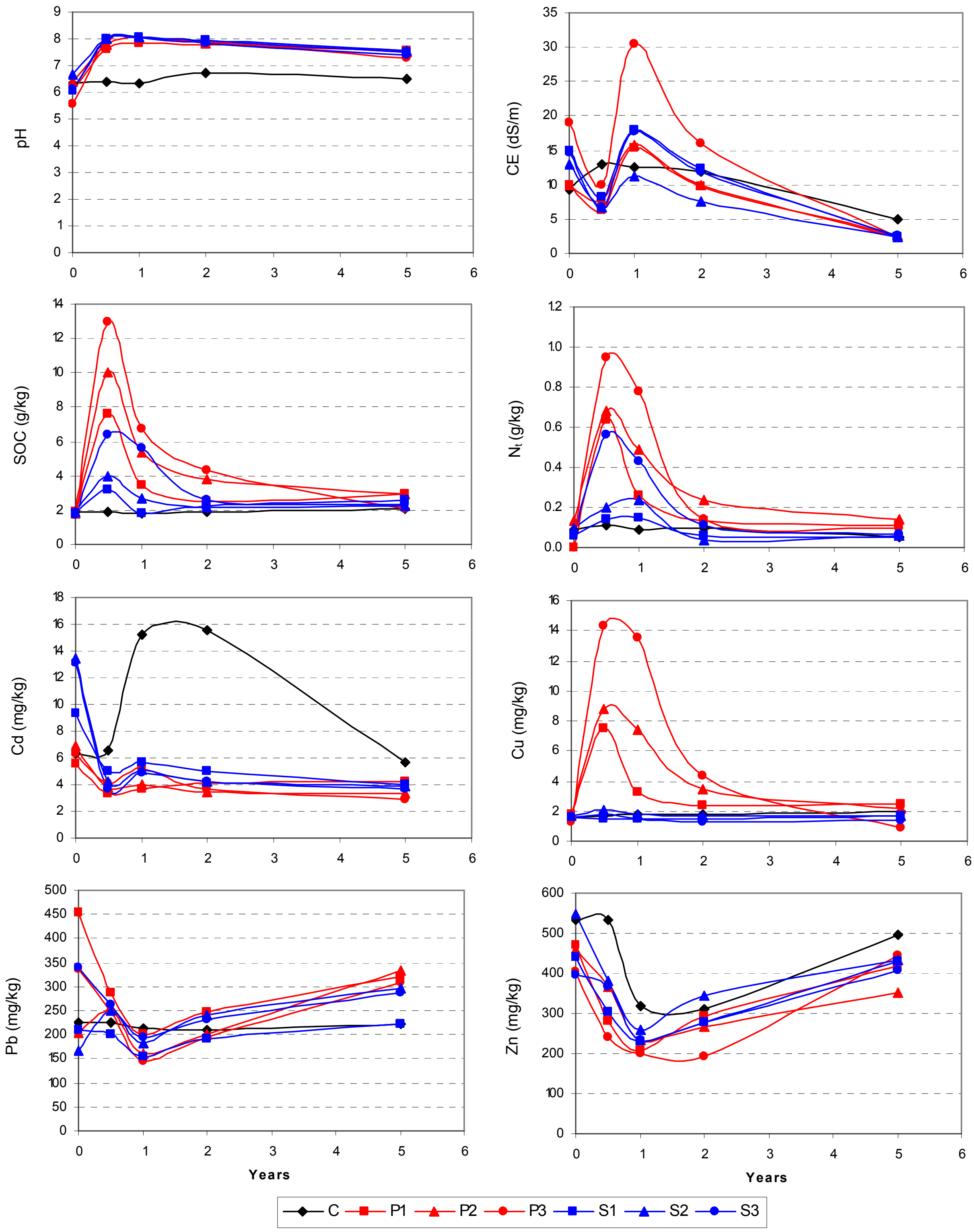

Figure 1. Evolution of pH, electrical conductivity (EC), soil organic carbon (SOC), total nitrogen (Nt) and bioavailable metals in El Lirio plots (see the text for the meaning of plots abbreviations).

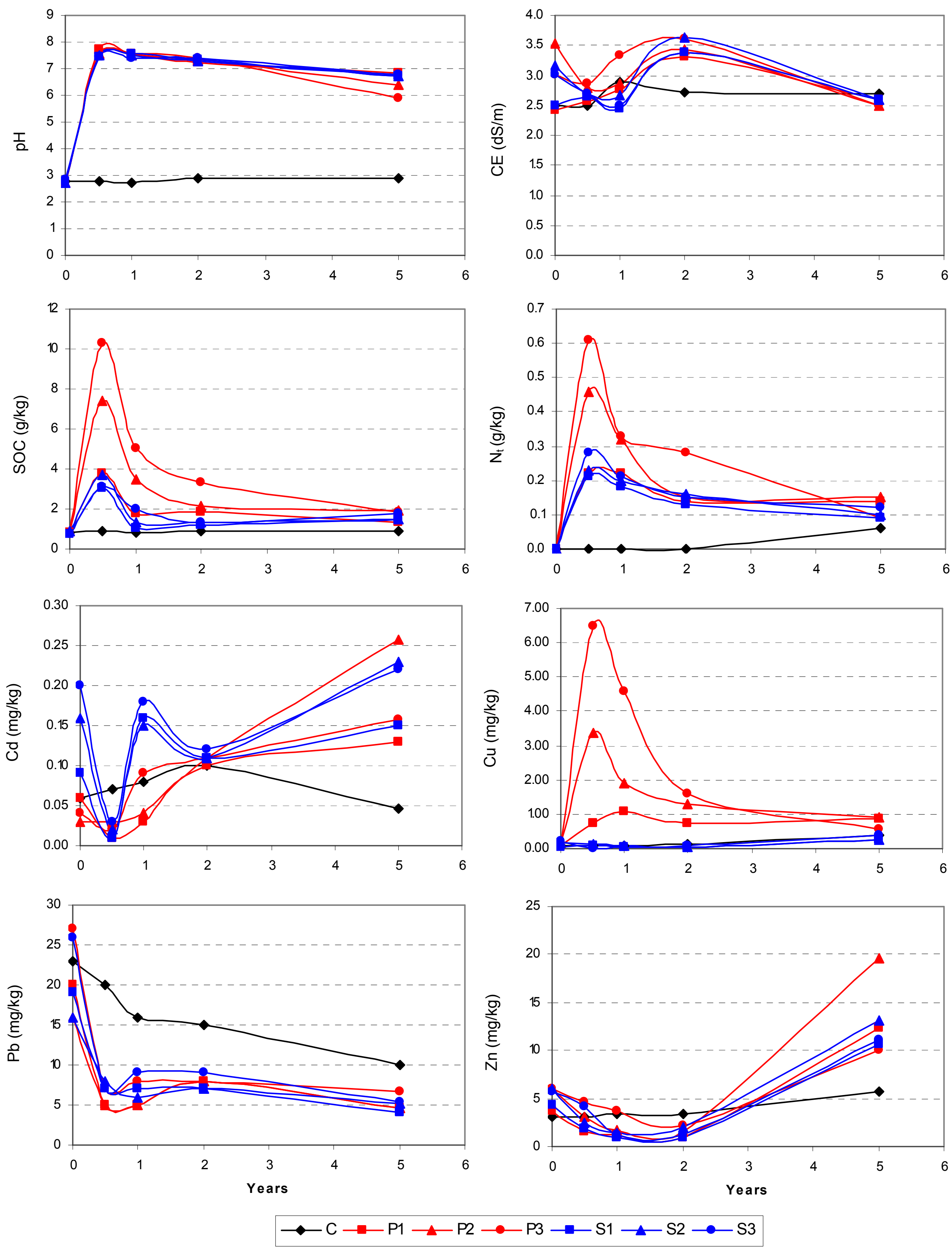

Figure 2. Evolution of pH, electrical conductivity (EC), soil organic carbon (SOC), total nitrogen (Nt) and bioavailable metals in Brunita plots (see the text for the meaning of plots abbreviations).

The evolution of soil properties and available metals for 5 years are represented in Figures 1 (El Lirio) and Figure 2 (Brunita). After the application of amendments, we observed an increase in pH in both ponds, being higher in Brunita, since the initial pH value in this pond was extremely low (<3). The pH remained practically stable with time, without differences among treatments, although it tended to decrease after 5 years, mainly due to decreases in carbonates content (data not shown). With regards to EC, we observed an increment after one year of amendments application, owing to the high quantity of salts provided by the

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organic amendments and the solution of carbonates. After two years, there is a decreasing trend in EC, owing to leaching of soluble ions. SOC and N_t initially increased with the application of amendments, mainly in P plots. This increase was in general terms related with the dose of application. However, the values of these two properties decreased owing to leaching and mineralization, shifting down after 5 years of applications to values slightly higher to control.

Regarding total metals, Cd, Cu, Zn and Pb were above European legislation thresholds, and did not change with time (data not shown). Bioavailable metals decreased as general pattern in the amended plots in both ponds. However, we detected slight increments in Pb and Zn in El Lirio, and in Cd and Zn in Brunita in amended plots after 5 years of monitoring. The possible explanation for this behavior is difficult owing to the different factors implied in the mobility of heavy metals and their interactions with soil properties. The detected slight decreases in pH and solubilization of carbonates may have likely contributed to increments in bioavailability of some metals. Moreover, the fact that we have also detected increments in the control plot in some metals could be indicating changes in bioavailability of these metals owing to water and wind erosion of surface particles that migrate to other zones, thereby exposing subsurface soils. In addition, the parent material is rich in Cd, Pb, Cu and Zn sulfides. Thus, oxidation processes of these sulfides may have also released some metals to the soil. On the other hand, decreases in soil organic matter could have had and important effect, since the application of organic amendments initially immobilized metals by complexation (Zanuzzi 2007). Biovailable Pb and Zn in El Lirio were positively correlated with plant richness and vegetation cover, whilst Cd and Zn were also positively correlated with plant richness in Brunita. This could indicate that the natural establishment of vegetation could be influencing the availability of these metals. In fact, plant roots are known to exude organic compounds capable of complexing metals, which can increment the metals availability in the rhizosphere, and this process differs among different plant species (Jones 1998; Almeida *et al.* 2006). Plants release some labile compounds to soil to promote the availability and uptake of nutrients, provoking also the availability and uptake of heavy metals (Séguin *et al.* 2005).

Conclusion

The application of pig manure and sewage sludge together with marble wastes has proved to be effective for long-term decrease in the bioavailability of most toxic heavy metals present in two tailing ponds from SE Spain, besides maintaining pH close to neutrality. Despite the initial decrease in SOC and N_t, mineralization and leaching have lead to levels of organic matter only slightly higher in comparison to control plots. Since increments in some bioavailable metals have been monitored, future studies are needed to determine the causes, or mitigate this trend by new applications of organic amendments.

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