Research article

Evaluation of remediation techniques in soils affected by residual contamination with heavy metals and arsenic

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A B S T R A C T

Residual soil pollution from the Aznalcóllar mine spill is still a problem in some parts of the affected area, today converted in the Guadiamar Green Corridor. Dispersed spots of polluted soils, identified by the absence of vegetation, are characterized by soil acid pH and high concentrations of As, Pb, Cu and Zn. *Ex situ* remediation techniques were performed with unrecovered soil samples. Landfarming, Composting and Biopiles techniques were tested in order to immobilize pollutants, to improve soil properties and to promote vegetation recovery. The effectiveness of these techniques was assessed by toxicity bioassays: *Lactuca sativa* L. root elongation test, *Vibrio fischeri* bioluminescence reduction test, soil induced respiration test, and *Eisenia andrei* survival and metal bioaccumulation tests. Landfarming and Composting were not effective techniques, mainly due to the poor improvement of soil properties which maintained high soluble concentrations of Zn and Cu after treatments. Biopile technique, using adjacent recovered soils in the area, was the most effective action in the reduction of soil toxicity; the improvement of soil properties and the reduction in pollutants solubility were key to improve the response of the tested organisms. Therefore, the mixture of recovered soils with polluted soils in the areas affected by residual contamination is considered a more suitable technique to reduce the residual pollution and to promote the complete soil recovery in the Guadiamar Green Corridor.

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1. Introduction

Aznalcóllar pyrite mine (Sevilla, Spain) is considered one of the largest environmental disasters involving mine spill in the world (Nikolic et al., 2011). In 1998 the waste dump broke, spilling around 36×10^5 m^3 of acidic waters and 9×10^5 m^3 of toxic tailings into the Agrio and Guadiamar rivers (Simón et al., 2001). The total affected area was 45 km^2 of soils, mainly with agricultural use. Widespread wastes were mainly composed by high concentrations of As, Pb, Cu and Zn (Aguilar et al., 2004a). These elements infiltrated irregularly in depth depending on soil properties, although the buffer capacity of the affected soils strongly minimized the negative effects on the environment (Cabrera et al., 1999; Aguilar et al., 2007; Simón et al., 2008). In the years following the spill, a quick and expensive soil remediation program was applied to restore the affected area, concluding with the establishment of the Guadiamar Green Corridor (GGC) (CMA, 2003). The main remediation actions performed included: removal of tailings and heavily polluted topsoil; applications of amendments to reduce mobility and bioavailability of pollutants (liming, iron-rich clayey materials, and organic matter) and soil phytostabilization (Aguilar et al., 2004b; Simón et al., 2008). The long-term ageing process in the area (18 years) has modified the potential toxicity in soils. Soils acts as natural pollution filter retaining metals, but under natural conditions these retained pollutants can lead to harmful effects. Soil properties largely control the mobility, bioavailability and therefore, potential toxicity of metals for environment, including living organisms (Sheppard and Evenden, 1988). In general, ageing process decrease toxicity in soils over time (Lock and Jannsen, 2003), and the long process of natural stabilization had decreased the concentration of residual pollution; however, residual soil pollution problems are still detected in the GGC (Martín et al., 2015). Affected soils are nowadays a source of pollution with high risk of dispersion that should be blocked to immobilize toxicity and finish, finally, the remediation started 18 years ago. Polluted areas are located in first 18 km downstream from the waste dump; this persistent pollution

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in some places of the GGC may be due to the speed of the first cleanup operation where removal of tailings was deficient and part of tailings remained mixed with soils in the upper 30 cm (Aguilar et al., 2007; Simón et al., 2008).

Over last years a great number of soil remediation techniques have been developed, treatments are currently safer, cleaner, less cost effective and more environmental friendly (Kulshreshtha et al., 2014). Recovering polluted areas is essential to prevent the deterioration of the environment, as well as control humans and other living organism exposures to hazardous chemicals (Mulligan et al., 2001; Pavel and Gavrilescu, 2008). Residual contamination and toxicity in polluted soils by heavy metals are generally evaluated by using bioassays. Direct responses of organisms exposed to potentially polluting elements obtained by bioassays are indicative of the actual risk of the pollutants, taking into account their bioavailability (Petänen et al., 2003; Romero-Freire et al., 2015a). Most common applied bioassays can be divided into two groups: a) those using a liquid phase (soil extract, pore water, leachate, etc.), and b) those using the soil solid phase (Farré and Barceló, 2003; Martín et al., 2010). To assess environmentally relevant soil toxicity, the use of a diverse set of exposure routes, as well as the maximal number of organisms, is recommended (Romero-Freire et al., 2016).

Unrecovered soils of the GGC were subject to remediation from an ex situ study. In order to immobilize involved pollutants and breakdown the dispersion risk, with the final aim of finding the best procedure to completely recovered the study area. The present work evaluates different remediation techniques focusing on easy applicability and low cost. Once applied the remediation techniques, bioassays with some of the most important groups of organisms (primary producers, detritivores and microbes) were performed to estimate the ecotoxicological risk.

2. Materials and methods

2.1. Soil sampling and analysis

Unrecovered soils located in the GGC, near to the tailing pond closed down after the accident, were identified using satellite images as areas with absence of vegetation, surrounded by regenerated areas with vegetation (Fig. 1). In total 5 plots without vegetation were selected. In each experimental plot composite samples were taken by mixing 200 g of top soil (0–10 cm) from each corner and centre of a square 1 m per side. Samples of both polluted (BS) and recovered (RS) soils were mixed and thoroughly homogenized to obtain representative soil sample of each paired plot. The main soil properties (Table 1) were analyzed in all cases.

Before analysis, soil samples were air dried at room temperature and passed through a 2-mm sieve, this fraction was used to characterize the main soil properties and for the toxicity bioassay. Soil texture was determined by the Robinson pipette method (Soil Conservation Service, 1972); calcium carbonate content by volumetric gases (Barahona, 1984); pH in a soil:water ratio 1:2.5 with a 914 pH/Conductometer Metrohm; total organic carbon (OC) was analysed by a LECO® TruSpec CN (St. Joseph, MI, USA) after soil samples were acid-washed (HCl 1 mol/l for 24 h) to remove carbonates, following Ussiri and Lal (2008); soil:water extract (1:5) was prepared to determine the electrical conductivity (EC) using a Eutech CON700 conductivity-meter; cation exchange capacity (CEC) were determined according to the methodology of the Soil Conservation Service (1972).

Total concentrations of main pollutants (T): As, Pb, Cu and Zn were determined by X-ray fluorescence in a NITON XLt 792 analyser, with a 40 kV X-ray tube with Ag anode target excitation source, and a Silicon PIN-diode with a Peltier cooled detector. The procedure followed the manufacturer's instructions and the

Fig. 1. Image of Sector 1 in the Green Corridor of the Guadiamar river, where spots corresponded to bare soils. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

recommendations of the Method 6200 (US EPA, 1998). Soluble metal concentrations (S) were obtained from soil:water extract 1:5 and measured by ICP-MS in a PE SCIEX ELAN-5000A spectrometer.

Soil-water partition coefficient (Kd) was calculated as the radio of the total metal concentration in soil (Xx T mg kg^{-1} dry soil) and soluble metal concentration (Xx S in mg l^{-1}), as a normalization of soluble concentration data (Blaser et al., 2000). Risk quotients (RQ) were calculated dividing the measure on-site metal concentration by a sensitive screening value; in this case we selected as screening values the metal concentration of the recovered adjacent areas (RS) which showed vegetation cover, assuming these areas had no ecological risk. RQ values were calculated both for total and water extractable metal concentrations. RQ values higher than one indicate pollution risk (US EPA, 2007). In addition, RQs were also calculated for the intervention level for other uses in Andalusia (Decree 18/2015) only for the total metal concentration.

2.2. Remediation treatments

With the aim to reduce mobility and bioavailability, prevent toxicity and promote the vegetation recovery of the soils. Three remediation techniques were performed in laboratory:

1. Landfarming (L): involving periodical tilling of polluted soils to remove the crust formed in the soil surface and to improve aeration.