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Risk assessment of an abandoned pyrite mine in Spain based on direct toxicity assays

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HIGHLIGHTS

- Risk assessment of an abandoned pyrite mine based on direct toxicity assays.
- Direct toxicity assessment versus chemical analysis for risk assessment.
- Total and available levels of trace elements did not correlate well with toxicity.
- Arsenic availability and mobility increased due to changes in soil properties.

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ABSTRACT

This research reports the risk assessment of an abandoned pyrite mine using direct toxicity assays of soil and groundwater samples taken at the site. The toxicity of As and heavy metals from mining soils to soil and aquatic organisms was studied using the Multispecies Soil System (MS-3) in soil columns. Ecotoxicological assessment was performed with soil samples diluted with a control soil at concentrations of 12.5, 25, 50 and 100% test soil/soil (w/w). In this way, changes in the mobility and bioavailability of soil contaminants due to changes in geochemical soil properties via soil dilution were studied. The toxicity of water samples was tested on algae and *Daphnia magna*. The assessment of the mining area indicated that the current presence of As and heavy metals at the site may cause injuries to soil and aquatic organisms in the entire research area. Moreover, this investigation demonstrated that changes in geochemical conditions can increase the availability of arsenic and, consequently, the environmental risk of these soils. A good correlation was not found between toxicity parameters and the concentrations of soil contaminants based on total and extracted element concentrations. This finding reinforces the usefulness of direct toxicity assays for evaluating environmental risk.

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1. Introduction

Today, there is a growing concern towards the environmental effects of mine tailing sites (Antunes et al., 2011; Frouz et al., 2011; Kapusta et al., 2011; Cerqueira et al., 2012; Ribeiro et al., 2013). Tailings are produced during ore processing and are characterized by elevated levels of heavy elements, which can be released into the environment by erosion and leaching processes. In most cases, mining areas show high levels of hazardous elements in surface water, groundwater and soil, which can pose serious geochemical risks to human health and the environment (Anawar et al., 2006; Hofmann et al., 2008). This threat is aggravated by the long-term persistence of hazardous elements in the environment.

Risk assessment methodologies have been widely applied for the management of contaminated sites. However, their application to mining sites affected by tailing contamination is more limited (Kim et al., 2005; Lee et al., 2006; Moreno-Jimenez et al., 2011). In a first-tier approach, an ecological risk assessment is based on geochemical analysis, where concentrations measured in soil are compared to established thresholds. These accepted levels are based on the worst possible scenarios: toxicity data on the most sensitive species and the application of the most protective safety factors. Under these assumptions, the risk may be overestimated and may result in unnecessary remediation (Alexander, 2000; Ollson et al., 2009). A risk assessment based on geochemical analyses is highly simplified and does not take into account factors such as the bioavailability of a contaminant or the simultaneous presence of different contaminants, which can affect toxicity and exposure estimates (McLaughlin et al., 2000; De Zwart and Posthuma, 2005; O'Halloran, 2006). These facts are of the utmost importance for hazardous elements. The availability of hazardous elements in the soil is highly

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dependent on soil properties (Cerqueira et al., 2011). Moreover, hazardous elements can be present in different geochemical forms with different geochemical and toxicological properties that can be transformed from one into another due to environmental changes. To have a more complete impression of the degree of pollution and toxicity of a contaminated site, it is recommended to consider alternative approaches that more accurately reflect specific site conditions. Thus, risk assessment in mining sites should integrate both chemical and toxicological assays (Antunes et al., 2011; Chapman et al., 2012).

Direct toxicity assessment, conducted with natural samples taken at the site, allows the measurement of the toxicity of complex mixtures of contaminants and can enhance the realism and certainty of the risk assessment. Although these techniques have an increasingly important role, they are not generally available in existing guidelines for ecological risk assessment on contaminated sites (Fernandez et al., 2006; Semenzin et al., 2008). Therefore, the ecotoxicological risk assessments based on direct toxicity assays need to be validated through field studies performed with natural samples.

The application of bioassays to contaminated site assessments requires selecting an appropriate set of test species and measurement endpoints to be applied at the investigated site. Microcosms are considered one of the higher-tier options to assess toxic substances and contaminated soils (Schaeffer et al., 2010). More complex than single toxicity assays, microcosms consist of systems in which an assemblage of species is exposed simultaneously. This allows one to consider the interactions among species that may influence toxicity, hence increasing realism.

In this research, a multispecies system in soil microcosms, termed a "Multispecies Soil System" (MS-3), was used for the ecotoxicological evaluation of an abandoned pyrite mine in Bustarviejo (Madrid, Spain). This system has previously been applied to characterize geochemical substances and polluted soils (Fernandez et al., 2005; Garcia Frutos et al., 2010). In the MS-3 system, the organisms were selected from different trophic levels and included taxonomic groups that cover essential ecological roles for sustainable soil use. The mobility of contaminants and possible risks to the aquatic environment (groundwater and surface water) can also be determined through watering and subsequent leaching processes.

In this paper, a case study that utilized direct toxicity assays to assess site-specific risk in an abandoned pyrite mine is presented. The aims of this work were: i) evaluating the potential of direct toxicity assays using the microcosm system (MS-3) for assessing multi-element contaminated soils in a mining area, ii) assessing changes in mobility and bioavailability of soil contaminants due to changes in geochemical soil properties via soil dilution and iii) comparing results based on direct toxicity assays and geochemical data.

2. Materials and methods

2.1. Site description

Our research site was the area surrounding the Mónica pyrite mine, near the village of Bustarviejo (Sierra de Guadarrama, Madrid, Spain). Mining activities were carried out here from 1427 until 1980, and a group of galleries and pyritic dumps remain. The site extends across 200,000 m^2 within the La Mina stream valley, between the following UTM coordinates: 30 T − X = 0438606, Y = 4524302; X = 0437797, Y = 4523518, where a shrub land (higher sites) and a woodland (lower sites) are developed. Two freshwater streams (with water depth between 10 and 15 cm) were present at the studied site: La Mina and La Barranca.

2.2. Soil samples

Based on the total element concentrations derived from a previous research (Moreno-Jimenez et al., 2011), the sampling points were designed to represent the entire area. Four soil samples were selected to represent different zones according to mine distance and the level of As and metals in the soils 2 and 3 (S2 and S3) had the highest hazardous element concentrations and were found nearest the mine (3–312 m); soil 4 (S4) denoted intermediate distance sites with intermediate contaminant levels (459–657 m) and soil 5 (S5) possessed contaminant level representative of distant sites (771–1229 m) with soil contaminant levels close to background levels in this zone (De Miguel et al., 2002). The sampling points are shown in Fig. 1. Control soil was collected from a field located near Madrid (Spain). This soil was also used to prepare the dilution series of contaminated soils. Control and contaminated soils were each taken from the topmost soil layer (0–20 cm), air-dried and sieved (2 mm mesh). Table 1 details the main physico-chemical characteristics and element concentrations of control and test soils.

2.3. Water samples

Water samples were taken from streams in the surroundings of the mine and sampling locations are detailed in Fig. 1. Samples A1 and A2 were taken from a stream that goes through the mine and leaves without being diluted by adjacent streams; A1 is within and A2 is outside of the mine. Sample A3 was taken upstream of the mine to obtain background levels for waters in the site. Samples A4 and A5 were taken in the La Mina and La Barranca streams, which cross the mine's surroundings. Sample A9 was taken downstream from the confluence of adjacent streams at the most distant site. Surface waters (100 mL) were sampled in plastic flasks. Samples for ecotoxicological assessment were stored at 4 °C and analyzed as soon as possible. Samples for chemical analyses were supplemented with HNO_3 at a ratio of 1 mL of HNO_3 per 40 mL of water. Non-filtered samples were stored at 4 °C for a maximum of 20 days before further analysis.

2.4. Ecotoxicity assay

Contaminated soils were tested at four dilutions (100, 50, 25 and 12.5% test soil, w/w). Dilutions of polluted soil with control soil were prepared on a dry-weight basis and were obtained by mechanically mixing the soils in a B50 Solid V-mixer (Lleal, S.A.). Soils were assessed

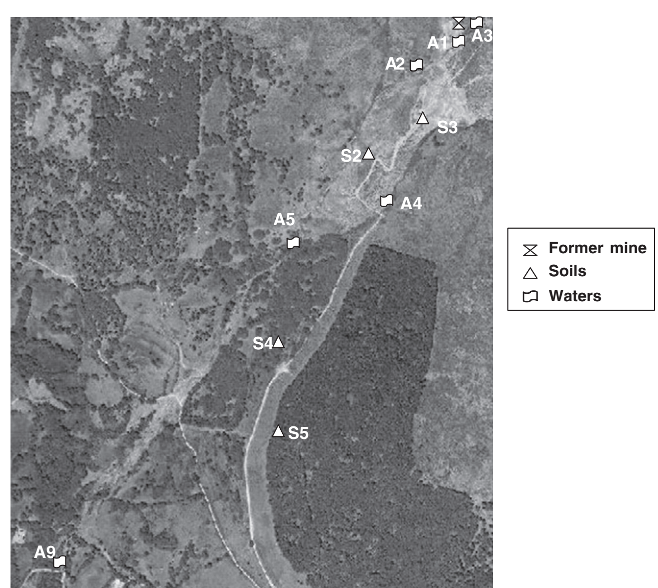

Fig. 1. Orthophoto of soils adjacent to the Mónica mine. Soil (S2, S3, S4 and S5) and water (A1, A2, A3, A4, A5 and A9) sampling points are shown in the figure.