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Pesticide mobility and leachate toxicity in two abandoned mine soils. Effect of organic amendments

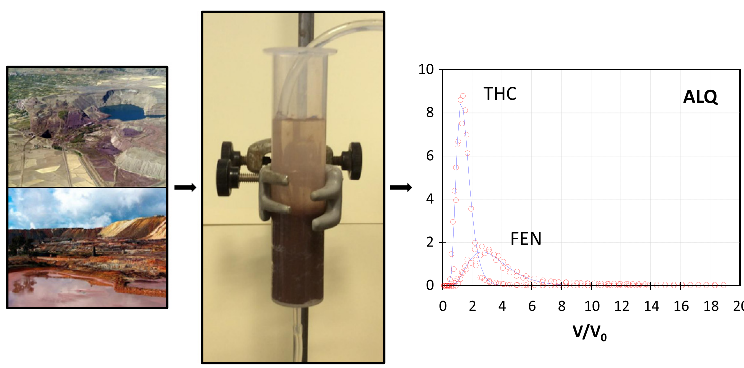
José Antonio Rodríguez-Liébana, M. Dolores Mingorance, Aránzazu Peña *

Instituto Andaluz de Ciencias de la Tierra (IACT), Consejo Superior de Investigaciones Científicas-Universidad de Granada (CSIC-UGR), Avda. de las Palmeras, 4, 18100 Armilla, Granada, Spain

HIGHLIGHTS

- Mine soils are degraded landscapes which need to be restored through revegetation.
- Soil columns to evaluate pesticide and element mobility from two Spanish mine soils
- Thiacloprid and fenarimol mobility reduced by application of organic amendments
- Only As in leachates at hazardous levels, despite the high soil element content
- The toxicity of the eluates diminished after amendment addition.

GRAPHICAL ABSTRACT



Mine soils — Soil column — Breakthrough curves

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ABSTRACT

Abandoned mine areas, used in the past for the extraction of minerals, constitute a degraded landscape which needs to be reintegrated to productive or leisure activities. However these soils, mainly composed by silt or sand and with low organic matter content, are vulnerable to organic and inorganic pollutants posing a risk to the surrounding ecosystems and groundwater. Soils from two mining areas from Andalusia were evaluated: one from Nerva (NC_L) in the Iberian Pyrite Belt (SW Andalusia) and another one from the iron Alquife mine (ALQ) (SE Andalusia). To improve soil properties and fertility two amendments, stabilised sewage sludge (SSL) and composted sewage sludge (CSL), were selected. The effect of amendment addition on the mobility of two model pesticides, thiacloprid and fenarimol, was assessed using soil columns under non-equilibrium conditions. Fenarimol, more hydrophobic than thiacloprid, only leached from native ALQ, a soil with lower organic carbon (OC) content than NC_L (0.21 and 1.4%, respectively). Addition of amendments affected differently pesticide mobility: thiacloprid in the leachates was reduced by 14% in NC_L-SSL and by 4% in ALQ-CSL. Soil OC and dissolved OC were the parameters which explained pesticide residues in soil. Chemical analysis revealed that leachates from the different soil columns did not contain toxic element levels, except As in NC_L soil. Finally ecotoxicological data showed moderate toxicity in the initial leachates, with an increase coinciding with pesticide maximum concentration. The addition of SSL slightly reduced the toxicity towards *Vibrio fischeri*, likely due to enhanced retention of pesticides by amended soils.

Abbreviations: A254, Absorbance at 254 nm; ALQ, Alquife soil; BTC, Breakthrough curves; CDE, Convection–dispersion equation; CSL, Composted sewage sludge; DOC, Dissolved organic carbon; EC, Electrical conductivity; FEN, Fenarimol; HIX, Humification index; HPLC, High performance liquid chromatography; NC, Nerva soil; NC_L, Limed Nerva soil; OC, Organic carbon; R, Retardation factor; SSL, Stabilised sewage sludge; THC, Thiacloprid; V/V_0, Relative pore volume.

* Corresponding author. Tel.: +34 958 230000x190119; fax: +34 958 552620.
E-mail address: aranchaph@iact.ugr-csic.es (A. Peña).

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1. Introduction

Abandoned mining areas have a negative influence on environmental and economic development. They were used in the past for the extraction of minerals and exploitation of the deposits but are no more in use, implying a major source of pollution of the surrounding environment, through a combination of eolian dispersion and water erosion processes (Mendez and Maier, 2008; García-Gómez et al., 2014). They constitute large areas of derelict land whose reintegration as productive land requires taking severe actions for the purpose of recovering mine soils for economic activities. Mine tailings lack nutrients supportive of biological growth (N, P, K), have a pH ranging from highly acidic (pH 2) to alkaline (pH 9) depending on the carbonate content and acid-generating potential of the tailings (Mendez and Maier, 2008), are mainly composed by silt or sand and contain almost no organic matter, lost as a result of initial stripping from the site to be mined. These two last features, highly related with soil ability to hold and release chemical compounds in solution (Fernandes et al., 2003), show that these soils are prone to pollutant leaching and groundwater contamination. Revegetation of these mine tailings is thus a good strategy to cope with this situation, because plant canopy serves to reduce eolian dispersion while plant roots help prevent water erosion and leaching (Asensio et al., 2013).

Full restoration of these areas will require the establishment of a functional ecosystem through revegetation which demands organic fertilization. Improvement of soil properties by addition of organic wastes is a usual strategy to restore these areas for revegetation purposes (Alvarenga et al., 2008; Mingorance et al., 2014), thus avoiding waste disposal to the environment. Organic wastes, with high organic matter content, affect soil fertility and water holding capacity and improve the overall soil structure and nutrient content, favouring soil reclamation. However, pollutants either present in the soil by past mining activities (metals), or added with the organic wastes or through the use of pesticides to control pests in the plants used for revegetation, are susceptible to reach the soil environment (Marín-Benito et al., 2013; García-Gómez et al., 2014). Understanding the physico-chemical processes involved in pollutant dynamics is an important issue to minimize water source contamination and properly assess the requirements of these soils, intended to be implemented for recreational or leisure activities.

The environmental fate of metals, abundant in these soils, has been the subject of numerous researches in recent years (Gilchrist et al., 2011; Deng et al., 2011; Asensio et al., 2013). However, the potential hazard of pesticide leaching from treatments to plants grown in these soils has not been yet evaluated.

To do this, two contrasting mine soils from Andalusia (south of Spain) were selected: one located in one of the largest sulphide deposits in the world (Nerva, Huelva, western Andalusia), with extremely acid pH and heavily contaminated with toxic elements and the other one from an abandoned iron ore mine (Alquife, Granada, eastern Andalusia), with basic pH and slightly polluted. The ability of both soils to retain two model pesticides, the polar insecticide thiacloprid and the fungicide fenarimol of intermediate polarity, was evaluated using soil columns. The effect on pesticide mobility of addition of organic wastes (sewage sludge and composted sewage sludge), previously selected for revegetation strategies (Mingorance et al., 2014), was also established. Finally, the chemical composition and toxicity to *Vibrio fischeri* of the leachates were assessed to establish the potential hazard of the different treatments.

2. Materials and methods

2.1. Soils and amendments

Two soils from Andalusia (south of Spain) devoted in the past to mining activities were selected: one situated near Riotinto in the province of Huelva (SW Spain), used for copper extraction and the other one placed in Alquife, in the province of Granada (SE Spain), aimed at iron extraction. The locations of both mining sites are presented in Fig. 1S in the supplementary material. The soils were collected from the upper 20 cm, air dried and sieved (<2 mm). The fine earth fraction corresponded in both cases to sandy loam soils (55% sand, 14% clay for the former and 64% sand, 8% clay for the latter). The soil from Riotinto site, very acid (pH 2.4), was limed with Carbocal (Azucarera Ebro), a residue rich in calcium carbonate (83.4%) to correct soil acidity and named as NC_L (Table 1). It displays low organic carbon (OC) content and higher electrical conductivity (EC), while the soil from Alquife (named ALQ) presents alkaline pH with low EC and OC content (Table 1). Major and toxic elements for both soils are also shown in Table 1. More information about both sites can be found elsewhere (Rodríguez-Liébana et al., 2013).

Two organic amendments from wastewater treatment plants were employed: stabilised sewage sludge (SSL) from the plant of Granada (SE Spain), and composted sewage sludge (CSL) from the plant of Sevilla (SW Spain). Sewage sludges were subjected in the urban water treatment plant to an aerobic digestion and mechanical dehydration. Then they were air-dried in the laboratory for several weeks and sieved <2 mm before use. Main properties and element contents are also presented in Table 1. Amended soils consisted in NC_L soil mixed with 2% SSL and ALQ soil mixed with 5% CSL. This study takes part of a project aiming at the restoration of both mining sites through revegetation. Therefore, the selected amendment doses took into account an effective increase in soil OC (Table 1) and previous results reflecting the ability of establishment of plant species in both mining areas (Mingorance et al., 2014 and unpublished results).

2.2. Pesticides

Thiacloprid (THC), a neonicotinoid insecticide and fenarimol (FEN), a pyrimidine systemic fungicide, were employed. Standards (purity ≥ 98%) were used without further purification (Dr. Ehrenstorfer, Germany). Their octanol/water partition coefficients (log K_{ow}) are 1.26 and 3.69, and their solubility in water is 185 and 13.7 mg L^{-1}, respectively (Tomlin, 2003). Their environmental DT_{50} values range between 7 and 21 d for THC and >365 d for FEN. The Groundwater Ubiquity Score (GUS) index for THC (1.44) indicates a low leaching potential, while that of FEN (2.72) can be considered as moderate (Footprint

Table 1
Some properties of the mine soils (NC_L and ALQ) and the organic amendments, stabilised sewage sludge (SSL) and composted sludge (CSL).

	NC_L	ALQ	SSL	CSL	NC_L-SSL2	ALQ-CSL5
pH	6.8	8.2	7.2	6.8	7.0	8.0
EC (dS m^{-1})[a]	1.9	0.07	2.8	3.0	2.3	0.66
OC (%)	1.4	0.21	36	10	1.8	0.37
HIX	5.74	1.41	0.43	2.21	1.91	4.19
Fe_2O_3 (%)	23	28	3.3	4.8		
CaO (%)	0.13	15.9	13.0	15.5		
MgO (%)	0.53	1.6	0.99	1.5		
MnO (%)	0.05	0.97	0.05	0.11		
K_2O (%)	1.95	2.11	1.11	1.46		
Na_2O (%)	0.41	0.49	0.06	0.26		
P_2O_5 (%)	0.51	0.10	7.8	4.1		
S (mg kg^{-1})	8320	127	b.d.	14,012		
Sr (mg kg^{-1})	55	171	2327	312		
As (mg kg^{-1})	3951	49	b.d.	b.d.		
Cu (mg kg^{-1})	694	49	676	314		
Cr (mg kg^{-1})	97	b.d.	169	154		
Pb (mg kg^{-1})	3976	b.d.	1163	b.d.		
Zn (mg kg^{-1})	120	70	2470	934		
Ni (mg kg^{-1})	b.d.	b.d.	140	71		

Element content by X-ray fluorescence (XRF).
b.d., below detection.
[a] EC measurements at 1:2.5 ratio (w:v) for non-amended (NC_L and ALQ) and amended soils (NC_L-SSL2 and ALQ-CSL5) and at 1:10 ratio for pure amendments (SSL and CSL).