

Application of remediation techniques for immobilization of metals in soils contaminated by a pyrite tailing spill in Spain

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Abstract. Remediation techniques for soil pollution have been studied in the aftermath of a tailing spill from a pyrite-mine holding pond in Aznalcóllar (southwest Spain). Given the extent of the accident and the characteristics of the affected area, we conclude that, after the removal of the tailings, the only feasible remediation measure involves chemical immobilization of the pollutants. The best treatment tested proved to be liming in combination with amendment materials such as soils rich in iron oxides and clay. Monitoring for 3 years has demonstrated that the system is effective for reducing the solubility of the most mobile forms of the main pollutant elements, although further monitoring is recommended.

Keywords: Pyrite spill, soil pollution, remediation, metal contamination, arsenic, heavy metals, Spain

INTRODUCTION

In 1998, a breach in the holding pond of the pyrite mine in Aznalcóllar (southwest Spain) spilled $2 \times 10^6 \text{ m}^3$ of tailings (floated pyrite sludge) and $4 \times 10^6 \text{ m}^3$ of acidic water containing high concentrations of Fe, S, Zn, Cd, Cu, As, Pb, Tl into the Agrío and Guadiamar river basins, which affected some 55 km^2 of land used predominantly for crops and grazing.

Since this event, studies have been made to assess the extent of contamination of the surface water, groundwater and soils not only in the affected zone, but also in the adjacent uncontaminated areas (Aguilar *et al.* 1998; Alastuey *et al.* 1999; Simón *et al.* 1999).

The first remediation measure was the physical removal of the tailings. The percentage of land area exceeding permitted levels was established for each element (Aguilar *et al.* 1999a). The area percentages seriously affected were 1% for Cd, 13% for Cu, 11% for Tl, 30% for Pb, 80% for Zn and 98% for As (Aguilar *et al.* 1999b). In addition, the mobility of the pollutants was estimated as water-soluble concentrations, revealing that soluble As exceeded the limit of 0.04 mg kg^{-1} (Bhon *et al.* 1985) in 83% of the land area; soluble Pb exceeded the limit of 1 mg kg^{-1} (Ewers 1991) in

40% of the area, and soluble Cd exceeded the limit of 0.03 mg kg^{-1} (Ewers 1991) in 49% of the affected area.

Given the high percentage of seriously contaminated land, the aim of the present work was to formulate the necessary remediation measures appropriate to local conditions.

MATERIALS AND METHODS

The amendments were applied to the affected area in the summer of 1999 and repeated in 2000. The application rate of sugar-refinery scum (pH 8.89, CaCO_3 content 38%) was between 2 and 4 kg m^{-2} depending on the contamination level of the soils. The amendment rate with material rich in iron oxides and clay was between 0.5 and 1 kg m^{-2} , applied in 2000 only in the most polluted sectors. To study the effect of the treatments, we monitored the basin over time: before (1998), during (1999), and after (2001). We focused on the most polluted soils, those without lime, with pH slightly below 7, and with very low organic carbon content ($\geq 1\%$). These soils were subdivided into loams, and sandy loams with high gravel content. The contaminated area was monitored with a sampling network established on a grid of $400 \times 400 \text{ m}$. At each intersection and in the centre of each cell, a square $10 \text{ m} \times 10 \text{ m}$ was sampled (the four corners and centre pooled) at three depths: 0–10 cm, 10–30 cm and 30–50 cm. Soil samples were finely ground ($< 0.05 \text{ mm}$) and digested in strong acids ($\text{HNO}_3 + \text{HF}$). The elements were determined by ICP-MS with a Perkin Elmer Sciex-Elan 5000A.

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Table 1. Properties of the soils treated with the pollutant solution obtained by oxidation of the tailings.

Soil	OM (%)	Clay ^a (%)	CEC (cmol _c kg ⁻¹)	Fe _d (%)	pH	CaCO ₃ (%)
1	4.5	13	12	1.0	7.5	0
2	1.5	13	5	2.2	5.0	0
3	2.0	12	6	1.5	7.5	0
4	0.8	50	14	3.0	7.0	0
5	0.4	5	3	0.6	8.5	0
6	0.5	5	3	0.4	8.5	18

^a Clay particle size < 2 μm.

OM = organic matter; CEC = cation exchange capacity, Fe_d = citrate-dithionite extractable iron.

RESULTS AND DISCUSSION

After the removal of the tailings and the topmost centimetre of the polluted soils, the pollution persisted at high concentrations due to the combined action of the machinery and the rainfall, which caused the tailings to penetrate the soils and increased the pollution in a highly irregular distribution pattern. Therefore, the remediation measures focused on the immobilization of the pollutants. To examine the soil properties involved in the retention of the contaminants, we carried out an experiment with six different unpolluted soils of the area (Table 1). We analysed the concentration of metals after treating the soils with the pollutant solution prepared by oxidation of tailings from the spill. The percentages of Cu and Zn (Figure 1) indicated that the soils most effective in retaining contaminants were

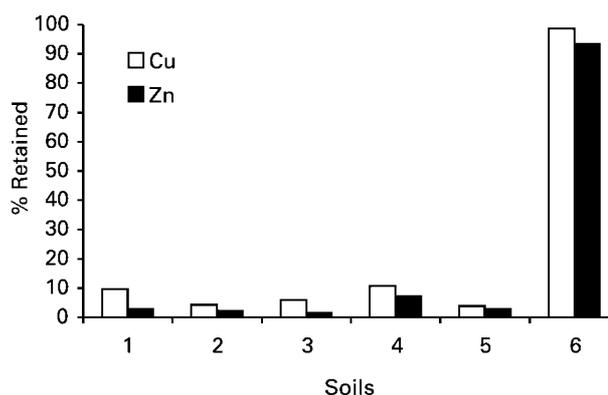


Figure 1. Percentage of Cu and Zn retained by different soils in Table 1 (means of duplicates).

rich in CaCO₃ (retention > 90%). Soils rich in clay and iron oxides also retained substantial percentages of the contaminants. Therefore, effective immobilization of the contaminants in the affected soils would require the addition of CaCO₃ (liming) and, to a lesser extent, clay and iron oxides.

However, the initial application rate of lime proved to be inadequate. The natural oxidation of the sulphides in the tailings caused a fall in pH to values below 2.0 in many areas. In these areas liming was repeated five or six times to achieve stable neutralization. After liming, the only element that remained soluble in substantial quantities,

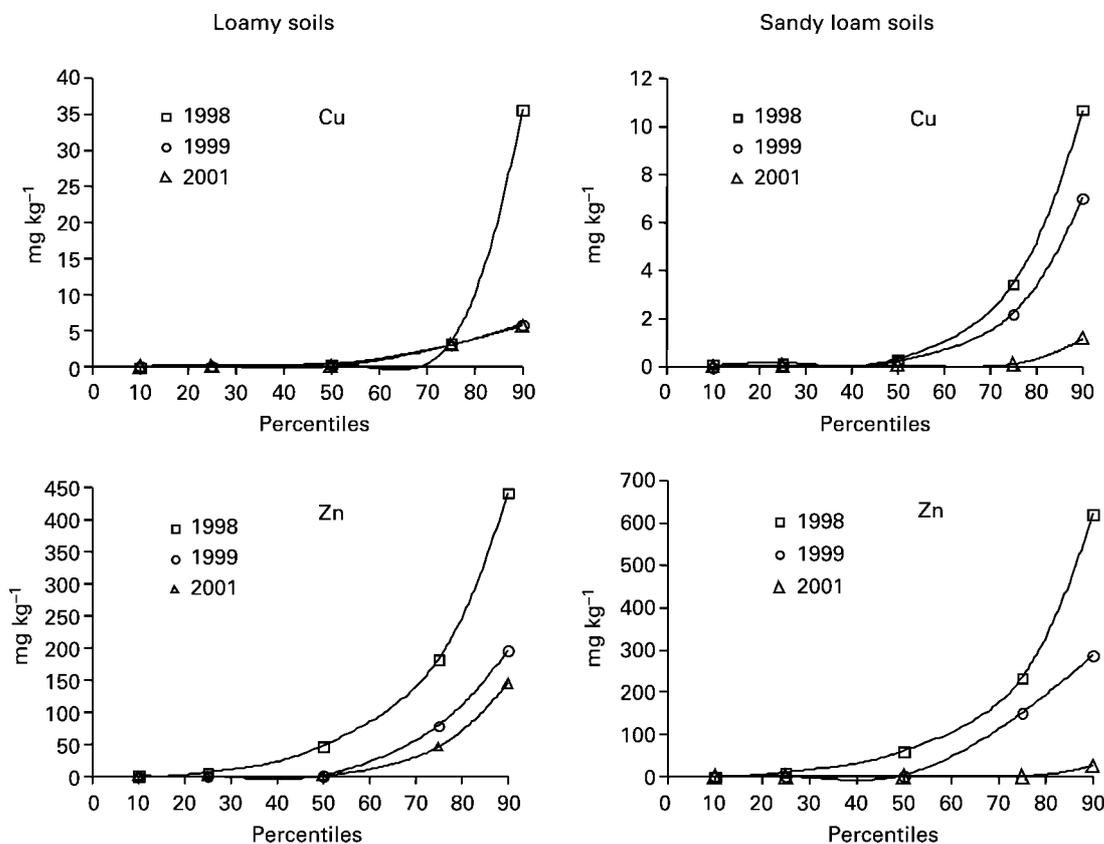


Figure 2. (Continued).

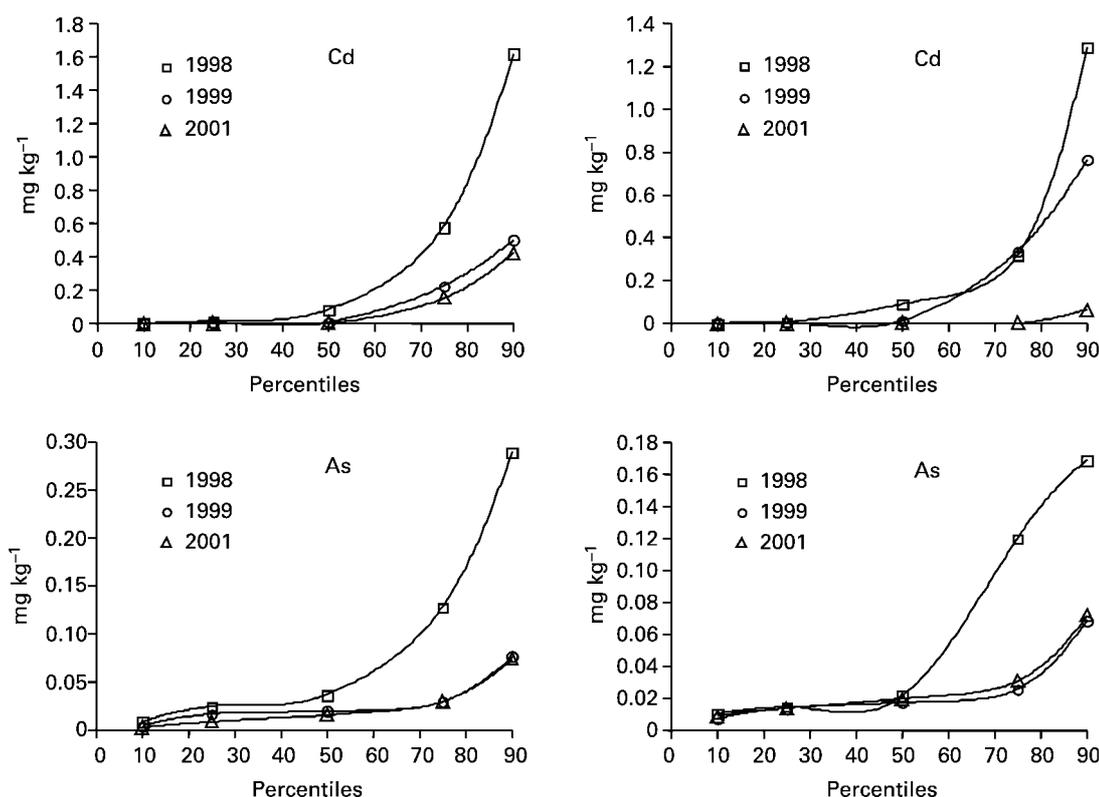


Figure 2. Change over time of water-soluble Cu, Zn and Cd in loamy and in sandy loam soils (% of all samples for each group), after treatment with CaCO₃ and materials rich in iron oxides and clay.

regardless of pH, was As. An amendment rich in iron oxides and clay was applied to immobilize this soluble As. The effects of treatments on the solubility of contaminants are in Figure 2. The water solubility diminished notably from 1998 to 1999, particularly in the case of As. The decrease from the year 1999 to 2001 was minor or negligible except for Cu, Zn and Cd in sandy loams, indicating that these soils require a second application of the amendments. Further monitoring of this contamination is needed.

ACKNOWLEDGEMENTS

The authors thank the Environmental Ministry of the Regional Government of Andalusia, Spain, for financial support, and Mr David Nesbitt for the English translation and comments.

REFERENCES

- Aguilar J Dorronsoro C Fernández E Fernández J García I Martín F Ortiz I & Simón M 1998. Contaminación de suelos por el vertido tóxico de la mina de Aznalcóllar. Simposio Minería y Medio Ambiente en la Cuenca Mediterránea. Cuevas de Almanzora, Almería pp 13–24.
- Aguilar J Dorronsoro C Galán E & Gómez L 1999a. Criterios y estándares para declarar un suelo como contaminado en Andalucía. Metodología, toma de muestras y análisis para su investigación. In: *Investigación y Desarrollo Ambiental en Andalucía*, ed Universidad de Sevilla. Sevilla Spain pp 45–59.
- Aguilar J Dorronsoro C Fernández E Fernández J García I Martín F Ortiz I & Simón M 1999b. Contaminación de suelos por vertido tóxico minero en el entorno del Parque Nacional de Doñana (Sevilla, España). Proceedings of the 14th Congreso Latinoamericano de la Ciencia del Suelo. Universidad de la Frontera. Temuco Chile p 529.
- Alastuey A García-Sánchez A López F & Querol X 1999. Evolution of pyrite mud weathering and mobility of heavy metals in the Guadiamar valley after the Aznalcóllar spill, south-west Spain. *Science of the Total Environment* 242(1–3), 41–55.
- Bhon HL McNeal BL & O'Connor GA 1985. *Soil Chemistry*. Wiley Interscience J Wiley & Sons New York.
- Ewers W 1991. Standards, guidelines and legislative regulatory concerning metals and their compounds. In: *Metals and their compounds in the environment*, ed E Merian, VCH Publishers Weinheim Germany pp 707–711.
- Simón M Ortiz I García I Fernández E Fernández J Dorronsoro C & Aguilar J 1999. Pollution of soils by the toxic spill of a pyrite mine (Aznalcóllar, Spain). *Science of the Total Environment* 242(1–3), 105–115.

Received April 2004, accepted after revision September 2004.