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Restoration strategies in the Guadiamar area of southern Spain: evaluation of success ten years after the Aznalcóllar accident

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Abstract
This study summarizes the main results obtained by the research group from the Instituto de Recursos Naturales y Agrobiología de Sevilla during ten years of study in the mine spill affected area of the Guadiamar river (SW Spain). This work is focussed on 1) trace element changes in soil (total and available concentrations) and plants (native and reforested), and 2) evaluation of the effectiveness of assisted natural remediation in the restoration of polluted soils.

Introduction

In the early hours of 25th April 1998, a failure of the tailing dam wall occurred at 'Los Frailes' open-pit pyrite mine (Aznalcóllar, 45 km west of Seville, Spain). A spill of 5-6 million m^3 of toxic tailings (sludge and acid water) flowed down through the courses of the Guadiamar and Agrio rivers. It began one of the most serious ecological disasters in Spanish environmental history. About 4500 ha of agricultural land were affected by the pollution. Apart from the economical disaster, the proximity of the mine to the Doñana National Park made the accident, if possible, more serious.

The first analysis of soils showed severe trace element contamination (mainly As, Cd, Cu, Pb, Tl and Zn). This contamination largely affected the superficial layer of the sludge-affected soils, with high element concentrations in the topsoil (around 40 cm) that strongly decreased at deeper layers.

The clean-up operation started officially at the beginning of May of 1998. First of all, a clean-up program was established to remove the toxic sludge from the surface. Toxic sludge and a variable layer of topsoil (10-30 cm) were removed mechanically. The tailings and the topsoil collected were placed back in the Aznalcóllar open pit. During the first phase of the clean-up (until December 1998) $7 \cdot 10^6$ m^3 of sludge and topsoil were removed. Then, other re-cleaning operations took place at the end of 1999 and $1 \cdot 10^6$ m^3 of sludge and topsoils were removed.

A second remediation phase was carried out by adding organic matter and calcium-rich amendments. The Regional Government 'Junta de Andalucía' supported by advice from different experts decided to give priority to the immobilization of the contaminants. Addition of amendments is a common practice for immobilization of trace elements and improvement of soil conditions. Soils can naturally reduce mobility of heavy metals as they are retained by sorption, precipitation and complexation reactions. This natural attenuation process can be accelerated by the addition of amendments. Vegetation cover also prevents wind-erosion and dispesion of contaminated particles and reduces water pollution by interception of a substantial proportion of the incident precipitation. The Regional Government purchased affected lands, which were farms with some fragmented forests and savannah-like woodlands and any agricultural practice was banned. The 'Guadiamar Green Corridor' programme was implemented, with the aim of providing a continuous vegetation belt for wildlife to migrate along the Guadiamar River basin between the Doñana (south) and the Sierra Morena mountains (north). Revegetation on the alluvial terraces started in 1999. Depending on local habitat conditions, the target tree and shrub species selected to afforest were those typical of riparian forests (such as white poplar and willow) or those typical of drier upland forests, such as holm oak, wild olive, rosemary, retama brush, lavender, oleander. The application of amendments and the development of a plant cover played an important role in the restoration of the physical, chemical and biological properties of these contaminated soils. Assisted natural remediation was used at a large-scale to solve a serious trace element pollution problem.

Materials and methods

To determine the effectiveness of the remediation, different studies on trace metal content in soils and plants after sludge removal and the subsequent remediation process were carried out.

The strategies developed for soil sampling in the Guadiamar river valley were: 1) intensive sampling in different zones of the soil profile (0-20 and 20-40 cm) after sludge removal in the north section of the river valley carried out in October-December of 1998; 2) extensive sampling in affected soil (0-25 cm) and in soil of the riparian forest of the river valley (0-25 and 25-40 cm) between October 1999 and October 2007.

Plants were sampled at different sites of the area. From 1999, we have analyzed native vegetation such as grasses and trees growing in restored and unrestored soils, and the species used in the afforestation along the Green Corridor. We have also monitored seedling establishment of different species in polluted sites. Moreover, from 2007 we also have been assessing the risk associated with managing horse-grazed pasture (non-edible livestock).

Total metal and S concentrations in soil samples (< 60 μm) were determined after *aqua regia* digestion in a microwave oven. Potentially available trace elements were determined by extracting samples with 0.05 M EDTA solution. Soil $CaCl_2$-soluble trace element concentrations were determined in 1:10 soil sample (2 mm): 0.01 M $CaCl_2$ extracts. Plant material was analyzed for N by Kjeldahl digestion. Mineral nutrients (P, K, Ca, Mg and S) and trace elements (As, Cd, Cu, Pb, Tl and Zn) were extracted by wet oxidation with conc. HNO_3 under pressure in a microwave oven. Mineral nutrients and trace elements in the extracts of soils and plants were determined by

ICP-OES. The accuracy of the analytical methods was assessed through BCR analysis (Community Bureau of Reference).

Results and discussion

Soils

Results of intensive sampling carried out in several patches of these soils showed that the degree of trace element pollution was independent of the type of soil. Table 1 shows mean and standard deviation values of trace elements in different soils of the affected area. Standard deviations are very large due to high spatial variability. Mean trace metal concentrations were generally much higher than background values for unpolluted soils in the Guadiamar river valley (Cabrera et al. 1999). In many cases, means were higher than those found before the removal of sludge deposited on the soil surface. This anomaly seems to be due to the sludge left behind on the soil surface and that buried in the soil during sludge removal.

Table 1. Means and standard deviation (SD) of trace metal concentrations for different samplings.

Sampling		As	Cd	Co	Cr	Cu	Hg	Mn	Ni	Pb	Tl	Zn
		Soil affected by the spill (0-20cm)										
1998	Mean	86.8	1.86	12.5	61.7	98.8	0.25	602	22.9	263	2.41	541
2002	Mean	153	4.44	14.3	51.7	155	0.40	1217	32.3	321	-	462
	SD	*121*	*1.91*	*12.7*	*32.2*	*93.0*	*0.42*	*1989*	*21.5*	*203*	-	*253*
2005	Mean	153	2.32	13.4	82.9	110	0.36	563	25.5	291	1.16	491
	SD	*104*	*1.34*	*2.41*	*10.2*	*39.0*	*0.24*	*150*	*4.62*	*188*	*0.85*	*192*
		Soil non affected by the spill										
1998	Mean	18.9	0.33	12.4	68.6	30.9	0.06	678	26.9	38.2	0.70	109
2002	Mean	21	0.35	13.8	91.8	31.0	-	688	29.5	60.1	0.28	117
		Phytotoxic concentration (Kabata-Pendias &Pendias, 1992)										
		15-50	3-8	25-50	75-100	60-125	0.3-5	1500-3000	100	100-400	1	70-400

Higher values of As, Hg and Pb – the less mobile elements - were observed in the first kms from the tailings dam, the section of the river that became the more contaminated after the spill, and that had to be submitted to further clean-up. However, we found that the contamination caused by other trace elements such as Cd, Zn and Cu, was similar along the river basin. The total concentration of the contaminants in the soil should not be the most important fraction to study in environmental research. Bioavailability of contaminants is of crucial importance for the assessment of environmental quality and their possible risk through the food chain. After liming and manuring, mean concentrations of available (EDTA and $CaCl_2$-extractable) trace elements in surface soils (0-10 cm) were greater than values for unaffected soils of the same area. However, extractable fractions remained constant (or even decreased) with time.

Plants

Native vegetation: In unrestored areas, trace element concentrations in the dry matter of native grasses were higher than in restored places (Madejón et al. 2002). Also, the deposition of contaminated dust was very high as shown by the analyses of unwashed samples. Nevertheless, element concentrations in plants measured in 2001 were much lower that those observed in 1999. Concentrations of trace elements in trees along the Green Corridor were low. Only willow and poplar growing in soil with low pH values presented concentrations of Zn and Cd higher than phytotoxic values. Figure 1 shows results of soil and plant sampling performed to study the use of white poplar (*Populus alba* L.) as a biological trace metal indicator in soils of Guadiamar riparian forest affected by the spill (Madejón et al. 2004).

Pastures

Analysis performed in 2007 showed trace element concentrations are now below maximum tolerable limits for horses, although autumn grazing may pose a risk from soil contamination of herbage and direct soil ingestion. Faecal analysis showed regulated absorption of essential elements, while non-essential elements seemed to be preferentially excreted. Nevertheless, periodic monitoring is recommended in view of the long-term chronic trace element exposure in these systems.

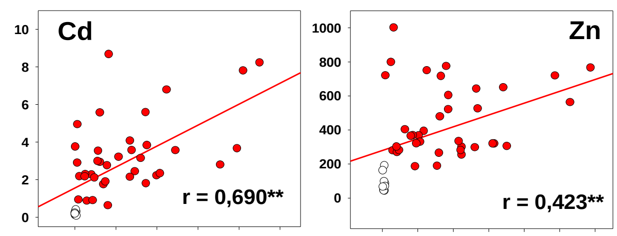

Figure 1. Regression analysis between values (mg kg^{-1}) of Cd and Zn in plant (Y) and soil (X)

Seedling establishment in polluted sites

Abiotic factors such us high irradiance and summer drought can be more important for seedling survival than soil pollution. Facilitation by shrubs plays an important role in the restoration of these degraded areas

Conclusions

Assisted Natural Remediation has been a reliable technique for reclamation and stabilization of the contamination of the soils affected by the Aznalcóllar accident.

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