The Cartagena–La Unión mining district (SE spain): a review of environmental problems and emerging phytoremediation solutions after fifteen years research POCIS

Samuel Content and Con

Héctor M. Conesa^{*} and Rainer Schulin

DOI: 10.1039/c000346h

After mining in the Cartagena–La Unión Mining District (SE Spain) was discontinued in 1992, various studies have shown that large amounts of toxic metals continue to be transferred with the spread of unstabilized mining wastes to the nearby ecosystems. Local creeks seem to be important pathways carrying eroded materials from the headwaters to the nearby coastal areas of the Mediterranean Sea. Studies have shown the presence of high metal concentrations in the sediments of riverbeds and in river mouths and adjacent coastal marshes (e.g. 500 mg kg-¹ As; 12 000 mg kg-¹ Pb). Also, some nearby agricultural areas are affected (up to 10 mg kg⁻¹ Pb in lettuce leaves). Metal transfer into biota has been demonstrated in creek sediments in relation to benthic organisms (up to 222 mg kg^{-1} Pb in molluscs). The mining wastes in the area are spontaneously colonized by native plant species. On the tailings, most of the plant species are grasses (e.g. Lygeum spartum, Piptatherum miliaceum); in polluted salt marshes, halophytic species dominate (e.g. Arthrocnemum

Institute of Terrestrial Ecosystems, ETH Zurich, Universitaetstrasse 16, CH-8092, Zürich, Switzerland. E-mail: hector.conesa@ env.ethz.ch; Fax: +41 44 633 1123; Tel: +41 44 632 8605

macrostachyum). Metal uptake by plants is in general low $(10 \text{ mg kg}^{-1}$ for Cu; <200 mg kg-¹ Pb; <500 mg kg-¹ Zn). Preliminary tests have shown the suitability of amendments (e.g. lime, fertilizer, pig manure) to improve the establishment of certain vegetation on the tailings. Phytostabilization appears to be a promising technology to decrease erosion in the tailings. However, tailings must be individually analysed in order to determine their geostructural stability, as in addition, mechanical stabilization will be needed in some cases to prevent collapse.

1 Mining activities in the Cartagena-La Unión mining district

Former mining areas are frequently the sources of environmental problems even many years after the closure of the mining operations. Current mining activities in most developed countries are carried out under environmental laws which require adequate restoration of affected land. However, mining operations which ceased before such regulations were enforced, continue to be a source of health and environmental risks due to the absence of remediation or restoration activities.¹ This is the case in the Cartagena–La Unión Mining District (Fig. 1), which is located on the Mediterranean coast of southeastern Spain. Mining and metal smelting made this district one of the most important industrial areas on the Iberian Peninsula, including its related smelting industries, from the time of the Roman empire until its closure two decades ago. The ore found in this zone was primarily mined for iron, lead and zinc, as the main metal components. Iron is present in oxides, hydroxides, sulfides, sulfates, carbonates, and silicates; lead and zinc occur in sulfides, carbonates, sulfates, and leador zinc-bearing (manganese, iron) oxides.²

The coastal Sierra Minera crosses the Mining District from West to East parallel to the Mediterranean coast. The terrain is low-lying (<400 m), but drops in steep slopes and runs to the coast. The area is characterised by a semi-arid Mediterranean climate. The annual rainfall averages 275 mm and mainly falls during spring and autumn. The annual average temperature is 17° C and

Environmental impact

Environmental studies in former mining sites usually focus on specific issues e.g. geochemistry, metal transfer, etc. but it is difficult to give a general vision of the problem within a single article. For this reason, reviews of these sites are necessary to integrate all the different studies and to give a better view of the pathways of pollutants to biota. In addition it is possible to generate more suitable proposals for remediation. After the mining closure the mining district of Cartagena–La Unión has been monitored by different researchers attending to: groundwaters, sediments in creeks, agricultural lands, marine fauna, mining wastes, tolerant metal biological communities, food chain, etc. This has provided an incredible "open" lab where metal pathways have been described. As a final step before carrying out remediation options we show in this manuscript a global view of this ecosystem and the relationships between the different ecological ''actors'' which are strongly influenced by the metal pollution.

Fig. 1 Location of the studied area.

the annual evapotranspiration rate is 857 mm per year. The vegetation is scarce and mainly consists of small forests with Pinus halepensis and thickets of xerophytic shrubs (e.g. Atriplex halimus, Helichrysum decumbens, Lygeum spartum).

The 50 km² of the Mining District includes five towns or villages with a total population of around 20 000 inhabitants. Another 200 000 people live in the surroundings, including the city of Cartagena. During the summer the population is increased by tourists who are attracted by the Mar Menor lagoon and the beaches of the Mediterranean Sea.³

The intensive mining activities have dramatically affected the local environment, in particular from the middle of the 19th century, coinciding with the introduction and development of modern metallurgy and smelting. In the middle of the 20th century open cast mines were developed and new flotation techniques in refineries were implemented. At that time there was a corresponding increase in processed ore and associated wastes. Total metal production increased to the early 1980s when external (low metal prices) and internal factors (such as the environmental concerns and the exhaustion of ore reserves), resulted in a deep crisis of the local mining sector⁴ which finally led to the definitive closure of mines in November 1991. Further historical information and socioeconomic data were given by Conesa et al.¹

This article describes the impacts on soils and hydrology that have resulted from the disturbance of the area by the former activities. It also addresses options for environmental restoration using noninvasive techniques based on the research which has been done since the mines were closed. Being surrounded by different kinds of natural ecosystems (lagoon, sea, salt marshes, agricultural lands) the area can be considered an ideal large-scale field study site where the dynamics of envi-

ronmental cycling of mining derived trace elements may be studied.

2 Impacts in the environment

2.1 Impacts in soils

Degradation of soils is usually one of the major environmental problems in mining areas. The excavation of open cast mines leads to denuded rock surfaces which usually provide a very hostile environment for the growth of plants. In addition, as these rock surfaces are exposed to the atmosphere, oxidation reactions occur and may lead to the generation of acid mine drainage. Mine spoils resulting from the excavation and the disposal of wastes from ore refining activities substantially modify the orography and hydrology.

García-García⁵ classified the surface affected by different types of mining wastes in the Cartagena–La Unión mining district (Table 1 and Fig. 2) according to their origin and characteristics. In total 8.82 km2 were found to be directly affected by mine deposits. Mine spoils (untreated materials from open pits) and mine tailings (wastes from the refining process) represented more than 70% of the total affected area and almost 80% of the total volume of waste deposits. Mine spoils are characterized by steep slopes $(30-39)$, homometric texture and often high metal concentrations.⁶ Environmental concerns relate to the geostructural instability due to large volumes

and low capacity to support vegetation, which results in high erosion risks. Tailings are usually characterized by low pH values, high heavy metal concentrations, lack of nutrients, low water retention capacity, high electrical conductivity and steep slopes.7,8 These factors make tailings adverse environments for plants and, as a consequence, their surfaces usually remain bare and exposed to erosion. Erosion processes create risks in two ways: (1) the structural stability of tailings may be seriously affected by water erosion, increasing the risk of collapsing especially in extreme meteorological situations or due to earthquakes.⁹ As a result, large areas may become polluted due to the spread of metal-rich waters, as in the case of the tailings dam failure at Aznalcollar in 1998 in southern Spain;¹⁰ (2) the release of metals from mine sites over time mainly through acid mine drainage and erosion (water/wind) 11 which may lead to wide spread contamination over large areas. In addition, chronic exposure to toxic dust blown from tailings can result in health risks for populations living in the vicinity. Were Article On 14 Apple 1911. The control of the state University of the transfer on 14 Apple 2010. The control of the state of t

Ortega et al.¹² classified the local tailings (averaging 20 m height and 40 000–80 000 m2) according to their environmental risk. They considered that 16 tailings posed a high risk due to acid mine drainage generation and high incidence of erosion. Restoration works or in some cases, the complete removal of the tailings were recommended. For 15 tailings even through acid generation was not a problem, erosion and dust generation were concerns. Fourteen tailings were in good condition and had already been removed or capped.

Water erosion was recognised as the main erosion factor,⁸ although in the long term, wind erosion, was also considered a risk. García-García⁵ found dust layers

Table 1 Summary of total areas affected by mine waste deposition according to García-García^s

Mining element	Number of structures	Area/km ²	Volume/m ³
Mine spoils	32	4.21	136
Mine tailing	89	2.18	23
Mines wastes in sea	3	0.83	25
Gravimetric spoils	119	0.65	3.73
Underground spoils	176	0.48	3.01
Gossans	11	0.26	6.93
High size wastes		0.06	0.59
Smelting wastes	19	0.13	0.66
Excavations materials from wells	1902	0.02	0.51

Fig. 2 Description of mining impacts in the area.

of more than 50 cm on soils situated in the proximity of some tailings. Nevertheless, water erosion was considered of greater concern due to the short high intensity rainfalls, which are typical for the local climate and which can transport large quantities of wastes through creeks in a short time over large distances. In addition, as mentioned before, water erosion can substantially increase the risk of collapse. Tailings usually consist of a sequence of layers with different texture and density reflecting their deposition history. Indeed, in 1972 and after high rainfall, the local tailing ''Brunita'' collapsed, causing an avalanche which killed one person and spread large amounts of mining wastes over the adjacent municipal area.⁵ If infiltration water is held back by layers of low permeability in the absence of adequate drainage systems, then slides may occur in certain conditions (non proper basement, long return period rainfall events or seismic event) in wet layers weakly structured and cause the tailing to collapse.¹³

The mine tailings of the Cartagena–La Unión Mining District can be classified into two different groups according to their geochemical characteristics.⁸ Conesa et al.¹⁴ showed a complete geochemical characterisation of local tailings. According to these authors there are acid tailings with a pH of around 3, which showed high solubility of metals such as Zn or Cd (e.g. 14% of total Zn is easily

mobilized in water extracts). Neutral pH tailings are also present with low metal water solubility but, at the same time, highly extractable with chelating agents such as EDTA. The main components of the tailings were Fe $(11-26\%)$, Si $(8-13\%)$, Al $(2-4\%)$ and S $(2-3\%)$. Trace elements with ecotoxicological significance were Zn (9100 mg kg⁻¹), As (1900 mg kg⁻¹), Cd (10–34 mg kg-1) and Pb (5000–7000 mg kg-1) (Table 2). The neutral tailings were characterized by the presence of nonoxidize minerals such as quartz and gypsum, whereas the acidic tailings were characterized by the presence of oxidised minerals (e.g. magnetite) and reduced ones (e.g. sphalerite). Oxidation of minerals in the tailings is the main source of acidity in the mine drainage. To prevent this process some of tailings have been capped with a mixture containing lime. However, many tailings are still at risk of oxidation because no capping layer has been added or it has been eroded. Aracil et al.¹⁵ studied columns composed of material collected from the acid tailings of the area and found differences of up to 3 pH units between tailing samples taken from the surface (pH 4) and samples from 1 m depth (pH 7). In the same way, electrical conductivity decreased from >10 dS m^{-1} at the surface to \leq 5 dS m⁻¹ at 3-4 meters depth.

Soils from the nearby Cartagena plain (Fig. 1) were found to have a geochemical background of 12.6 mg kg^{-1} Cu, 9 mg kg^{-1} Pb and 41 mg kg^{-1} Zn¹⁶ (Table 2). However, these values can not be used as reference levels for the mining district area because of its different geochemistry. Heavy metal background concentrations of agricultural soils developed on parent material in the mining area have not been

Table 2 Summary of heavy metal concentrations found in tailings and in surrounding areas and comparison with some threshold values. All data are in mg kg-1 ; n.a.: no available data

		As	Cd	Cu	Pb	Zn	Reference
Cartagena–La Unión sites affected	Mine tailings in the area	n.a.	n.a.	150	4000	12 000	51
by mining wastes		n.a.	n.a.	180	2000	2000	53
		1900	8.8	380	7000	5400	14
		350	34	84	5200	9100	
	Salt marshes in the Mar Menor	n.a.	n.a.	110	8000	6900	26
	lagoon	500	9.1	75	7000	7100	29
	Portman Bay sediments	n.a.	n.a.	150	8000	20 000	54
	Crop land near mine tailing	n.a.	n.a.	21	$200 - 500$	$200 - 900$	37
Regional thresholds and guidelines	Geochemical backgrounds in the nearby Cartagena plain	7.0	0.32	12.6	9.3	41.4	16
	Environmental thresholds in the nearby Cartagena plain	16	0.50	30	57	90	

established. Normally, analyses published in technical reports of some local crops lands are used as reference levels. According to these reports the metal concentration of agricultural lands near the mining area vary between 77–160 mg kg-¹ Cu, 28–150 mg kg-¹ Pb and 93–400 mg kg-¹ Zn.¹⁷

2.1.1 The Portman Bay pollution. New extraction techniques introduced in the middle of the 20th century modified the traditional way of working, increasing the mineral production but also the quantity of wastes generated in the area. The factory "Lavadero Roberto" located in Portman Bay (Fig. 2), was the largest metal refinery in Europe when it was established in 1957. Up to 10 000 tonnes of wastes were dumped daily into the bay. These contained large amounts of ore minerals such as lead carbonate, lead sulfide, iron sulfide, as well as reagents employed in the refining processes such as cyanides, sulfuric acid, xanthate, etc. Dumping wastes into Portman Bay stopped on March 1990 due to socialpolitical pressure. During the operational period from 1957 to 1990, more than 57 million tons of wastes were dumped into the Mediterranean Sea at Portman Bay. Over half of these materials deposited locally, filling completely the bay, which originally was more than 10 meters deep in the centre, and displacing the shore line 700 m towards the sea. The remaining material, was swept onto the continental $shelf.¹³$ Martinez-Frias¹⁸ considered Portman Bay ''the most contaminated bay in the entire Mediterranean, and a perfect example of ecotoxic pollution of a coastal environment by mine tailings''. We have the matched on 14 April 2010. We have the state of the matched particle in the halo matched by a state of the matched on 14 April 2010. The matched online the state university of the matched online to the matched

The sediments, which now fill the former Bay, show hydromorphic properties, indicating ''salt marsh'' dynamics (wet–dry periods). Analyses of sediments showed high metal concentrations: 7800 $\text{mg}\,\text{kg}^{-1}$ Zn, 6000 $\text{mg}\,\text{kg}^{-1}$ Pb, 5.9 $\text{mg}\,\text{kg}^{-1}$ Cd, 75 mg kg⁻¹ Cu and 1700 mg kg⁻¹ As.¹⁹ In total, an area of around 10 km² of the submerged continental shelf is impacted by mining.²⁰

Portman Bay has been the centre of local politics for the last twenty years. Various projects have been proposed to attempt to rejuvenate economic activities and address the pollution problem. These proposals include the removal of sediments from the bay $({\sim}2\,300\,000\,\mathrm{m}^3)$, and

their transfer into a nearby pit, creating a stable beach and building a yacht sport port. These remediation works may generate acute or chronic toxicity in local marine fauna by re-suspending toxic sediments.²¹

2.2 Impacts on hydrology

2.2.1 Surface water streams. The hydrology of the area has been dramatically affected by the mining activities. There are seven main creeks drainage the mining area (Fig. 2 and 3). The water regime of these streams reflects the seasonal character of the Mediterranean climate: for most of the year they remain dry and carry water only following short intensive rainfall events. Permanent water streams are restricted to some spring exits and discharges from mining galleries. Due to the steep slopes of the area, runoff waters can reach high speeds, increasing erosion processes. Five of the creeks flow into the Mar Menor lagoon (Miedo, Matildes, Beal, Ponce, Carrasquilla) and two to the Mediterranean Sea (El Gorguel, Portman). The creeks which flow into the Mediterranean Sea are shorter (\sim 3 km total length) and steeper (\sim 10%) than those ones which flow into the Mar Menor lagoon $(7-12 \text{ km})$ (Fig. 2 and 3). The creeks which flow into the Mar Menor lagoon (Fig. 2 and 3) have an average slope of around 3%, have steep headwaters (10%) but relatively long and flat lower reaches (slope $\leq 1\%$). The lower reaches consist of salt marshes and wetlands where most of the sediments are deposited before the water discharges into the lagoon. The Mar Menor lagoon is one of the biggest hypersaline coastal lagoons in the Mediterranean Sea. The lagoon and its salt marshes cover an area of around 15 000 ha. They are protected by official laws and conventions: the area has been a Ramsar international site since 1994 and includes five Sites of Community Importance (SCI); it is considered a Special Protected Area of Mediterranean Interest (SPAMI), established by the Barcelona Convention in 2001; and a Site of Community Importance (SCI) to be integrated in the Nature 2000 Network (EU Habitats Directive).

Negative impacts of the mining and associated activities (refining, smelting) on the local creeks were first noted during the 19th century when the wastes in riverbeds formed deposits more than 3 m thick.²² The wastes from the refining process were generally dumped into the streams that drained the area. In 1955 some public restrictions prohibited the mining companies from dumping wastes to form mining tailings.²³ However, tailings are located at the headwaters or in the riverbeds of the seven creeks and few have undergone any environmental restoration. Erosion is a significant issue due to bare areas and the short but high intensity rainfall. Large volumes of contaminated material can be relocated into and throughout the creek system (Fig. 4). The seven aforementioned creeks have tailings at their headwaters or along their riverbeds (Fig. 2).

Analyses undertaken by some authors24,25 along creeks (Table 3) showed that mining wastes were effectively transported to the respective creek mouths. Pavetti et al.,²⁵ for Gorguel creek (Fig. 2), showed positive correlations between the soluble anions and metals

Fig. 3 Profiles of local creeks from headwater to mouth.

Fig. 4 Metal exposure pathways from mining wastes disposal sites to biota. Continuous lines are non-biotic pathways. Dashed lines are biotic pathways.

concentrations in the slopes of the tailings located at the creek headwater and contents in the flowing creek water. The metal concentrations found by the same authors in flowing water after rainfall (Table 3) reached values of 1000 mg L^{-1} Zn and 1.8 mg L^{-1} Pb. Sediments showed an average of 7000 mg kg^{-1} Pb and 10 000 mg kg-¹ Zn. Similar results have been obtained by several authors^{5,24,26} for the Beal Creek (Table 3).

At some salt marshes located at creek mouths at the Mar Menor lagoon, such as the Miedo Creek, agricultural and urban discharges mix with the mining wastes. Here, mining materials deposited appear as bare areas with high metal concentrations (up to 62 280 mg kg⁻¹ Zn; 725 mg kg-¹ As, 16 800 mg kg-¹ Pb).²⁷ In addition to particle- or colloid-bound transport, and due to the low pH of the runoff, there is also a considerable transport of dissolved metals. These dissolved metals precipitate rapidly when in contact to the sea water of the lagoon whereas particle-bound metals remain suspended longer and affect a wider area.²⁸ High metal concentrations have been found at all creek mouths. The most polluted stream is the Beal creek where the highest metal concentrations were reached (e.g. 500 mg kg^{-1} As, 15 mg kg-¹ Cd, 200 mg kg -¹ Cu, 12 000 mg

 kg^{-1} Pb, 7000 mg kg^{-1} Zn).²⁹ This area is considered the most polluted point of the Mar Menor lagoon in relation to mine discharges with all the related flood plain deeply affected by the presence of mining wastes.²⁶ The other creeks showed lower contamination (100 mg kg^{-1} for As, 20 mg kg^{-1} Cd, 40–70 mg kg^{-1} Cu, 2000 mg kg^{-1} Pb, 3000 mg kg^{-1} Zn).^{5,26,29} Environmental consequences of mining wastes discharges into the lagoon have been already reviewed by Conesa and Jimenez.³ These authors described the metal transfer from the mining area to the ecosystem of the lagoon, where high metal concentrations have been found in sediments (e.g. 3000-7000 mg kg^{-1} Zn, $30-42$ mg kg⁻¹ Cu, 10 000 mg kg⁻¹ Pb), macrophytes and benthic organisms.

2.2.2 Groundwaters. From a hydrogeological point of view, the Sierra de Cartagena–La Unión aquifer behaves as a single hardrock aquifer, outcropping over an area of approximately 100 km2 . This aquifer underlies the Campo de Cartagena basin and the Mediterranean Sea, and it is difficult to define the aquifer boundaries with accurately. The aquifer is composed of geologic materials from the Internal Zones of Betic Ranges, mainly schists, quartzites, phyllites, limestones and marbles, and ranges between 400 and

Table 3 Gorguel and Beal creek characterization.^{5,25,26}

Table 3

Gorguel and Beal creek characterization.^{5,25,26}

Table 4 Metals and pH characteristics of groundwaters according to Robles-Arenas *et al.*³⁰ Values are average. Maximum and mininum are in brackets.

Parameter	Units	Open pits	Mining wells	European drinking standards ⁶⁰	WHO drinking standards ⁶¹	a lower number of species but with more constant development in relation to acidic tailings, in which a higher number of
pH		$2.8(3.0-2.5)$	$6.3(7.8-2.0)$			species grew (due to the higher pH range in relation to the natural surroundings
$\rm EC$	$dS~m^{-1}$	$9.8(10-9.1)$	$5.1(21-1.0)$	2.5		
SO_4^{2-}		9580 (9650-9500)	3068 (40 310 - 54.7)	250	250	soils) but with greater annual fluctua-
Cl^-		428 (593–264)	756 (5757–65.9)	250	250	tions. Table 5 shows metal accumulation
Cd		$0.56(0.96 - 0.16)$	$0.3(8-0)$	0.005	0.003	in spontaneous vegetation which growing
Fe	$mg L^{-1}$	$36.1(72.3-0)$	$19.3(1260-0)$	0.200		in different mining wastes. Most species
Mn Ni		89.4 (93.0–85.6) $0.86(1.05-0.70)$	$26.2(436-0)$ $0.2(3.8-0)$	0.050 0.020	0.500 0.020	growing on tailings belong to the Grami-
Pb		$0.47(0.77-0.07)$	$0.1(2.8-0)$	0.010	0.010	neae Family. However, plant communi-
Zn		$370(581-159)$	$153(4093-0)$	$\qquad \qquad$	3	ties on mining wastes deposits near the sea
		or pits have disturbed former piezometric levels. Robles-Arenas et al. ³⁰ showed that			ously colonized by plant species that show adaptation to metal contamination and saline soils: ³¹ these plant communities,	Some of the grasses identified $(e.g.$ Pipthaterum miliaceum) could be used as pasture. Even though the tailings are not
		infiltration and aquifer recharge in the area are determined by the existing			which are formed by halophytic species	
		underground net of mining galleries. Some pits (Fig. 2) reached the ground-	(Sarcocornia ramossisima,	fruticosa, Arthrocnemun	Salicornia macro-	suitable for cattle grazing, soils on the surrounding areas, may contain high metal concentrations with no evident
		water level and oxidation of rock surfaces has led to pH values between 2 and 3			strachyum) and others species typical from salt marshes (Phagmites australis	
			and	Tamarix canariensis),	support	
		(Table 4), including high dissolved heavy				phytotoxic effects and may be used for grazing with a risk potential. Therefore, plant metal uptake may pass unnoticed
		metal concentrations (e.g. 159–581 mg L^{-1} Zn). ³⁰ Mining wells showed wide pH			a diverse bird fauna. ³¹ Also, the mining wastes dumped into the Mar Menor	
		range values (7.8–2.0) which caused high			lagoon and in the Mediterranean Sea	
		variability in the dissolved metal and			have strongly affected the respective bio-	
		anion concentrations. Based on average			logical communities. In the Mar Menor	
		values for this area and, according to the			lagoon, significant metal transfer was	by farmers. Cattle should be prevented from grazing on soils affected by depo- sition of mine tailings material. Although the concentrations of metals taken up through roots and accumulated in plant tissues in this area are generally
		standards for drinking water recom-			found to occur from polluted sediments to	low (Table 5), plant contamination by
		mended by European Union ⁶⁰ and World			macrophytes ³² and molluscs. ²⁹ On the	metal rich dust and direct soil ingestion

Some pits (Fig. 2) reached the groundwater level and oxidation of rock surfaces has led to pH values between 2 and 3 (Table 4), including high dissolved heavy metal concentrations (e.g. 159–581 mg L^{-1} Zn).³⁰ Mining wells showed wide pH range values (7.8–2.0) which caused high variability in the dissolved metal and anion concentrations. Based on average values for this area and, according to the standards for drinking water recommended by European Union⁶⁰ and World Health Organization,⁶¹ the groundwaters are not adequate for human drinking (Table 4). The drinking water in the populations surrounding the mining district is provided from sources located in the interior ranges from Murcia region, and therefore, not affected by the local mining. Nevertheless, the use of local groundwaters for the irrigation of private gardens is taking place and this issue may generate an undesirable transfer of metals to consumable vegetables if no monitoring of water is carried out.

2.3 Metal transfer to biota

Metal transfer pathways from tailings to biota are shown in Fig. 4. The duration of mining activities and dispersion of mining wastes to the surrounding environment have resulted in pollutant uptake by local ecosystems. In some cases new ecological communities have developed directly on mining waste sediments.²⁶ At Portman Bay, in spite of the high metal concentrations, some areas have been spontaneously colonized by plant species that show adaptation to metal contamination and saline soils:³¹ these plant communities, which are formed by halophytic species (Sarcocornia fruticosa, Salicornia ramossisima, Arthrocnemun macrostrachyum) and others species typical from salt marshes (Phagmites australis and Tamarix canariensis), support a diverse bird fauna.³¹ Also, the mining wastes dumped into the Mar Menor lagoon and in the Mediterranean Sea have strongly affected the respective biological communities. In the Mar Menor lagoon, significant metal transfer was found to occur from polluted sediments to macrophytes³² and molluscs.²⁹ On the Mediterranean Sea, similar results have been found around the Portman Bay area.33,34

The mine tailings in the Cartagena–La Unión Mining District are situated on the sierra, generally perched on the slope of the mountains. There is no physical barrier between mining wastes and surrounding biota. The natural colonization by plant species of these sites is slow since the physicochemical characteristics of these sites are not suitable for most plant species. Nevertheless, some plant species can spread easily in these environments profiting from the lack of competition.³⁵ Annual species often show stress resistant physiology, and can grow under poor fertilizer and low water conditions. As a result of long-term natural selection, annual species have exhibited an extensive adaptive capacity.⁵⁰ Conesa et al.^{8,36} described the local plant communities which are

Some of the grasses identified (e.g. Pipthaterum miliaceum) could be used as pasture. Even though the tailings are not suitable for cattle grazing, soils on the surrounding areas, may contain high metal concentrations with no evident phytotoxic effects and may be used for grazing with a risk potential. Therefore, plant metal uptake may pass unnoticed by farmers. Cattle should be prevented from grazing on soils affected by deposition of mine tailings material. Although the concentrations of metals taken up through roots and accumulated in plant tissues in this area are generally low (Table 5), plant contamination by metal rich dust and direct soil ingestion are additional potential exposure pathways.

Fauna identified includes reptiles such as, Bedriagai's Skink (Chalcides bedriagai) herbivores mammals, such as rabbits (Oryctolagus cuniculus) and Iberian hare (Lepus granatensis), as well as, further in the food chain, carnivores mammals such as genets (Genetta genetta), foxes (Vulpes vulpes) and rapacious birds such as Hieraaetus fasciatus (Bonelli's Eagle). Studies of metal transfer from plants to animals have not yet been carried out. The few available data are not representative.⁵

Flood plain soils besides creeks have been intensively affected by mining wastes after occasional floodings. These soils include salt marsh and agricultural areas. In the case of salt marsh soils, toxicity due to metal transfer through the food chain has become a big concern, in particular, for birds nesting. Here, significant

amounts of metals may enter the food chain through the consumption of halophytes with high metal concentrations

(Table 5).²⁶ Conesa et al.³⁷ studied metal transfer from a tailing into a nearby agricultural area used for lettuce crops. Despite being a hot spot with high metal concentration $(e.g. 510 \text{ mg kg}^{-1} \text{ Pb}, 910 \text{ mg kg}^{-1} \text{ Zn}),$ metal uptake was still low due to the high soil pH. Lettuce leaves showed Pb concentrations within tolerance limits for human health $(< 0.3$ mg kg⁻¹ in fresh weight). The essential micronutrients Cu and Zn were in the range of optimal contents (10–28 mg kg^{-1} Cu, 60–85 mg kg-¹ Zn). The high pH of the local soils seems to limit metal accumulation by plants.³⁸ Nevertheless, there is still the risk of direct ingestion of soil by cattle since after harvest, the land is often used as pasture.

3 Remediation options

Traditionally, soil remediation techniques have been described as either in situ (nonexcavated soil) and *ex situ* (soil is excavated). Among the latter, the remediation can be achieve ''on site'' (soil is excavated and remediated in the same site) or ''ex site'' (soil is excavated and transported over long distances to a facility which will effect the cleansing). Conventional remediation techniques (e.g. soil washing, thermal desorption, soil oxidation) generally have drawbacks such as generating additional wastes that require disposal and are not suited for the treatment of soils which are to be re-used for agricultural or similar purposes of plant/ biomass production. The regulators tend to favour in situ techniques which imply the non transport of the soil, trying to achieve a soil disposal as close to the source as possible.^{55,56} The idea of in situ soil recycling instead of dig and dump has been included in official regulations such as the Directive 2008/1/EC concerning integrated pollution prevention and control.⁵⁷ Phytotechnologies (application of science and engineering to study problems and provide solutions involving plants58) have been shown to be an effective and promising low cost tool for the in situ stabilization of metal contaminated sites.⁵⁹ Moreover, these techniques may improve the soil fertility, favour the ecological development of the ecosystem and, at the same time, maintain the aesthetic values of the landscape.¹

3.1 The phytostabilization option

Former mining lands are considered to be suited to non-invasive remediation technologies due to the huge areas to be treated. In addition, aesthetic considerations have increased their importance due to the growing recognition of the mining heritage values.¹ Among the available remediation technologies, phytostabilization is a particularly promising option.³⁹ In this sense, the studies carried out in the Cartagena–La Unión mining district after mining closure in 1991 (Fig. 2) have provided the base for the implementation of phytostabilization. This base should include, according to Mendez and Maier:⁴⁰ (a) the identification of plants in the region adapted to the local soil and climate conditions with low metal uptake in shoots and (b) the evaluation of suitable amendments (compost, fertilizer, irrigation) in order to facilitate the establishment of the plants. Both issues have been already provided by preceding studies in the Cartagena–La Unión area: a plant selection showing low rates of metal uptake have been described in Table 3. Most of the tested candidate plants accumulated less than 10 mg kg^{-1} Cu, 200 mg kg⁻¹ Pb and <500 mg kg⁻¹ Zn. Among them, few plant species with higher Pb concentrations were the two Asteraceae, Helichrysum decumbens (390 mg kg⁻¹) and Dittrichia viscosa (510 mg kg-1). The highest Pb uptake (960 mg kg^{-1}) was found in leaves from Arthrocnemun macrostachyum, from the surroundings of Portman Bay. In any case, revegetating tailings should be fenced in order to keep out larger herbivores mammals.

Also, some soil amendments have been already tested under controlled lab conditions for their suitability to enhance revegetation on the acidic as well as the neutral tailings. Conesa et al.⁴¹ found that liming was necessary to increase the growth of Lygeum spartum on acid tailings whereas the addition of fertilizer had no significant effect. However, fertilization resulted in a significant growth response of Lygeum spartum, Piptatherum miliaceum and Zygophyllum fabago on neutral mine tailings, in particular the latter two species.⁴²

The addition of pig manure in combination with lime strongly increased the spontaneous establishment of vegetation, leading to a plant cover of 25–40% within one year.⁴³

Although it is not possible to recreate the original uncontaminated environment, successful phytostabilization is a form of remediation, because the establishment of a self-sustaining vegetative cover reduces the risk of uncontrolled pollutant transfer into the environment along non-biotic pathways (water and air erosion) as well as along biotic ones (Fig. 4). Combining phytostabilization with a partial capping of the most acidic spots could further reduce acid mine drainage. However, preliminary field studies performed on the tailings from Cartagena–La Unión district have shown that the establishment of vegetation is not enough to guarantee sufficient structural stability of the tailings. This means that as a first measure, mechanical stabilization is required to prevent structural collapse before a stable vegetation can grow.⁴⁴

3.2 The costs of phytostabilization

Apart from Portman bay, there are currently no restoration plans for the whole mining district. One of the main problems of phytotechnologies is the difficulty to come up with convincing cost/benefits analyses. In the economic point of view, phytoremediation was presented as novel low cost remediation technology. However, we must include time consumption as an additional cost and then phytoremediation takes an uncertain cost that is difficult to evaluate. Research in phytotechnologies so far has been focused more on solving scientific and technical questions than on analysing the economical aspects and demonstrating commercial feasibility. More efforts in developing rates, modelling, treatment times and monitoring schemes are still necessary to provide a better base for the implementation of phytoremediation in practice.^{45,46}

Conventional engineering methods proposed to remediate contaminated soils are easier to evaluate in the economic point of view because they are based in previously known rates which allows the prediction of feasible time scales. It is difficult to value phytotechnologies because the soil can not be used productively while there are long remediation periods. For this reason, phytotechnologies are relegated as projects with low economic added value. Such projects are usually restricted to marginal areas without short term economic value, such as former mining areas,⁴⁰ abandoned shooting ranges⁴⁷ or post-industrial sites.⁴⁸

In some cases, phytotechnologies are used after conventional remediation schemes, such as the removal of highly polluted materials (''dig and dump''), in order to control the residual pollution and restore the ecological functions as it has been shown in the area affected by the toxic spill in Aznalcollar (Southeast Spain)⁴⁹ Here, a ''green corridor'' has been established on over 2000 ha of metal contaminated land coming from the spill after the mine tailings-dam failure in 1998. Following removal of the most contaminated topsoil, the establishment of vegetation, combined with soil conditioners, reduced dust and metal leaching, providing an ecological connection between the Donaña World Heritage Park in the South and the Sierra Morena mountains in the North.⁵⁹

According to preliminary economic evaluations, the phytostabilization (including the addition of amendments) of tailings from the Cartagena–La Union- Mining District would cost between 12 000–30 000 euros per tailing. This is negligible compared to the cost of the mechanical works needed to prevent structural collapse of the tailings, which are estimated to be two orders of magnitude higher.⁴⁴ However, conventional methods to clean-up soils (e.g. by soil washing) or landfill disposal would still be much more expensive due to the large volumes of the tailings (370 000– 750 000 m³).

Two decades after ceasing mining activities, wastes from the tailings of the Cartagena–La Unión Mining District still continue to contaminate terrestrial and aquatic ecosystems in the surrounding areas. Wind and water erosion are predominant processes in the transfer of the pollutants. Contamination of coastal soils is taking place through the local creeks that drain the mining district and carry substantial amounts of sediments with the run-off of heavy rainfall events. The amelioration of tailings erosion is of primary importance in any attempt to remediate the situation. Phytostabilization appears to be a very promising option to protect the surface of the tailings against erosion and to prevent mechanical collapse. Preliminary studies of suitable plants and amendments have been already performed. These studies have also shown that, in addition, conventional engineering is necessary in some tailings to prevent collapse. A comprehensive land management scheme needs to be established in order to control the risks of further contaminant transport through the food chain and to keep health risks or a harmless or at safe tolerable level. Next, some and amountained by the method of the method in the controlled by Pennsylvania State Controlled by Pennsylvania State University of the method of the metho

All these operations should involve not only the local and regional governments, but also local communities (e.g. farmers, urban planners).

Acknowledgements

To Dr Armando Ripolles for his valuable comments and to a native English colleague for his suggestions. Assessment of environmental data came from Dr Francisco J. Jimenez-Carceles belonging to the environmental consultant BIOCYMA (Biología, Calidad y Medio Ambiente) under its R&D activities program (Alcantarilla, Murcia, Spain).

References

- 1 H. M. Conesa, R. Schulin and B. Nowack, Ecol. Econ., 2008, 64, 690-700.
- 2 I. S. Oen, J. C. Fernández and J. I. Manteca, Econ. Geol., 1975, 70, 1259–1278.
- 3 H. M. Conesa and F. J. Jiménez-Cárceles, Mar. Pollut. Bull., 2007, 54, 839-849.
- 4 P. M. Egea-Bruno, in Patrimonio geológico minero y desarrollo regional, ed. I. Rábano, I. Manteca, C. García, Instituto Geológico y Minero de España, Madrid, Spain, 2003. pp. 31–42.
- 5 C. García-García Ph.D. Thesis, Universidad Politécnica de Cartagena, Cartagena, Spain, 2004.
- 6 J. M. Martínez-Orozco, F. Valero-Huete and S. González-Alonso, Landscape Urban Plann., 1993, 23, 195–207.
- 7 M. H. Wong, Chemosphere, 2003, 50, 775– 780.
- 8 H. M. Conesa, Á. Faz and R. Arnaldos, Sci. Total Environ., 2006, 36, 1–11.
- 9 G. García, H. Conesa and Á. Faz, in Patrimonio geológico y minero y desarrollo regional, ed. I. Rábano, I. Manteca, C. García, Instituto Geológico y Minero de España, Madrid, Spain, 2003, pp.295– $\frac{299}{10}$ J. O.
- Grimalt, M. Ferrer and E. Macpherson, Sci. Total Environ., 1999, $242, 3-\overline{11}$.
- 11 W. Salomons, J. Geochem. Explor., 1995, 52, 5–23.
- 12 M. Ortega, E. Nicolás, M. A. Esteve, A. Torres and L. Ramírez-Díaz, in Problemática ambiental y desarrollo, ed. R. Ortiz-Silla, V Reunión Nacional de Geología ambiental y Ordenación del Territorio. Sociedad Española de Geología Ambiental y Ordenación del Territorio, Murcia, Spain, 1993, Vol. 1, pp. 307–316.
- 13 P. Martos-Miralles, A. Sansano Sánchez, P. Baños Páez, J. A. Navarro Cano and T. Méndez Pérez, Medio Ambiente y Empleo en la Sierra Minera de Cartagena– La Unión. Edita Fundación Sierra Minera. La Unión (Murcia), 2001.
- 14 H. M. Conesa, B. H. Robinson, R. Schulin and B. Nowack, Appl. Geochem., 2008, 23, 1232–1240.
- 15 E. Aracil, Á. Faz, P. Martínez-Pagán, S. Martínez-Martínez, J. A. Acosta, T. Fisher, U. Maruri, in Proceedings of the 9th International Mine Water Association Congress ed. J. Loredo and F. Pendas, 5th–7th September 2005 Oviedo, Spain,
Departamento de Explotacion y Explotacion y Prospeccion de Minas, 2005. pp. 273–279. Published on 14 April 2011. Download Control Control
	- 16 M. J. Martínez-Sánchez and C. Pérez-Sirvent, Niveles de fondo y niveles genéricos de referencia de metales pesados en suelos de la Región de Murcia. Universidad de Murcia. Región de Murcia, Consejería de Desrrollo Sostenible y Ordenación del Territorio. Technical Report, Murcia, Spain. 2007.
	- 17 H. M. Conesa, Informe Agronómico sobre la finca de "Las Jacobas". Technical Report. Universidad Politécnica de Cartagena, Cartagena, Spain. 2003.
	- 18 J. Martinez-Frias, Nature, 1997, 388, 120. 19 M. J. Martínez-Sánchez, M. C. Navarro, C. Pérez-Sirvent, J. Marimón, J. Vidal, M. L. García-Lorenzo and J. Bech, J. Geochem. Explor., 2008, 96, 171–182.
	- 20 IEO (Instituto Español de Oceanografía). Estudio de la contaminación de la Bahía de Portmán. Instituto Español de Oceanografía, Centro Oceanográfico Mar Menor. Techcnical Report, Murcia Spain, 1984.
	- 21 A. Cesar, A. Marín, L. Marín-Guirao and R. Vita, Sci. Mar., 2004, 68, 205–213.
	- 22 J. B. Vilar and P. M. Egea, *La minería* murciana contemporánea (1840–1930). Universidad de Murcia, Academia Alfonso X El Sabio, Excmo. Ayuntamiento de Cartagena, CajaMurcia, Spain. 1990.
- 23 J. B. Vilar, P. M. Egea and J. C. Fernández, La minería murciana contemporánea (1930– 1985). Instituto Tecnológico Geominero de España, Madrid, España, 1991.
- 24 G. García, Á. Faz and H. M. Conesa, Water, Air, Soil Pollut.: Focus, 2003, 3, 243–250.
- 25 F. G. Pavetti, H. M. Conesa, Á. Faz, R. Arnaldos and G. García, Terra., 2006, 24, 171–178.
- 26 J. Álvarez-Rogel, M. J. Ramos-Aparicio, M. J. Delgado-Iniesta and R. Arnaldos-Lozano, Fresen. Environ. Bull., 2004, 13, 274–278.
- 27 F. J. Jiménez-Cárceles, J. Álvarez-Rogel
and H. M. Conesa, Water, Air, Soil Pollut., 2008, 188, 283–295.
- 28 L. Marín-Guirao, J. Lloret, A. Marin, G. García and A. J. García-Fernández, Chem. Ecol., 2007, 23, 217–231.
- 29 A. María-Cervantes, F. J. Jimenez-Carceles and J. Alvarez-Rogel, Water, Air, Soil Pollut., 2009, 200, 289–304.
- 30 V. M. Robles-Arenas, R. Rodríguez, C. García, J. I. Manteca and L. Candela, Environ. Geol., 2006, 51, 47–64.
- 31 H. M. Conesa and A. Faz-Cano, in Advances in geoecology, ed. Á. Faz-Cano, A. R. Mermut, J. M. Arocena and R. Ortiz, Catela-Verlag, Germany, 2009, Vol. 40., pp. 287–294.
- 32 C. Sanchiz, A. M. García-Carrascosa and A. Pastor, Mar. Ecol., 2000, 21, 1–16.
- 33 D. Deheyn, M. Jangoux and M. Warnau, Sci. Total Environ., 2000, 247, 41–49.
- 34 J. Benedicto, C. Martínez-Gõmez, J. Guerrero, A. Jornet and C. Rodríguez, Cienc. Mar. 208, (34), pp. 389–398.
- 35 M. R. Macnair, Trends Ecol. Evol., 1987, 2, 354–359.
- 36 H. M. Conesa, G. García, Á. Faz and R. Arnaldos, Chemosphere, 2007, 68, 1180–1185.
- 37 H. M. Conesa, J. A. Pérez-Chacon, R. Arnaldos, J. Moreno-Caselles and Á. Faz-Cano, Water, Air, Soil Pollut., 2010, 208, 377–383.
- 38 M. C. Navarro, C. Pérez-Sirvent, M. J. Martínez-Sánchez, J. Vidal and J. Marimón, Chemosphere, 2006, 63, 484-489.
- 39 M. O. Mendez and R. M. Maier, Environ. Health Perspect., 2008, 116, 278–283.
- 40 M. O. Mendez and R. M. Maier, Rev. Environ. Sci. Bio/Technol., 2008, 7, 47–59.
- 41 H. M. Conesa, B. H. Robinson, R. Schulin and B. Nowack, Environ. Pollut., 2007, 145, 700–707.
- 42 H. M. Conesa, B. Nowack and R. Schulin, Water, Air, Soil Pollut., 2007, 183, 201–212.
- 43 A. Faz, D. M. Carmona, A. Zanuzzi and A. R. Mermut, The Scientific World Journal, 2008, 8, 819–827.
- 44 A. Faz, E. Aracil, J. A. Acosta, M. Alcaraz, H. Conesa, G. García, C. García, J. I. Manteca, I. Martínez, P. Martínez, M. A. Martínez, J. M. Peñas, T. Rodríguez, R. Rodríguez, and E. Trigueros, Evaluación de riesgo y definición de medidas correctoras en depósitos de lodos abandonados procedentes de procesos de actividad extractiva en la Región de Murcia. Aplicación al depósito "Brunita". Consejería de Economía, Industria e Innovación, de la Comunidad

Autónoma de Murcia. Dirección General de Industria, Energía y Minas (contract No 0978-1-0026) Technical Report. Cartagena, Spain, 2003.

- 45 L. A. Newman and Ch. M. Reynolds, Curr. Opin. Biotechnol., 2004, 15, 225–230.
- 46 L. Van Nevel, J. Mertens, K. Oorts and K. Verheyen, Environ. Pollut., 2007, 150, 34–40.
- 47 B. H. Robinson, S. Bischofberger, A. Stoll, D. Schroer, G. Furrer, S. Roulier, A. Gruenwald, W. Attinger and R. Schulin, Environ. Pollut., 2008, 153, 668–676.
- 48 C. J. French, N. M. Dickinson and P. D. Putwain, Environ. Pollut., 2006, 141, 387–395.
49 M. T.
- 49 M. T. Domínguez, T. Marañón,
J. M. Murillo, R. Schulin and B. H. Robinson, Environ. Pollut., 2008, 152, 50–59.
- 50 S. Wei, Q. Zhou and X. Wang, Environ. Int., 2005, 31, 829–834.
- 51 H. M. Conesa, Á. Faz and R. Arnaldos, Chemosphere, 2007, 66, 38–44.
- 52 C. Pérez-Sirvent, M. J. Martínez-Sánchez, M. L. García-Lorenzo and J. Bech, Fresen. Environ. Bull., 2008, 17, 1666–1671.
- 53 H. M. Conesa, Á. Faz, G. García and R. Arnaldos, Fresen. Environ. Bull., 2007, 16, 1076–1081.
- 54 G. García, H. Conesa, Á. Faz in Patrimonio Geológico y Minero y Desarrollo Regional. ed. I. Rábano, I. Manteca, C. García. Instituto Geológico y Minero de España, Madrid, Spain, 2003, pp. 295–299.
- 55 EC (European Comission). Guide to Cost-Benetfit analysis of investment projects. Evaluation Unit DG Regional Policy European Commission. Structural Fund-ERDF, Cohesion Fund and ISPA.2002.
- 56 BOE (Boletín Oficial del Estado), REAL DECRETO 9/2005, de 14 de enero, por el que se establece la relación de actividades potencialmente contaminantes del suelo y los criterios y estándares para la declaración de suelos contaminados. 2005. (BOE n°15 de 18.01.05), pp. 1833– 1843.
- 57 EU (European Union). Directive 2008/1/ EC of the European Parliament and of the Council of 15 January 2008 concerning integrated pollution prevention and control (29-01-2008).
- 58 UNEP (United Nations Environment Programme). Phytotechnologies. A Technical Approach in Environmental Management, Freshwater Management Series No. 7 2003, Available at: http:// www.unep.or.jp/ietc/publications/ freshwater/fms7/index.asp.
59 B. H. Robinson,
- H. Robinson, G. Bañuelos, H. M. Conesa, M. W. Evangelou and R. Schulin, Crit. Rev. Plant Sci., 2009, 28, 240–266.
- 60 Official Journal of the European Communities. Council directive 98/83/EC of 3 November 1998 on the quality of water intended for human consumption. 1998 available at: http://www.emwis.org/IFP/ Eur-lex/l_33019981205en00320054.pdf (accessed on 30-01-2009).
- 61 World Health Organization, Guidelines for Drinking-Water Quality, 2nd edition Geneva, Switzerland, 1993.