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Sulphide-mining impacts in the physical environment: Sierra de Cartagena–La Unión (SE Spain) case study

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Abstract The environmental impact and potential-risk assessment of an abandoned sulphide-mining site in a semiarid climate is presented here, by the study case of Sierra de Cartagena–La Unión (SE Spain), a 2,500-year-old mining district extending over an area of 100 km². The regional map illustrates the existence of 12 open-pits, 1,902 mining wells, 2,351 waste deposits, including 89 tailing dams and waste rock derived from mining processes. Mine wastes occupy an area of 9 km² and have an approximate volume of 200 Mm³. Mineralogical, physical and chemical data distinguish nine different types of mine and metallurgical waste. According to the concentration of sulphate and heavy metals in sediment, soil, rainwater, surface water and groundwater samples, it is possible to conclude that the impact of mine activities

occurs not only in the immediate mining area (100 km²), but also in the surrounding areas (an affected area of 1,000 km² approximately). The hydrochemical data show that groundwater, runoff water and some rainwater samples exceed Spanish and European water quality guideline values for water supply. The main geochemical process recognised is sulphide-mineral oxidation and later-generated sulphate dissolution by groundwater and runoff. Runoff and wind are the major mechanisms of metals and sulphate transport in the study area and adjacent zones.

Keywords Mine and metallurgical waste · Environmental impact and risk · Mine closure · Spain
Sierra de Cartagena–La Unión

Introduction

Mining activities take a direct impact on the environment. The natural water and its ecosystem can be affected in diverse ways: the hydrological pathways can be disrupted and new ones created, the rate of groundwater recharge may increase and surface-water and groundwater pollution may occur, among other effects (Younger and Wolkersdorfer 2004). Abandoned mine areas contain different types of residues from ore-processing operations that are typically characterised by high con-

centrations of heavy metals (Lee et al. 2001; Ashley et al. 2004). Environmental problems are worse in areas without a mining-site-restoration program. With mine closure, a hydrological process called groundwater rebound is produced, which is the recovery of the groundwater table from the dewatering cessation (Younger 1999; Younger et al. 2002). One consequence is the generation of acid-mine drainage, caused by the oxidation and hydrolysis of metal sulphides. The pH decrease allows metals to have a greater mobility (Banks et al. 1997; Younger 2001; Rodríguez and Candela 2004;

Ashley et al. 2004; Marguá et al. 2004). The geochemical form in which a metal exists strongly conditions its mobility and its effect on the environment. Dissolved heavy metals (e.g. Fe, Cu, Pb, Zn, Cd, Hg, Ni, Co) and metalloids (e.g. As, Sb) are mobilised by runoff to ephemeral streams, soil and sea, allowing their entrance into the trophic chain in aquatic and terrestrial ecosystems (Auernheimer et al. 1984; De León et al. 1982; Ashley et al. 2004).

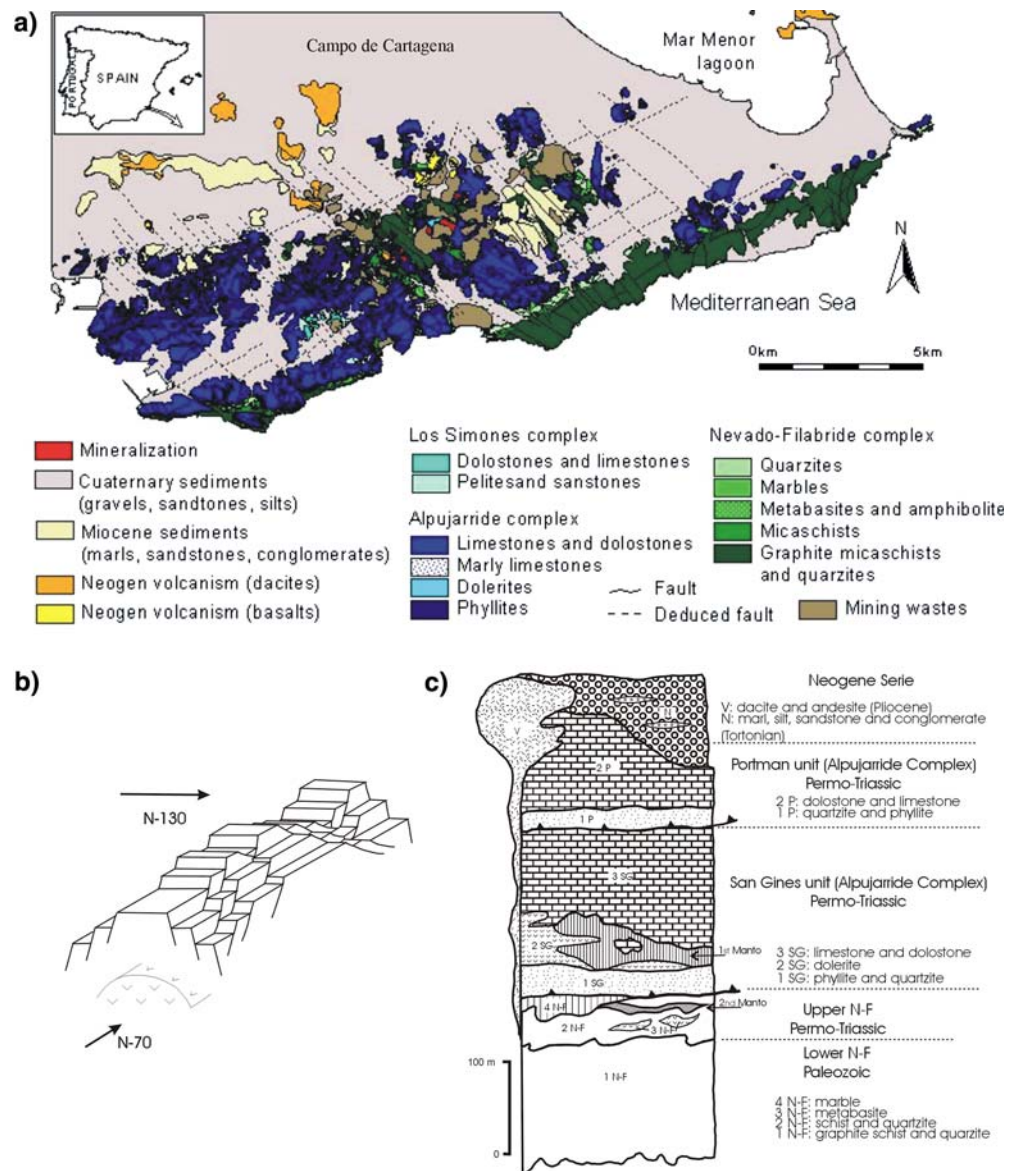
Not many studies have been conducted on mining sites in semiarid climates (Rösner 1998).

Sierra de Cartagena-La Unión is situated at the most south-eastern part of Spain (Cartagena, Murcia) (Fig. 1). The region contained one of the largest Pb–Zn

accumulations in the Iberian Peninsula. This region has been exploited for Ag, Pb, Zn, Cu and Fe from the Phoenician and Carthaginian times (Oén et al. 1975) until 1991. During these 2,500 years, the area suffered important environmental stresses. The sedimentation in Portman Bay of post-flotation wastes (sludges) was one of the worst environmental catastrophes related with mining activities in Mediterranean countries. The sedimentation took place between 1957 and 1990. Pipelines pumped the sludge to the Mediterranean Sea and marine currents transported approximately 57 million tons inside the bay.

Nowadays, this area is undergoing an important tourist and economic boom. As a consequence, an

Fig. 1 a Geological map, b schematic block diagram of Sierra de Cartagena-La Unión (Gagny and Marconnet 1994), c simplified litho-structural column of Sierra de Cartagena-La Unión central zone (Manteca and Ovejero 1992)



evaluation of the environmental impact in this derelict mine site and in the surrounding areas (Mar Menor and Mediterranean Sea) is needed. The Mar Menor Lagoon and its influenced area are included in the Ramsar Convention on Wetlands (Duran et al. 2003) and in the Coastal Area Management Programme by the UN Environment Programme (Da Cruz and Murcia Regional Working Group 2003).

This study characterises mine and metallurgical wastes, sediments and water, and reviews different sources and transport mechanisms of sulphates and heavy metals in a derelict mine site under semiarid climatic conditions.

Study area

The Sierra de Cartagena–La Unión is a coastal mountain range with an approximate E–W trend. It is limited by the Mediterranean Sea to the South and the East, and by the Campo de Cartagena basin to the North (Fig. 1a). It extends over an area of 100 km², with a length of 23 km. The highest elevation is the “Peña del Águila” (392 m a.s.l.). The northern slopes are gentler than southern slopes, the latter end as cliffs on the coast of the Mediterranean Sea. Over the years, 12 open-pits were excavated, 3,000 wells and kilometres of mining galleries were drilled, and hundreds of piles of mining waste and spoil were excavated and deposited.

The climate in Sierra de Cartagena–La Unión is typical semiarid Mediterranean, characterised by an annual mean precipitation of approximately 300 mm, with a range between 250 and 350 mm/year, distributed in a few intensive rainfall events. The southern slope is wetter than the northern due to air-moisture condensation from the Mediterranean Sea. The area shows a temperature range between –5.4 (January) and 40°C (August) (Font 1983). The annual average temperature is 17°C. Wind is always present in the study area, mainly the “Levante” (a wet wind with an E–W trend). The lowest wind speed is registered in autumn (15.6 km/h) and the fastest in spring (22.4 km/h). The potential evapotranspiration is approximately 900 mm/year (García 2004).

Due to the climate, soil development is scarce. Soil types are Halpic Calcisols, Petric Calcisols, Calcaric and Haplic Cambisols, Gipsiric and Calcaric Regosols, and some types of Leptosols. In many areas, they have been replaced by Terric and Hortic Anthrosols, Spolic Anthric Regosols, etc. (Hernández et al. 2004). Vegetation is composed mainly by shrubs; small areas are being reforested with *pine halepensis*. A lot of endemism has been reported (Sánchez-Gómez et al. 1998). Native plants in some cases grow on tailing dams (Conesa et al. 2006).

Geologic setting and mineralisation

Sierra de Cartagena–La Unión belongs to the Internal Zones of the Betic Cordillera. The Betic and Rift cordilleras, lying from north to south of the Alborán Sea, form an arc-shaped mountain belt joining across the Strait of Gibraltar. They were developed during the convergence between the African and Iberian plates (late Mesozoic to Cenozoic; Sanz de Galdeano 1990).

The Internal Zones comprise three complex nappes of variable metamorphic grade, which are from bottom to top: the Nevado-Filábride (N-F), the Alpujarride (Alp) and the Maláguide complex (MC) (Fig. 1). The grade of metamorphism decreases in each complex from bottom to top and from the lower complex to the upper. The N-F is divided into two parts: the lower is constituted by graphite micaschists, greyish quartzites and quartzitic schists, locally named “el muro” (the wall), with a minimum thickness of 500 m and of Paleozoic age or older. The upper N-F consists of micaschists, white quartzites, marbles and “green rocks,” it has a thickness of 60 m approximately and of Permo-Triassic age. “Green rocks” are massive bodies of ortho-amphibolites with chloritic schists. Discordantly overlaying the N-F is the Alp complex, which is constituted from bottom to top by San Gines Unit, Portman Unit and Gorguel Unit (Manteca and Ovejero 1992; Ovejero et al. 1976). All units present a detritic formation (epimetamorphics rocks, quartzites and phyllites), probably of Permian age, and a Triassic carbonate series. Intrusive bodies of diabases and dolerites in the carbonated material of San Ginés unit are present. Their thicknesses are approximately 30 m to Gorguel unit, 150 m to Portman unit and 250 m to San Ginés unit, where they are well developed. García-Tortosa et al. (2000) displayed that Gorguel unit is a small tectonic slice of the Portman unit, and the MC outcrops in the study area, occupying less than 1% of the Sierra area. MC has a detritic component (sandstone, quartzite, silt and conglomerate) and a carbonated member (limestone).

The tectonic complexes are partly covered by Miocene and Quaternary sediments (pelitic rocks, including sandy and conglomeratic levels) and affected by sub-volcanic (rhyolite–dacite and andesite) and volcanic events (alcalin basalt). These Tertiary formations are modified by tectonic movements. Posterior to the complexes being piled up, between the Eocene and Middle Miocene period, an extensional phase generated two important fault systems, N-70 and N-130 (Fig. 1a), which control the magmatic outcrops. Sierra de Cartagena–La Unión presents geological horst and graben features as a consequence of the reactivation of these faulting systems after the Middle Miocene (Fig. 1b). N-70 faults represent the trend of a great volcanic axis cut by a set of second-order horst and graben structures trending N-130 (Gagny and Marconnet 1994).

The main mineralisation is constituted by two strat-
 abound sulphide deposits, locally named “mantos,” on
 the carbonated sequences in the N-F (second manto)
 and Alp complex (first manto) (Fig. 1c). The minerali-
 sation can also be found disseminated in Miocenic
 materials, in gossans, stockworks and veins (Manteca
 and Ovejero 1992). The lead–zinc and associated ore
 deposits are described by Oén et al. (1975). Two mineral
 paragenesis appear in both stratabounds. The first is a
 chlorite–sulphide–carbonate–silica paragenesis, named
 “manto piritoso,” where sulphide minerals are pyrite,
 sphalerite, marcasite, galena and locally pyrrhotite,
 chalcopyrite, arsenopyrite, tetrahedrite and stannite are
 accessory constituents; carbonate minerals are siderite
 with Zn- and Mn-bearing varieties, and rarely calcite.
 Silica occurs as quartz. Clay minerals and chlorite are
 frequent. The second paragenesis is greenalite–magne-
 tite–sulphide–carbonate–silica, “manto de silicatos o de
 magnetita,” sulphide and carbonate minerals are the
 same of previous paragenesis. Greenalite is highly abun-
 dant, locally accompanied by chlorite, clay minerals, talc
 or minnesotaite. Magnetite is also plentiful, however
 rarely does it show oxidation in haematite. Silica occurs
 as quartz, opal, chert and veins of chalcedony. Miocenic
 disseminations consist of pyrite, marcasite, galena and
 are mixed with chlorite and quartz, accessory minerals
 are pyrrhotite and chalcopyrite. In gossan zones, ores
 occur as an oxide–hydroxide–sulphate–carbonate–silica
 association; oxides are goethite, haematite and magne-
 tite, and manganese oxides. Among the sulphates are
 barite, anglesite, jarosite, alunite, anhydrite and gypsum;
 carbonates are calcite, siderite, cerussite and smithson-
 ite; silica appears as quartz, chert, calcedony and opal;
 and finally, clay minerals (vermiculite, metahalloysite
 and dickite) are locally abundant.

There is a controversy with regard to the genesis of
 the mineralisation; there are two hypotheses. The first
 hypothesis establishes a mineralisation generated by
 hydrothermal activity related to Tertiary volcanism
 (Oén et al. 1975; Kager 1980). The second hypothesis
 considers two metallogenetic phases, the main phase
 being pre-orogenic, and the second associated with the
 Neogene volcanism (Guardiola 1927; Pavillon 1969; O-
 vejero et al. 1976).

Surface water and groundwater hydrology

The hydrographical network mainly consists of ten
 creeks, only operational during heavy rainfall events.
 Five of them flow into the Mediterranean Sea and the
 remaining into the Mar Menor Lagoon, with the longest
 being 10.5 km (Miedo, northern face) and the shortest
 2.8 km (Portman, southern face) (Fig. 2b, c). In the
 northern face, the creek beds disappear before arriving

to the Mar Menor lagoon except when the creek is
 forced into an artificial channel.

From a hydrogeological point of view, the Sierra de
 Cartagena–La Unión aquifer behaves as a single hard-
 rock aquifer, outcropping over an area of approximately
 100 km². This aquifer underlies the Campo de Carta-
 gena basin and the Mediterranean Sea, being difficult to
 define the aquifer boundaries with accuracy. The aquifer
 is composed of geologic materials of the Internal Zones
 of Betic Cordillera, mainly schists, quartzites, phyllites,
 limestones and marbles, and ranging between 400 and
 800 m of thickness (Fig. 1c). The impervious basement
 is the lower N-F unit (schist and quartzite). It shows
 secondary porosity due to the intensive tectonic activity,
 mining activities and, to a lesser extent by karstification.
 The aquifer recharge exclusively originates from rain-
 water infiltration; according to CHS (1991, unpublished
 data) the 30% of rainwater is infiltrated. The discharge
 is produced by intense evaporation from large diameter
 wells and open-pit lakes (“Brunita,” “Gloria” and “Los
 Blancos II”: Figs. 2, 3a, b). Moreover, on the northern
 slope two springs exit (“El Chorrillo” and “La Fuente”)
 and a seepage from a mining gallery (“Horno ctra. 33”).
 On the southern side, there is discharge through four
 mining galleries [“Galería Portman” (Fig. 3c), “Túnel
 Lilian” (Fig. 3d), “Túnel José Maestre” and “Molienda
 Semiautógena”] and two springs (“Gorguel” and
 “Calzada romana”). Also, water is extracted from wa-
 ter-supply wells for the existing industries and golf-field
 irrigation; however extraction volumes are not known
 with accuracy. According to 1993 data (IGME-MOP-
 TMA 1996), 1.4 h m³ were pumped. Water flow to the
 Campo de Cartagena hydrogeologic unit and to the
 Mediterranean Sea must exist. Discharge to the Medi-
 terranean Sea is estimated to be 0.3 h m³/year by CHS
 (1997). Flow to the Campo de Cartagena remains un-
 known.

Available hydrogeological data are local values of
 transmissivity, ranging between 10 (IGME-MOPTMA
 1996) and 960 m²/day (T. Rodríguez, unpublished data),
 and scattered groundwater heads.

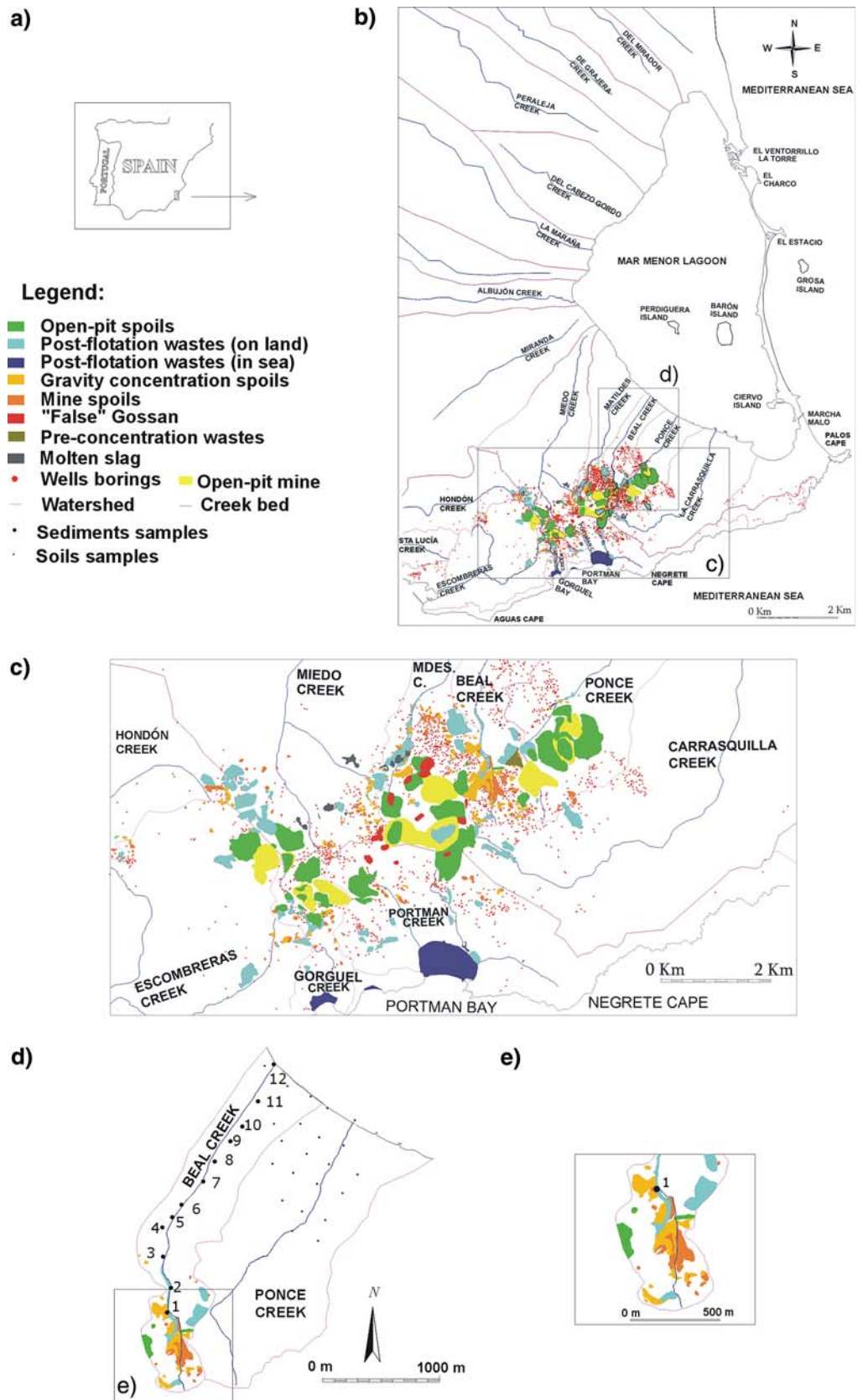
Materials and methods

To characterise water, sediments and wastes in Sierra de
 Cartagena–La Unión, old mine reports and biblio-
 graphical information were reviewed and three field-
 work campaigns were carried out.

Field work

In the first campaign (September 2000–May 2001), an
 inventory was performed of mine and metallurgical

Fig. 2 a Study-area location, b affected area by mining activities, c mining and metallurgical wastes distribution, d stream sediments and soil-sampling sites (García 2004), and e detailed scheme of Beal creek



wastes, mining wells and open-pits with the development of corresponding maps. Samples of each type of waste were collected using a scoop, and immediately stored in plastic bags to avoid moisture loss (5–10 kg per sample). Samples of efflorescence salts were collected at the same time (approximately 100 g per sample). In the second field work campaign (January to March 2003), 108 water samples were collected (102 from wells, 2 from springs, 2 from seepages in 2 mining galleries and 2 from bigger mine-pit lakes) and groundwater levels were measured in each well (388 data points). For each sample, “in situ” pH, electric conductivity (EC) and temperature were measured with a multiparameter-recording device (pH/Cond 340i/SET). Two water samples were collected at each point in 100-mL bottles, the first one for water physicochemical characterisation and the other to determine concentration of metals. The latter was acidified “in situ” (with KNO_3) and filtrated with 0.45 μm millipore filters. All were stored at 4°C and sent to the laboratory. Twenty rainwater samples, each from different rain events, were collected at a local meteorological station for the period from October 2002 to April 2003.

In September 2002, additional samples of sediment were collected and stored in plastic bags, 12 samples from Beal creek and 1 from the Mar Menor backshore (2–4 kg per sample).

Analysis of water and solid-material samples

Physicochemical characterisation of water was performed by a commercial laboratory. Major parameters determined were Na^+ , K^+ , Ca^{2+} , Mg^{2+} , HCO_3^- , Cl^- , SO_4^{2-} and NO_3^- ; total alkalinity; hardness; pH; EC and total dissolved solids (TDS). Heavy metal concentration was obtained by ICP-MS (Ni, Zn, Cd, Pb and Sr) and AAS (Fe and Mn).

In mining waste and sediment samples, grain-size distribution and mineralogical composition were estimated. The grain-size distribution analysis was done by two methods: wet sieving and laser-diffraction technology (Mastersizer 2000; Malvern). Mineralogical composition was determined by XR diffraction; pH of residues was obtained by dilution of samples in double distilled water in a 1:2.5 (solid/liquid) ratio according to Buurman et al. (1996).

Mineralogy of efflorescence sulphate salts was determined by XR diffraction.

Environmental risk (leaching test)

To analyse the behaviour of mining and metallurgical wastes in contact with water, a leaching test was carried out. In this leaching test, Milli-Q water (pH = 5.5) was used as the extractant, in accordance with the German

Standard Method DIN 38414-S4 (DIN-NORMEN 1984). Particle sizes less than 10 mm in each sample were used. The leaching process was carried out during 24 h in a temperature-controlled room. The solid/liquid ratio used in the leaching test was 1/10. After completion of the leaching period, the sample was centrifuged and undissolved waste separated by filtration using a membrane filter of pore size 0.45 μm . EC, pH and Ni, Pb, Cu, Zn and Cd content was measured in the effluent. The leaching procedure was repeated three times on each waste sample.

Results

Inventory of mining activity proofs

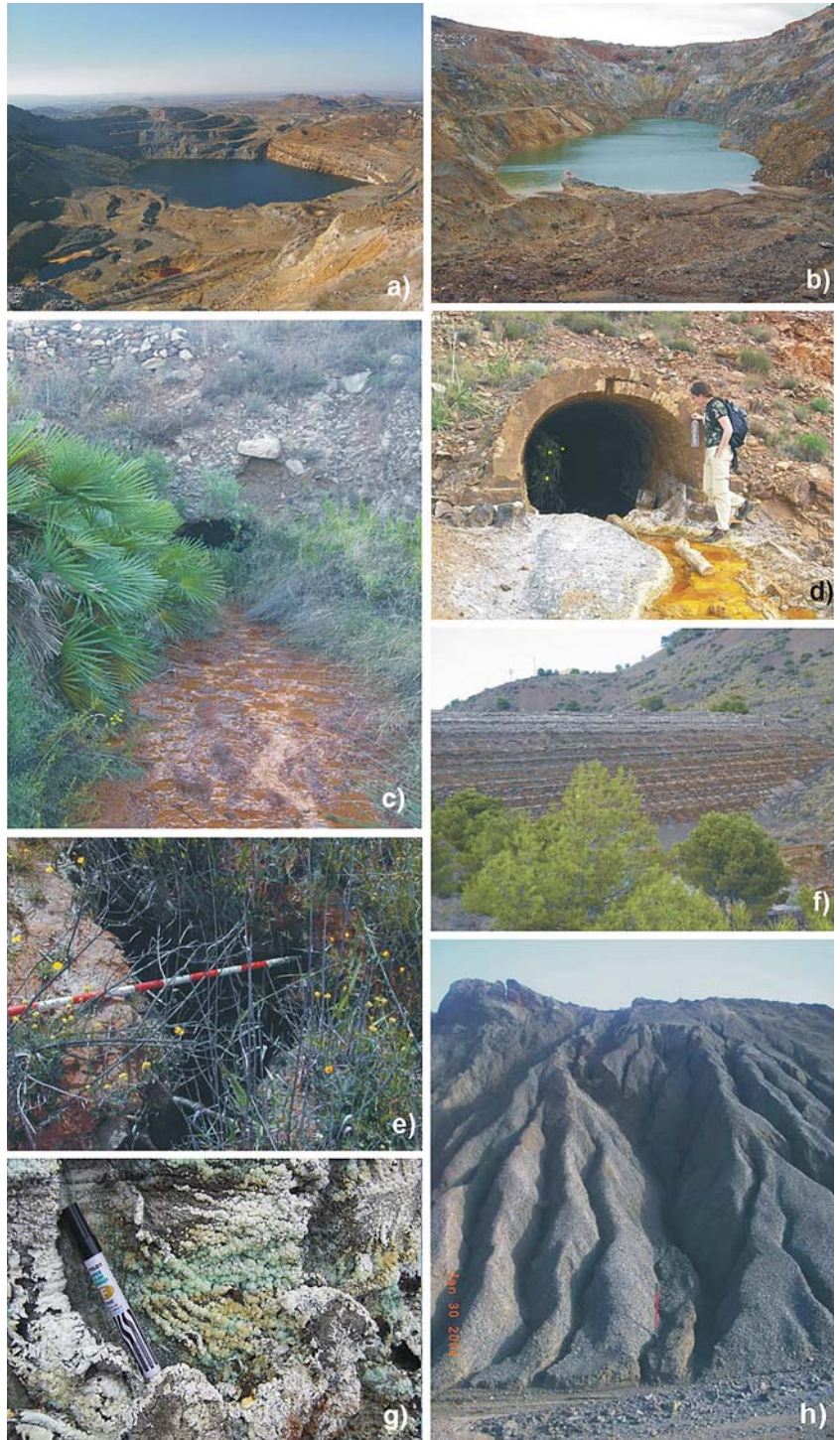
The cartography shows the geometrical characteristics and spatial distribution of the 12 mining open-pits, 1,902 exiting wells and 2,351 waste deposits (Fig. 2b, c). Nowadays, three open-pits are filled with wastes from metallurgical, construction and industrial processes, and another three are occupied by lakes. Inventoried wells had different diameters (< 0.5 to > 4 m), different cross-sections (irregular, circular, oval or polygonal) and depths (< 20 to > 225 m). Only 388 wells contain water. The waste deposits inventoried included 2,110 accumulations from open-pits, mines, galleries and well excavations; 11 “false” gossan dumps, which contain oxidised minerals from the covering layer of mineral deposits without any industrial value. The remaining waste deposits were originated from metallurgical processes; 89 tailing dams on land and two in two Mediterranean bays consisting of sludge from post-flotation process, another 139 waste-rock piles from pre-concentration processes, melting and gravimetric separation methods. Overall, they occupy an area of 9 km^2 and an approximate volume of 175 Mm^3 on land and 25 Mm^3 in the sea (Gorguel and Portman bays). A large volume of waste materials exists in creek beds and plains. Despite dumping of mining wastes in creek was banned in 1956 (Vilar et al. 1991), tones of waste have been deposited.

Characteristics of waste and sediment samples

Mining and metallurgical wastes

Stratification, layers with different thicknesses, desiccation cracks, badlands and efflorescent salts can be observed in waste deposits (Fig. 3). According to the type of mine activity, mineral processing and disposal methods, nine types of mining and metallurgical wastes can

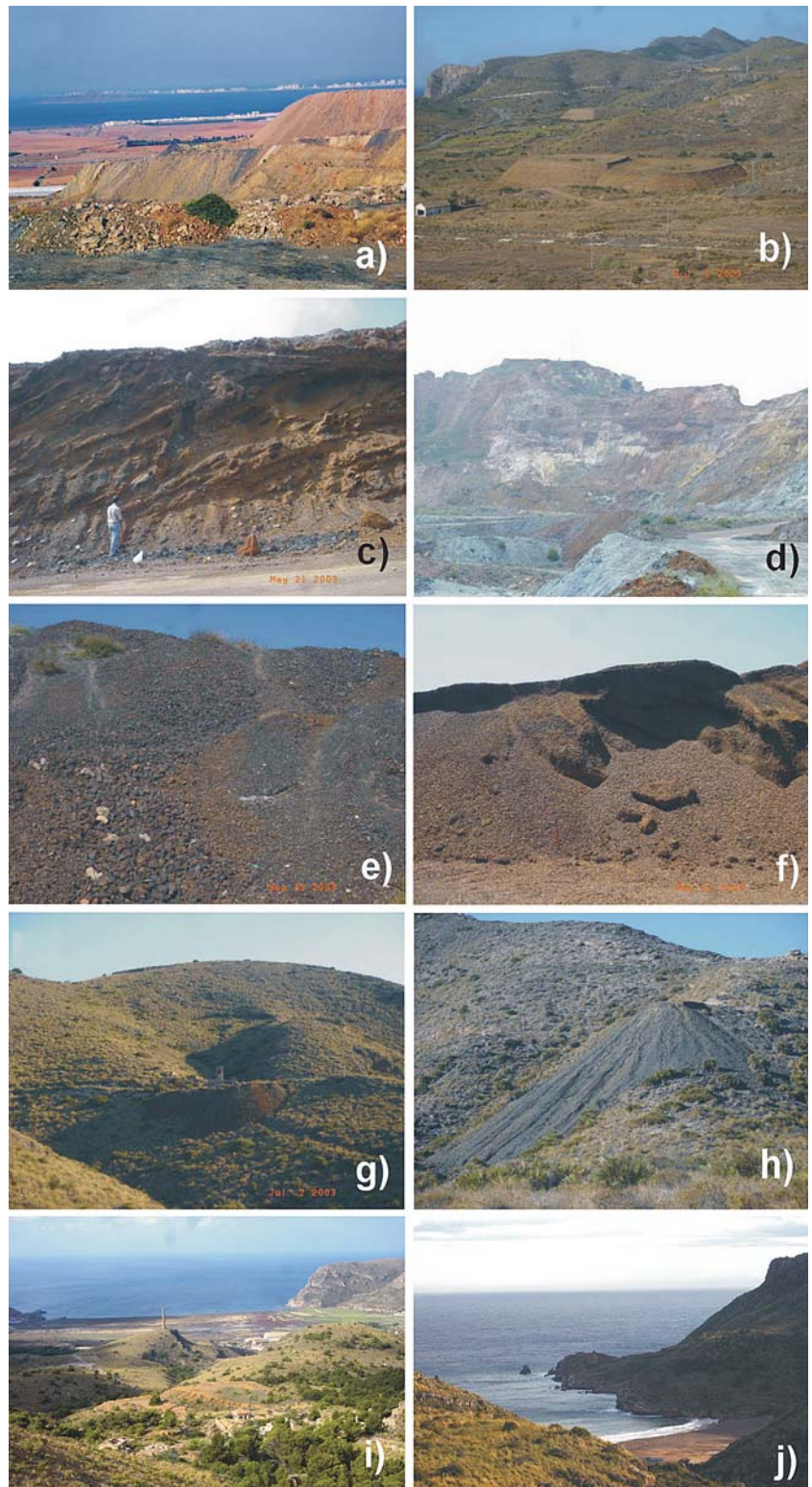
Fig. 3 **a** “Brunita” open-pit lake, **b** “Los Blancos II” open-pit lake, **c** Portman Gallery (seepage), **d** Lilian Tunnel (seepage), **e** a tailing crack, **f** stratification in a tailing dump of post-flotation wastes, **g** sulphate salts efflorescent, and **h** bad lands in a tailing dam



be defined (Fig. 4). The grain sizes range from cobbles to clay (Fig. 5a). The main fractions are sand and silt. The grain-size distribution curves of post-flotation sludge in Beal creek are different from the representative curve (Fig. 5) considered for this mining process in the Sierra, due to a different grinding process.

Mining wastes are mainly composed of: quartz, haematite, kaolinite, pyrite and magnetite (Tables 1, 2), emphasising the presence of chalcopryrite in “false” gossan and galena in post-flotation sludge deposited on land. Galena, chalcopryrite, spharelite, dolomite, calcite, greenalite, pyrrhotite, muscovite, chlorite, feldspar, sid-

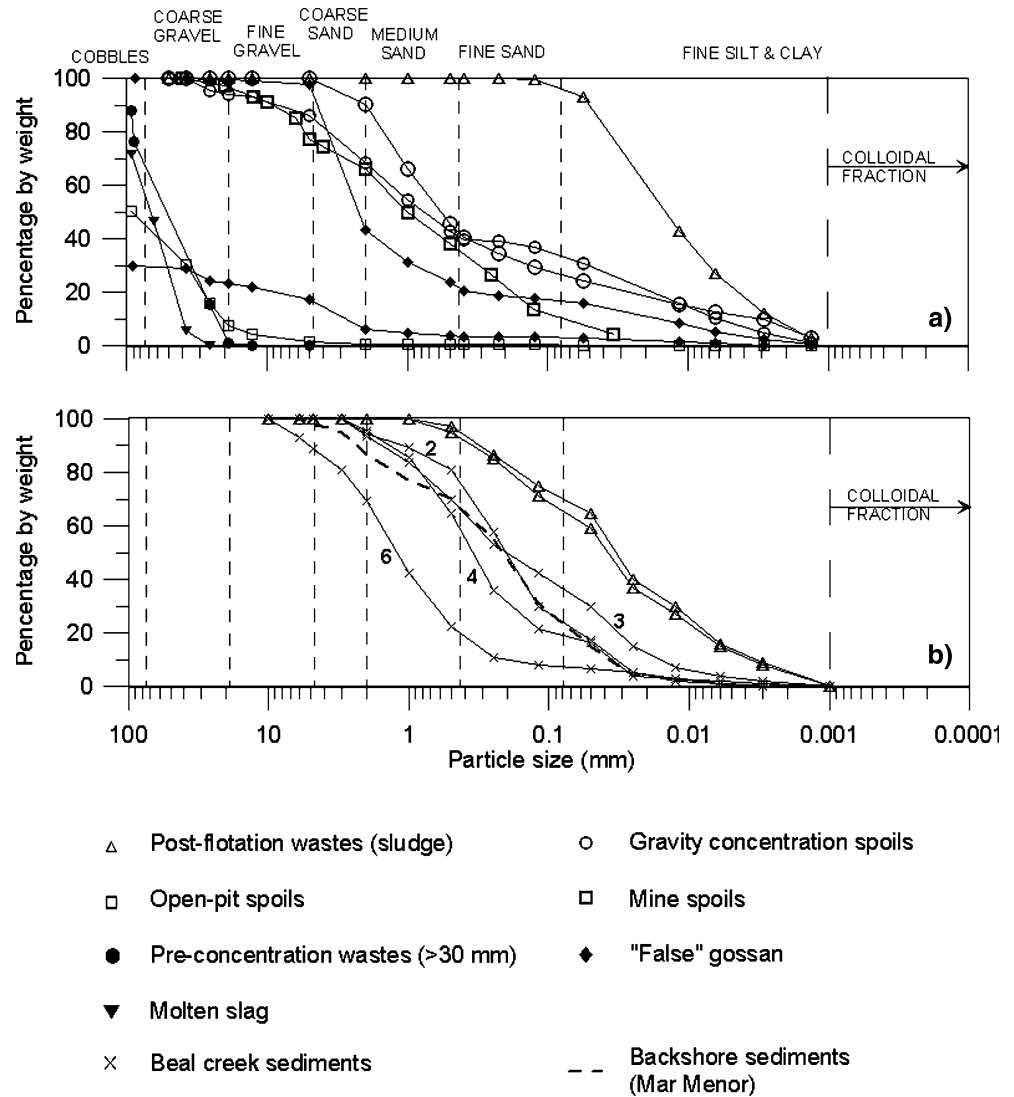
Fig. 4 Photographs of each type of mining wastes: **a** open-pit spoils, **b** post-flotation wastes, **c** gravity concentration spoils, **d** “false” gossan, **e** molten slag, **f** pre-concentration wastes, **g** mine spoils, **h** well borings, **i** post-flotation sludge in Portman Bay and **j** post-flotation sludge in Gorguel Bay



erite and gypsum are present at concentrations less than 5% by weight. The chemical composition shows that mine and metallurgical wastes have important Pb, Zn,

Fe, Mn, Cu, Cd and Ni concentrations. Fe, Mn, Pb and Zn contents are at least two orders of magnitude higher than other heavy metals (Table 2).

Fig. 5 Grain-size distribution of samples: **a** mine and metallurgical wastes, **b** Beal creek stream sediments and Mar Menor lagoon backshore and "Rosa" dam post-flotation wastes (location of 2, 3, 4, 6 and sampling points can be seen in Fig. 2d)



Stream and Mar Menor Lagoon sediments

Surface water allows the transport of particles and dissolved contaminants from the mining and metallurgical wastes transported by creeks to the Mar Menor lagoon and the Mediterranean Sea. To characterise this process, the Beal creek was selected as being a representative of the study area. The sediment transported by surface water in Beal creek mainly comes from tailing dams located in the upper creek part. In Fig. 5b can be observed the difference between the grain-size curves of the sediment samples collected along Beal creek and grain-size curves of wastes located upstream. According to chemical analysis, the sediment in the stream bed is strongly affected by solid particles rich in Pb, Zn and Cd. Figure 6 shows how metal concentrations vary along the stream bed to the lagoon. Pb and Zn mean concentrations are 39,000 and 2,000 ppm, respectively.

Top-soil samples from the Beal and Ponce flood plain (García 2004) have mean concentrations of: Pb_{total} 4,000 ppm, Zn_{total} 4,600 ppm, Cd_{total} 4.5 ppm and Cu_{total} 50 ppm.

Surface water and groundwater hydrology

The natural watersheds have been altered by open-pit excavations and waste deposition. These activities together with underground mines have modified the groundwater system.

The piezometric map reveals that the aquifer is divided into four main hydrogeologic blocks with different water-level ranges, although have the same dome-shape under the open-pits lineament (Fig. 7). This pattern may indicate the location of the main recharge area, because infiltration is promoted by

Table 1 Average mineralogical composition of mining and metallurgical wastes and efflorescence sulphate salts

	Open-pit spoils	Post-flot land	Post-flot sea	Gravity	Mine spoils	“False” gossan	Pre-concentration	Molten slag	Well spoils
Minerals in wastes (% by weight)									
Haematite	5.6	11.4	6.6	12.2	5.2	12.4	17.6		7.6
Magnetite	6.1	6.1	4.1	4.1	2.2	2.2	4.1		2.1
Galene		4.2	Trace	Trace	1.2	1.2	1.1		Trace
Greenalite	Trace	Trace	Trace	Trace		Trace	Trace		
Sphalerite	2.1	Trace	1.2	1.1	Trace	1.1	Trace		1.1
Chalcopyrite	4.2	1.5	1.2	1.2	Trace	6.3	Trace		2.5
Pyrrhotine		Trace	Trace	Trace	Trace	Trace	1.2		
Pyrite	3.1	7.1	6.1	8.2	5.2	5.6	10.1		7.1
Kaolinite	9.5	9.5	9.5	2.5	8.7	1.5	9.5		7.1
Dolomite	2.3	2.3		Trace	Trace	Trace	2.3		Trace
Calcite	Trace	1.2		Trace	Trace	Trace	Trace		1
Muscovite	3.2	1.1	1.3	1.1	1	1.1	Trace	1.1	1.2
Quartz	20.8	13.2	14.6	10.1	21.1	20.8	10.1	13.8	17.2
Chlorite	2.1	3.1	2.1	2.1	3.2	2.2	Trace		2.1
Ca feldspar	Trace	1.6	1.2	Trace	Trace	Trace	Trace		Trace
Na–Ca feldspar	Trace	1.7	1.3	2.1	Trace	Trace	Trace	1.2	Trace
Siderite	Trace	Trace	Trace	Trace	Trace	Trace	Trace		Trace
Minerals in efflorescence salts (% by weight)									
Rozenite		12.36	91.87						61.00
Gypsum		7.29	1.30	52.00		0.60	3.20		
Illite		1.59		2.70					
Quartz		2.84		1.00			6.74		
Chlorite	5.3	3.31		5.50			11.00		9.00
Apjohnite	7.80	30.19		4.50	87.80				
Halotrichite	2.20	1.53			2.20				
Starkeyite		9.03				1.35	4.61		
Hexahydrate		3.63				2.10	14.35		
Epsomite		13.44	1.2			8.90			

mining-induced higher fracturation. General flow directions appear to be parallel to N-130 faults system, this is the trend followed by mining galleries, indicating that the flow is conditioned by mining activities. Mining galleries mainly follow this path due to the fact that underground mines initially worked via veins in volcanic breccia zones and fault-crush zones with this strike.

Hydrochemical characteristics

A statistical summary of chemical data of water samples from the study area is shown in Table 3. The main characteristics of rainwater are: pH 7.14, 200.1 $\mu\text{S}/\text{cm}$ EC, 22.1 ppm SO_4^{2-} , 28 ppb Zn, 8.34 ppb Cd, 1.8 ppb Ni, 7.71 ppb Pb, 39 ppb Cu and 30 ppb Mn. Rainwater is $\text{Ca}^{2+}\text{-HCO}_3^-$ type or $\text{Ca}^{2+}/\text{Na}^+\text{-Cl}/\text{HCO}_3^-$ type (Table 3; Fig. 8).

The samples collected from surface water have an important volume of solids in suspension (5–30 g/L). The average physicochemical characteristics of runoff are: pH 3.67, 5,200 $\mu\text{S}/\text{cm}$ EC, 5,472 ppm SO_4^{2-} , 77.2 ppm Zn, 1.3 ppm Cd, 0.7 ppm Ni, 0.5 ppm Pb, 1.6 ppm Fe and 88 ppm Mn (Table 3; Fig. 8).

The range of pH values in samples collected from mining wells is 2–7.8. EC varies between 1,000 and 21,700 $\mu\text{S}/\text{cm}$, and sulphate concentrations oscillate

between 55 and 40,310 mg/L. Regarding heavy metal contents, they appear below the detection limit and several order of magnitude, ranges are: 0–4,093 ppm Zn, 0–8.0 ppm Cd, 0–3.8 ppm Ni, 0–2.8 ppm Pb, 0–1,263 ppm Fe and 0–436 ppm Mn (Table 3; Fig. 8).

Samples collected in the open-pit lakes have an average of heavy metals content of: 159–581 ppm Zn, 0.16–0.96 ppm Cd, 0.7–1.05 ppm Ni, 0.07–0.77 ppm Pb, 0–72.3 Fe ppm and 85.6–93 ppm Mn. Hydrochemical data from two outflowing mining galleries are: pH 2.3–5.6, 500–838 ppm Zn, 0.9–2.27 ppm Cd, 0.5–1.08 ppm Ni, 0.3–0.62 ppm Pb, 0.01–2.97 ppm Fe and 203–393.3 ppm Mn (Fig. 8).

The hydrochemical facies of mine water, including samples from mining wells, open-pit lakes and outflowing mining galleries are: sulphate (81%), magnesium (24%), sodium (16%) and calcium (6%), the remaining are combinations of all of them.

Leaching test

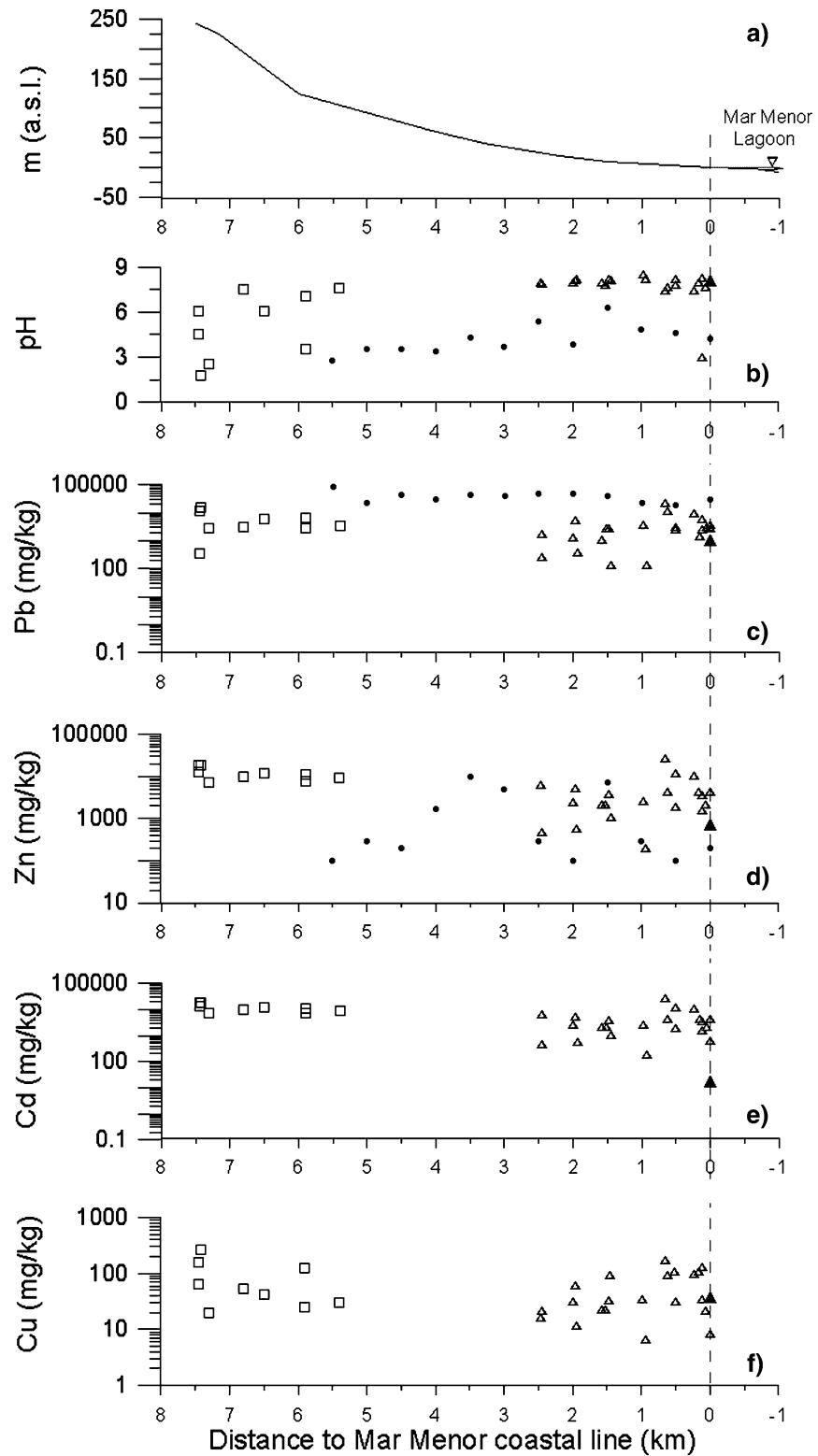
The results of leachability test are shown in Fig. 9 and Table 4. EC values and different metal concentrations of Ni, Pb, Cu, Zn and Cd decrease from the first to the third extraction, whereas pH increases. The post-flota-

Table 2 Chemical composition of mining and metallurgical wastes, minimum (Min) and maximum (Max) values

% by weight	Open-pit spoils		Post-flot land		Post-flot sea		Gravity		Mine spoils		“False” gossan		Pre-concentration		Molten slag		Well spoils	
	Max	Min	Max	Min	Max	Min	Max	Min	Max	Min	Max	Min	Max	Min	Max	Min	Max	Min
Mg	3.11	2.92	1.74	1.10	1.75	1.20	2.50	1.45	3.68	1.40	3.00	1.78	1.05	0.73	0.77	0.23	3.56	2.10
Al	8.79	3.45	7.25	3.20	8.31	5.23	3.04	1.20	5.40	2.56	3.78	2.06	1.34	0.45	2.98	1.80	9.85	4.23
Si	23.12	8.21	19.45	9.23	23.45	11.56	16.60	8.80	22.75	13.45	17.43	11.24	12.56	7.98	13.59	8.93	23.45	9.12
P	0.05	0.012	0.003	0.0023	0.0074	0.0056	0.03	0.0025	0.04	0.0098	0.04	0.007	0.02	0.0012	0.03	0.0021	0.09	0.005
S	1.79	0.89	3.37	0.70	2.57	1.78	3.55	0.0056	2.12	1.097	0.53	0.128	2.39	0.45	2.38	1.23	2.19	0.98
Cl	0.02	0.012	0.03	0.016	0.25	0.09	0.04	0.0021	0.01	0.0078	0.01	0.0056	0.02	0.0098	0.03	0.012	0.08	0.0056
K	0.24	0.14	1.37	0.34	1.37	0.0978	0.19	0.045	1.04	0.094	0.11	0.045	0.03	0.011	0.38	0.0162	1.58	0.65
Ca	1.19	0.34	2.25	1.09	2.37	1.23	1.12	0.023	1.35	0.075	0.65	0.234	0.51	0.29	1.19	0.56	1.22	0.73
Ti	0.32	0.02	0.018	0.0012	0.14	0.095	0.093	0.008	0.37	0.067	0.22	0.093	0.016	0.0095	0.19	0.021	0.25	0.06
Cr	0.006	0.004	0.0041	0.002	0.0051	0.0023	0.0038	0.0016	0.03	0.0045	0.01	0.0078	0.01	0.0093	0.01	0.0032	0.01	0.002
Mn	1.20	0.20	0.70	0.12	0.73	0.023	0.76	0.23	0.04	0.029	0.89	0.039	0.17	0.092	0.73	0.12	0.63	0.007
Fe	18.00	12.00	23.45	17.80	24.31	16.28	35.60	21.50	20.42	13.62	30.7	19.12	49.10	21.30	43.34	22.45	23.50	12.30
Ni	0.002	0.0011	0.0043	0.0031	0.0024	0.0019	0.0031	0.0017	0.004	0.0016	0.0031	0.0012	0.0025	0.0031	0.0023	0.0011	0.0023	0.0008
Cu	0.02	0.013	0.0023	0.0014	0.002	0.0015	0.0068	0.0021	0.0032	0.0012	0.004	0.0023	0.0032	0.0021	0.051	0.0007	0.0021	0.0015
Cd	0.0012	0.0009	0.0023	0.0014	0.0031	0.0015	0.0024	0.0017	0.0035	0.0013	0.0031	0.0008	0.0044	0.0025	0.0035	0.0024	0.0014	0.0007
Zn	1.08	0.36	1.02	0.243	1.057	0.23	1.15	0.24	1.07	0.21	0.97	0.3	0.76	0.23	1.097	0.54	1.10	0.10
Pb	0.56	0.20	0.65	0.23	0.61	0.334	0.61	0.31	0.83	0.23	1.08	0.34	1.17	0.31	1.71	0.34	0.57	0.27
As	0.0003	0.0001	0.0009	0.0005	0.0009	0.0004	0.0006	0.0004	0.0004	0.00063	0.00028	0.0009	0.0009	0.0006	0.0015	0.0004	0.0021	0.0006
Sr	0.01	0.002	0.01	0.010	0.010	0.010	0.010	0.010	0.010	0.010	0.010	0.010	0.010	0.010	0.010	0.010	0.010	0.010
Zr	0.01	0.002	0.01	0.010	0.010	0.010	0.010	0.010	0.010	0.010	0.010	0.010	0.010	0.010	0.010	0.010	0.010	0.010
Na	0.19	0.045	0.10	0.0009	0.85	0.085	0.085	0.085	0.085	0.0078	0.0078	0.0078	0.0078	0.0078	0.0078	0.0078	0.0078	0.0078
Ba	0.04	0.0034	0.004	0.0009	0.0009	0.0009	0.0009	0.0009	0.0009	0.0009	0.0009	0.0009	0.0009	0.0009	0.0009	0.0009	0.0009	0.0009
W.L.C.	5.8	6.70	6.50	5.30	5.90	4.79	7.20	6.71	7.10	5.87	7.10	6.43	5.20	4.90	5.60	5.10	5.18	4.98

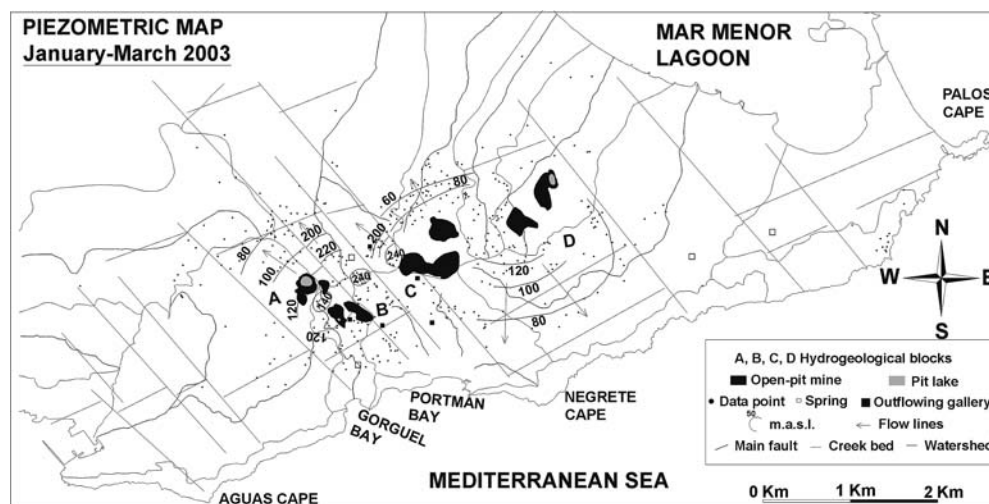
W.L.C. loss of weight by calcination

Fig. 6 **a** A topographic profile, **b** pH values, **c-f** Pb, Zn, Cd and Cu content in soils (Garcia 2004), Beal creek bed and Mar Menor backshore sediments (values of Cd and Cu concentration in stream sediment are unavailable)



□ Mining wastes • Stream Sediments △ Soil samples ▲ Lagoon Sediments

Fig. 7 Piezometric map for the period January–March 2003



tion sludge and gravimetric concentration spoils leach an important mass of Pb. In both cases, wastes have an acid pH (Fig. 9).

The mass of leached metals (Pb, Zn and Cd) in gravimetric concentration and post-flotation wastes with acid pH is higher than guideline levels. Pb concentration in both wastes is two orders of magnitude higher than the permissible value. Averages of Zn concentration in both waste extracts are one order of magnitude higher than the permissible value. Leached water strongly depends on the initial pH of waste (Fig. 9). Mining and metallurgical wastes with basic or alkaline pH ($\text{pH} > 7.5$) produce water with metal concentrations below the detection limits.

Discussion

Impacts on solid materials

In sediment samples from the Beal-creek bed (Fig. 6), Pb and Zn concentration ranges between 19,000 and 85,000 mg/kg and 100 and 10,000 mg/kg, respectively. García (2004) indicated that top-soil samples from Beal and Ponce flood plain had elevated Zn and Pb concentration, in the range of Pb 100–20,000 mg/kg and Zn 200–30,000 mg/kg (Fig. 6). The Spanish Ministry of Agriculture (R.D. 1310/1990) indicated the reference levels to agricultural soils, only for the addition of sludge as amendment, of 150 mg/kg Zn and 50 mg/kg Pb for agrarian soils with $\text{pH} < 7$, 450 mg/kg Zn and 300 mg/kg Pb for soils with $\text{pH} > 7$. Sediment samples have a $\text{pH} < 7$, where only 25% samples do not exceed the Zn guide value, whereas the Pb guide value is exceeded in all of them. Soil samples have a $\text{pH} > 7$, 13% of samples are below the permitted value for Pb and 5% for Zn. Lagoon sediment sample also exceeded

the guideline values with analysis results of Pb 950 ppm and Zn 650 ppm. This elevated concentration of heavy metals in soils and sediments has two origins; the first one from the beginning of mining activities, when wastes were spilled without control in the creeks (banned in 1956), and the second from the transport of metallurgical wastes (mainly post-flotation sludge) by runoff and wind activity, due to tailing dams erosion.

Metal concentration in the Mar Menor sediments has not undergone any noticeable change in the last few decades. Concentrations are similar to data given by Simonneau (1973), De León et al. (1982) and Sanchíz et al. (1999). Pollution sources remain the same and remediation has been minimal.

The leaching tests show that when acid wastes are in contact with water, they give the water an acidic pH, allowing metal leachability. These metals are carried to the creek bed and flood plains, to groundwater, agricultural zones, to the sea and natural ecosystems.

Environmental impacts on water

Natural flow directions of surface water and groundwater have been modified by mining activities. The natural water divides and stream-flow patterns have been changed by excavations and waste accumulations. The principal groundwater-flow direction is also affected by the main trend of mining galleries. They follow faults N-130 where mineralisation is located. To understand the aquifer, Sierra de Cartagena–La Unión a compartmentalised aquifer model, which consists of four main, poorly connected geological blocks, is proposed.

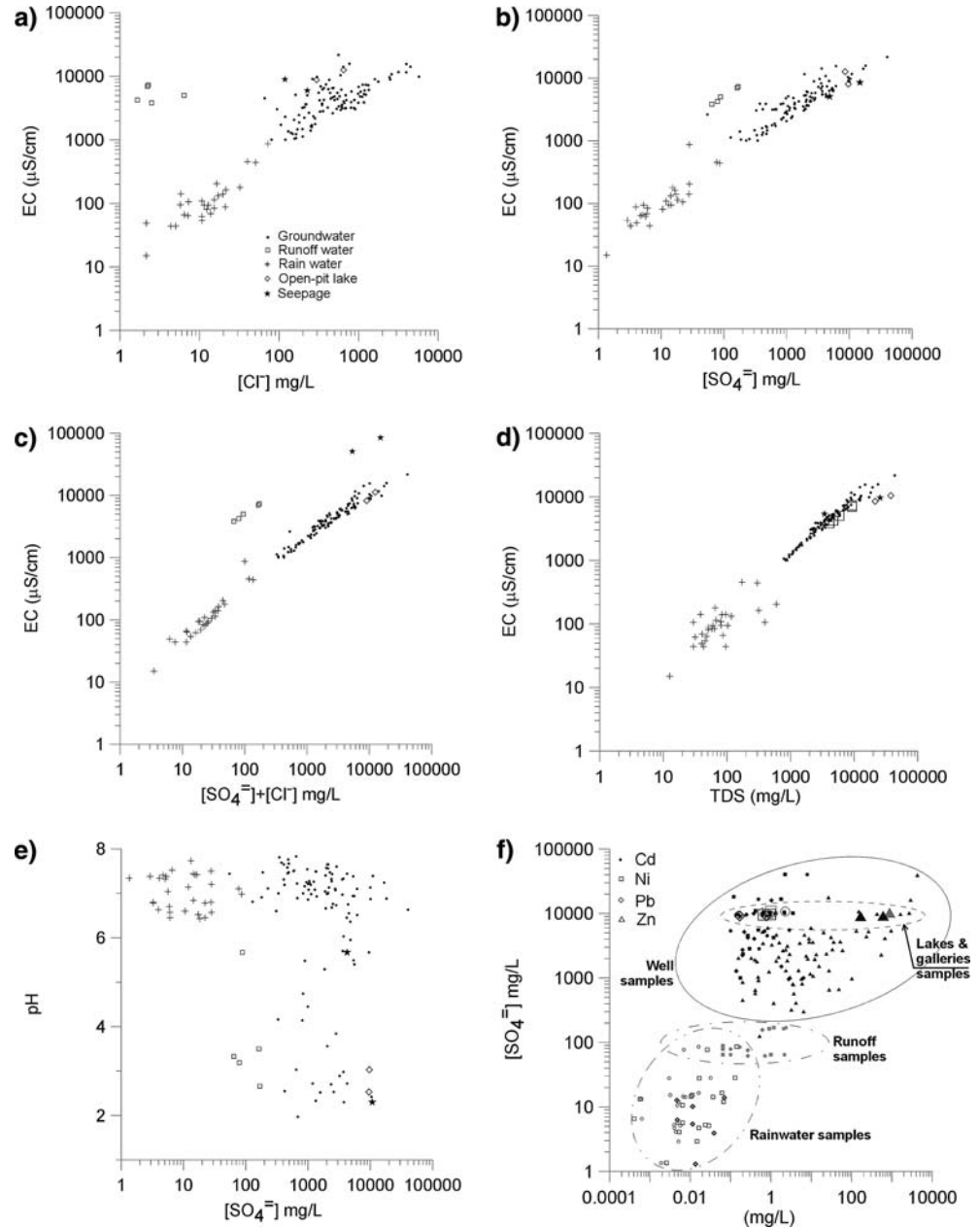
Hydrochemical data (Table 3) show that groundwater, runoff water and some rainwater samples exceed Spanish (R.D. 140/2003) and European (98/83/CE) water-quality guideline values for water supply, mainly

Table 3 Statistics of water samples chemical data (rainwater, surface water and groundwater, open-pit lakes and mining galleries) from the study area

	Rainwater					Open-pit lakes					Mining wells					Outflowing galleries					G.D.W.
	Av	Max	Min	SD	Av	Max	Min	SD	Av	Max	Min	SD	Av	Max	Min	SD	Av	Max	Min	SD	
Electric conductivity ($\mu\text{S/cm}$)	200.06	867	44	216.2	5,200	7,330	3,830	1,586	9,750	10,390	9,110	905.10	5,081	21,700	1,007	3,611	7,010	9,010	5,010	2,828.43	2,500
pH	7.14	7.5	6.45	0.33	3.67	5.67	2.66	1.16	2.78	3.03	2.53	0.35	6.3	7.8	2	1.6	3.985	5.67	2.3	2.38	6.5-9.5
Total alkalinity ($\text{CO}_3\text{Ca mg/L}$)	52.42	258.2	10.97	73.02	0	0	0	0	0	0	0	185	854.8	0	160.4	8.55	17.1	0	12.09	30	
Hardness ($\text{CO}_3\text{Ca mg/L}$)	26.42	99.77	4.75	25.53	2,732	3,530	2,140	585.1	7,093	8,034	6,151	1,332.10	2,557	15,743	296	2,295	3,847	4,163	3,530	447.61	60
TDS (mg/L)	159.61	603	29.68	162	6,621	9,242	4,056	2,479	12,393	12,850	11,936	646.22	5,396	43,600	783	5,676	9,147	12,429	5,864	4,641.80	
CO_3H^- (mg/L)	57.73	314.8	10.94	75.87	0	0	0	0	0	0	0	225	1,042	0	195.3	10.43	20.85	0	14.74		
SO_4^{2-} (mg/L)	22.11	85.64	2.91	24.81	5,472	8,126	3,094	2,455	9,583	9,650	9,516	94.75	3,068	40,310	54.7	4,817	7,485	10,736	4,234	4,597.61	250
Cl^- (mg/L)	20.67	72.17	4.36	19.03	107.1	227	59	69.98	428	593	264	233.04	756	5,757	65.9	942	180	227	132	67.32	250
NO_3^- (mg/L)	1.99	11.16	0	2.89	10	16.75	6	7.29	5.75	9.43	2.08	5.20	8.8	136	0	18.6	4.56	9.11	0	6.44	50
Na^+ (mg/L)	9.63	38.46	1.8	9.22	54.01	129.6	31	42.52	276	390	162	161.23	374	1,980	49.2	327.8	86.91	130	44.2	60.44	200
K^+ (mg/L)	4.91	35.36	0.28	9.1	1.76	6.3	0	2.81	7.72	10.82	4.62	4.38	24.1	320	3.4	37.5	3.72	6.3	1.13	3.66	150
Ca^{2+} (mg/L)	6.71	25.92	0.93	6.67	467	492	449	18.70	479	509	449	42.28	355	739	52.8	180.4	295	450	140	219.53	200
Mg^{2+} (mg/L)	2.54	8.51	0.45	2.2	381	584	221	153.6	1,432	1,679	1,185	349.12	397	3,550	16.2	500.2	756	927	585	241.81	50
NH_4^+ (mg/L)	9.18	73.5	0.14	18.17	0	0	0	0	0	0	0	0.9	37.23	0	4.48	0.04	0.08	0	0.06	0.5	
B (mg/L)	0.03	0.24	-	0.06	0.35	0.46	0.26	0.104	0.44	0.61	0.28	0.23	0.5	5.84	-	0.66	0.88	1.49	0.26	0.87	1
P_2O_5 (mg/L)	0.76	2.86	-	0.73	3.10	4.86	1.3	1.57	3.82	4.54	3.1	1.02	2.9	10.4	0.6	1.8	1.5	1.65	1.3	0.25	5
SiO_2 (mg/L)	1.68	20.46	0.14	5.02	29.1	37.89	7.72	12.54	51.86	64	39.97	16.81	25	130	7.2	23.91	24.9	42.1	7.72	24.32	
Fe (mg/L)	-	0.02	-	0.01	1.62	2.48	0.01	1.01	36.15	72.3	-	51.12	19.3	1,263	-	128.1	1.49	2.97	0.01	2.09	0.2
Mn (mg/L)	0.03	0.29	-	0.07	88	203	51.12	64.60	89.38	93	85.64	5.28	26.2	436	-	72.1	298	393	203	134.14	0.05
Ni (mg/L)	0.002	0.009	-	0.003	0.69	1.28	0.07	0.58	0.86	1.05	0.7	0.22	0.2	3.8	-	0.56	0.79	1.08	0.5	0.411	
Cu (mg/L)	0.039	0.154	0.012	0.048	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	
Zn (mg/L)	0.028	0.138	0.009	0.038	77.2	124.3	12.3	40.42	370.76	581	159	298.17	153	4,093	-	571.3	669	838	500	239.06	5
Cd (mg/L)	0.008	0.044	0.002	0.012	1.3	2.3	-	1.18	0.56	0.96	0.16	0.22	0.3	8.0	-	1.07	1.58	2.27	0.9	0.968	0.005
Pb (mg/L)	0.007	0.032	0.003	0.009	0.54	0.92	0.17	0.33	0.47	0.77	0.07	0.42	0.1	2.8	-	0.36	0.46	0.62	0.3	0.32	0.225

Av average, Max maximum, Min minimum, SD standard deviation, G.D.W. Spanish and European guideline drinking water, - below detection limits

Fig. 8 Concentrations comparison of each type of sampled water: **a** EC vs. chloride, **b** EC vs. sulphates, **c** EC vs. chloride plus sulphate, **d** CE vs. TDS, **e** sulphate vs. pH, **f** black symbols correspond to groundwater samples, grey symbols to runoff and white to rainwater. Bigger symbols show the concentrations of open-pit samples (black) and seepages from mining galleries (grey)



due to elevated sulphate, EC and Mn concentration. An exception occurs in the groundwater samples, water from the spring “La Fuente” is suitable for human consumption. This is the furthest water sample collected from the main mining area.

According to the main water component, rainwater is $\text{Ca}^{2+}-\text{HCO}_3^-$ or $\text{Ca}^{2+}/\text{Na}^+-\text{Cl}^-/\text{HCO}_3^-$ and groundwater is mainly $\text{Mg}^{2+}-\text{SO}_4^{2-}$ type, indicating the increase of sulphate and magnesium in the percolated water. This increase is produced by the interaction of infiltrated water with weathering products of sulphide minerals present in the surface of waste deposits, wells and mining

galleries, and the aquifer materials. The high concentration of sulphate in groundwater is due to the dissolution of different sulphate minerals generated by sulphide mineral oxidation. This oxidation is feasible by groundwater pumping while mining is active. The water-table drawdown allows oxygen and other gases to enter into mining wells and galleries, where sulphide minerals are present. When pumping ceased, the water level rebounded (there is a water column of 30 m in one open-pit lake) and sulphate dissolution was enhanced. Oxidation of specific sulphide minerals, such as pyrite and pyrrhotite, is acid-producing, it causes the pH decrease

Fig. 9 a Metal concentration in mining and metallurgical wastes; **b** results from leaching tests (DIN 38414-S4) for mining and metallurgical wastes according to the initial pH values of the mining waste

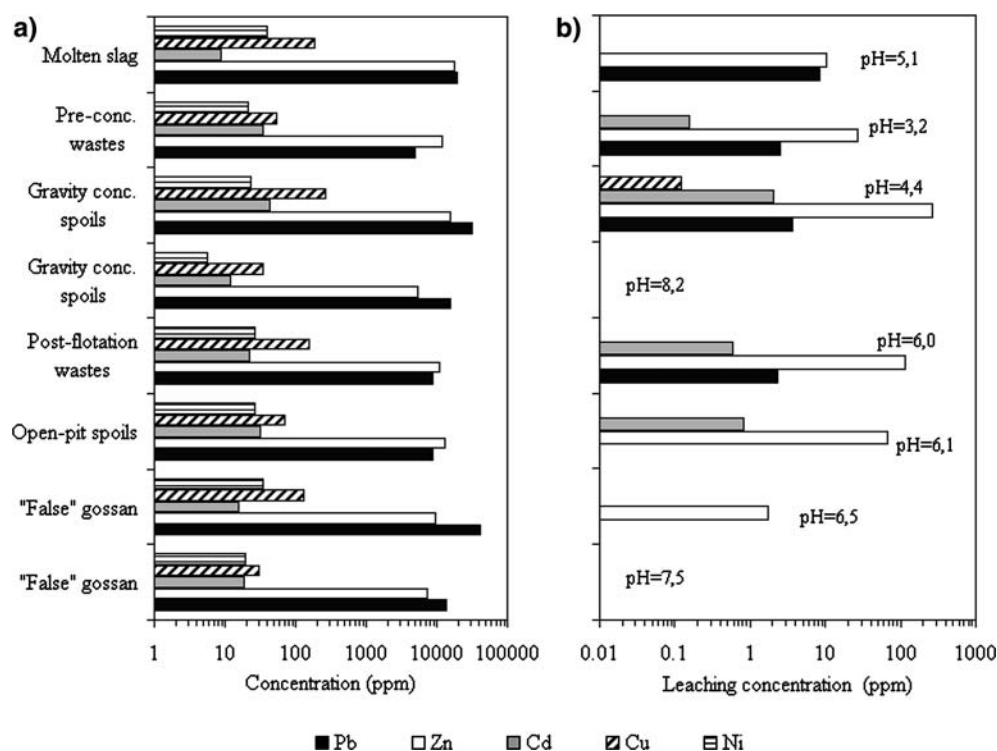


Table 4 Results from leaching tests (three replicates; F first, S second and T third)

Sort of waste	Replicate	pH	Electric conductivity (μS/cm)	Pb (ppm)	Zn (ppm)	Cd (ppm)	Cu (ppm)	Ni (ppm)
"False" gossan	F	7.5	1.34	<0.4	<0.1	<0.05	<0.1	<0.4
	S	7.8	0.51	<0.4	<0.1	<0.05	<0.1	<0.4
	T	8.0	0.18	<0.4	<0.1	<0.05	<0.1	<0.4
"False" gossan	F	6.5	0.48	<0.4	1.71	<0.05	<0.1	<0.4
	S	6.6	0.22	<0.4	0.77	<0.05	<0.1	<0.4
	T	6.7	0.14	<0.4	0.46	<0.05	<0.1	<0.4
Gravity concentration wastes	F	3.2	1.40	2.25	27.56	0.15	<0.1	<0.4
	S	3.4	0.43	3.29	4.29	<0.05	<0.1	<0.4
	T	3.5	0.28	5.02	2.06	<0.05	<0.1	<0.4
Open-pit spoil	F	6.1	2.60	<0.4	66.13	0.82	<0.1	<0.4
	S	6.6	0.67	<0.4	5.39	<0.05	<0.1	<0.4
	T	7.1	0.25	<0.4	0.62	<0.05	<0.1	<0.4
Post-flotation sludge	F	6.0	2.94	2.35	118.3	0.59	<0.1	<0.4
	S	6.1	2.32	1.68	30.33	0.17	<0.1	<0.4
	T	6.3	0.75	<0.4	9.59	<0.05	<0.1	<0.4
Post-flotation sludge	F	8.2	4,255	<0.02	<0.4	<0.007	<0.1	<0.4
	S	8.3	2,310	<0.02	<0.4	<0.007	<0.1	<0.4
	T	8.4	2,110	<0.02	<0.4	<0.007	<0.1	<0.4
Gravity concentration waste	F	4.4	4.76	3.55	264	2.03	0.13	<0.4
	S	4.7	1.46	2.99	46.36	0.37	<0.1	<0.4
	T	4.8	0.48	3.26	13.63	0.12	<0.1	<0.4
Molten slag	F	5.1	0.15	8.39	10.53	<0.05	<0.1	<0.4
	S	5.4	0.03	3.81	2.32	<0.05	<0.1	<0.4
	T	5.5	0.02	2.45	1.10	<0.05	<0.1	<0.4
NL (ppm)		4-13	50×10^3	0.5-1.0	2.0-5.0	0.1-0.2	2.0-5.0	0.5-1.0
NIPDWS (ppm)				0.025	5.0	0.005	0.005	0.02

NL regularity level, NIPDWS National Interim Primary Drinking Water Standard

and allows increase in the movement of metals. About 70% of the samples from mining wells do not have an acid pH (Fig. 8e), as carbonate materials of the aquifer neutralise the water acidity (Younger 2001).

Four groups of water samples (rainwater, seepage from mining galleries, surface water and groundwater) can be distinguished by the relationship between electrical conductivity and $\text{SO}_4^{2-} + \text{Cl}^-$ concentration in Fig. 8c. Electrical conductivity in each type of water is controlled by sulphate and chloride concentration (Fig. 8a–c). Runoff and seepage samples show a similar trend due to the fact that both cases are affected by the evaporation process and sulphate dissolution. There is a linear correlation between TDS and EC for each group of samples (Fig. 8d). Elevated TDS contents in different waters are due to dissolution of efflorescent sulphate salts. Heavy metal concentration in water samples displays a wide variation. Heavy metals and sulphate found in rainwater samples come from the suspended particles present in the atmosphere due to wind erosion of tailing dams.

As anticipated, samples with higher contents of heavy metals present the lowest pH values. These samples come from some mining wells, outflowing mining galleries and open-pit lakes, respectively. Heavy metal concentration is directly correlated with sulphate concentration (Fig. 8f). Sulphate concentration is higher in groundwater and runoff, independently of the pH value (Fig. 8e).

Rainwater hydrochemistry rapidly changes after falling over the soil surface, due to the dissolution of efflorescent sulphate salts (Fanfani et al. 1997; Hammarstrom et al. 2005) present on the tailing dams surface, increasing the concentration of dissolved and suspended sulphate and metals in runoff (Fig. 8).

These results agree with the conclusions of Gray (1996), who showed that the sulphate concentration and EC are more consistent indicators of mining influence than heavy-metal contents or pH values because they are affected by the environmental fluctuations.

Mar Menor water is also polluted, due to agricultural and mining influences. Metal contents in water from the mouth of Beal creek are: Zn 0.41 ppm, Pb and Mn 0.07 ppm.

Conclusions

The Sierra de Cartagena–La Unión is strongly affected by mining activities. The natural background of water, soil and sediment in this area is difficult to determine due to the long duration of mining activities. These activities have produced a progressive deterioration of groundwater, sediment and soil quality. High sulphate concentration and elevated EC in the groundwater and runoff water, and metals content in water, sediment and soil samples have been identified. If the concentration of Pb, Zn, Cd and Cu is analysed in wastes, soil and sediment in a longitudinal profile along a creek in the majority of samples the concentration of heavy metals exceeds the guidelines of the Spanish government. According to the obtained data, the mining area can be considered strongly polluted and wastes with acid pH values represent an environmental hazard, due to metals leachability. The main geochemical process identified in the study area is the oxidation of sulphide minerals by weathering of mining and metallurgical wastes and “in situ” mineralisation oxidation (allowed by the dewatering process). Later-water rebound allows the dissolution of oxidised minerals in deep mines. Physical and geochemical properties of waste deposits and climatic conditions, wind (always present in the study area) and water erosion (few heavy rainfall events in the hydrologic year), represent the main environmental risk factors. Rainwater dissolves the efflorescent sulphate salts generated on waste-pile surfaces, mobilising elevated concentrations of sulphate and heavy metals in acid water with important amount of suspended solids, allowing their entrance to the trophic chain in aquatic and terrestrial ecosystems. Wind transports fine particles from tailing dams to the surrounding areas, covering villages, fields and enter the sea.

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References

- Ashley PM, Lottermoser BG, Collins AJ, Grant CD (2004) Environmental geochemistry of the derelict Webbs Consols mine, New South Wales, Australia. *Environ Geol* 46:591–604
- Auernheimer C, Llavador F, Pina JA (1984) Chemical minority elements in bivalve shells. A natural model (Mar Menor, Spain). *Arch Sci Genève* 37(3):317–331
- Banks D, Younger PL, Arnesen RT, Iversen ER, Banks SB (1997) Mine-water chemistry: the good, the bad and the ugly. *Environ Geol* 32:157–174
- Buurman P, Van Lagen B, Velthorst EJ (1996) Manual for soil and water analysis. Backhuys Publishers, Leiden, The Netherlands, pp 291
- CHS (1997) Plan hidrológico de la cuenca del Segura. Memoria. Murcia, pp 363. http://www.mma.es/cuencas/segura/docum_plan.htm

- Conesa HM, Faz A, Arnaldos R (2006) Heavy metal accumulation and tolerance in plants from mine tailings of the semiarid Cartagena-La Unión mining district (SE Spain). *Sci Total Environ* (in press). DOI 10.1016/j.scitotenv.2005.12.008
- Da Cruz H, Murcia regional working group (2003) Programme for the integrated management of the Mar Menor coastline and its area of influence. Feasibility study. UNEP, Region of Murcia and Mediterranean action plan, 136 pp. [http://www.pap-thecoastcentre.org/camp-definitivo\(ing\).pdf](http://www.pap-thecoastcentre.org/camp-definitivo(ing).pdf)
- De León AR, Guerrero J, Farazo F (1982) Evolution of the pollution of the coastal lagoon of Mar Menor. *Proc. Vies Journées Étud Pollutions, Cannes, C.I.E.S.M.*, pp 355–358
- DIN-NORMEN (1984) DIN 38414-S4 Determination of leachability by water (S4). German standard methods for examination of water, wastewater and sludge. *Sludge and Sediments (group S)*
- Duran JJ, García de Domingo A, López-Geta JA (2003) Hydrogeological characterization of the Spanish wetlands included in the Ramsar Convention. 1:2.500.000 Map. Geological Survey of Spain
- Fanfani L, Zuddas P, Chessa A (1997) Heavy metals speciation analysis as a tool for studying mine tailings weathering. *J Geochem Explor* 58:241–248
- Font I (1983) Atlas climático de España y Portugal. Instituto Nacional de Meteorología, Madrid, pp 296
- Gagny C, Marconnet B (1994) Les minéralisations Pb–Zn du district de Cartagène (Espagne): un nouveau modèle structural. Application à la prospection. *Chon Rech Min* 516:25–38
- García C (2004) Impacto y riesgo ambiental de los residuos minero-metalúrgicos de la Sierra de Cartagena-La Unión (Murcia-España). Ph.D. thesis, Technical University of Cartagena, Spain, pp 424
- García-Tortosa FJ, López Garrido AC, Sanz de Galdeano C (2000) Las unidades alpujarrides y maláguides entre Cabo Cope y Cabo de Palos (Murcia, España). *Geogaceta* 28:67–70
- Gray NF (1996) Field assessment of acid mine drainage contamination in surface and ground water. *Environ Geol* 27:358–361
- Guardiola R (1927) Estudio metalogénico de la Sierra de Cartagena. *Inst Geol España Mem* 53:564
- Hammarstrom JM, Seal RR II, Meier AL, Kornfeld JM (2005) Secondary sulfate minerals associated with acid drainage in the eastern US: recycling of metals and acidity in surficial environments. *Chem Geol* 215:407–431
- Hernández J, García G, Conesa H, Faz Cano (2004) Polluted soils by mining and industrial activities in the “Campo de Cartagena” county (Murcia). In: Faz A, Ortiz R, García G (eds) Fourth international conference on land degradation. *Excursion Guidebook*, pp 67–83
- IGME-MOPTMA (1996) Recuperación de los usos de la Bahía de Portmán. Estudio geológico e hidrogeológico de la Sierra Minera (Murcia), pp 306
- Kager PCA (1980) Mineralogical investigation on sulfides, Fe–Mn–Zn–Mg–Ca–carbonates, greenalite and associated minerals in the Pb–Zn deposits in the Sierra de Cartagena, Province of Murcia, SE Spain. Ph.D. thesis, University of Amsterdam, GUA paper of Geology series 1(12):230
- Lee CH, Lee HK, Lee JC (2001) Hydrogeochemistry of mine, surface and groundwater from Sanggok mine creek in the upper Chungju, Republic of Korea. *Environ Geol* 40(4–5):483–494
- Manteca JI, Ovejero G (1992) Los yacimientos Zn, Pb, Ag–Fe del distrito minero de La Unión–Cartagena, Bética Oriental. In: García Guinea J, Martínez Frías J (eds) *Recursos minerales de España*, Madrid. CSIC, pp 1085–1101
- Marguí E, Salvadó V, Queralt I, Hidalgo M (2004) Comparison of three-stage sequential extraction and toxicity characteristic leaching tests to evaluate metal mobility in mining wastes. *Anal Chim Acta* 524:151–159
- Oén IS, Fernández JC, Manteca JI (1975) The lead–zinc and associated ores of La Unión–Sierra de Cartagena, Spain. *Econ Geol* 70:1259–1278
- Ovejero G, Jacquín JP, Servajean G (1976) Les minéralisations et leur contexte géologique dans la Sierra de Cartagena (Sud-Est de L’Espagne). *Bull Soc Géol France* (7), t. XVIII(3):613–633
- Pavillon MJ (1969) Les minéralisations plombo-cinzifères de Carthagène (Cordillères Bétiques, Espagne). Un exemple d’héritages successifs en métallogénie. *Mineral Deposita* 4:368–385
- Rodríguez R, Candela L (2004) Changes in groundwater chemistry due to metallurgical activities in an alluvial aquifer in the Moa area (Cuba). *Environ Geol* 46(1):71–82
- Rösner U (1998) Effects of historical mining activities on surface water and groundwater—an example from north-west Arizona. *Environ Geol* 33(4):224–230
- Sánchez-Gómez P, Guerra-Montes J, Coy-Gómez E, Hernández-González A, Fernández-Jiménez S, Carrillo-López AF (1998) Flora de Murcia. Claves de identificación e iconografía de plantas vasculares. Murcia, p 440
- Sanchíz C, García AM, Pastor A (1999) Heavy metals contents in soft-bottom marine macrophytes and sediments along the Mediterranean coast of Spain. *Mar Ecol* 21(1):1–16
- Sanz de Galdeano C (1990) Geologic evolution of the Betic Cordilleras in Western Mediterranean, Miocene to the present. *Tectonophysics* 172:107–119
- Simonneau J (1973) Mar Menor. Evolution sedimentologique et geoquimique recent du remplissage. Ph.D. thesis, University Paul Sabatier, France, p 172
- Vilar JB, Egea Bruno PM, Fernández-Gutierrez JC (1991) La minería murciana contemporánea (1930–1985). *Inst Tecn Geomin España*, Madrid, pp 256
- Younger PL (1999) Pronóstico del ascenso del nivel freático en minas subterráneas y sus consecuencias medio-ambientales. *Bol Geol Min* 110(4):407–422
- Younger PL (2001) Contaminación de las aguas subterráneas por productos de oxidación de sulfuros en una mina abandonada encajada en calizas masivas. In: Medina A, Carrera J, Vives L (eds) *Proceedings of the conference: Las caras del agua subterránea*. September 2001, Barcelona, Spain, vol. 1, pp 3–8
- Younger PL, Wolkersdorfer C (2004) Mining impacts on fresh water environment: technical and managerial guidelines for catchment scale management. *Mine Water Environ* 23:S2–S80
- Younger PL, Banwart SA, Hedin RS (2002) *Mine water. Hydrology, pollution and remediation*. Kluwer Academic Publisher, London, pp 442