The Mazarrón Pb–(Ag)–Zn mining district (SE Spain) as a source of heavy metal contamination in a semiarid realm: Geochemical data from mine wastes, soils, and stream sediments

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ABSTRACT

The Mazarrón epithermal ore deposits (SE Spain) formed in Miocene time in relation to the emplacement of dacitic–rhyodacitic domes. The Pb–(Ag)–Zn ore deposits are of the high sulphidation vein and stockwork type. There are two main mining sites: San Cristóbal-Perules (adjacent to the town of Mazarrón) and Pedreras Viejas. The area is located in the southern realm of a Miocene marine basin surrounded by mountains in its western, eastern and southern flanks. A main seasonal river (Rambla de las Moreras) crosses the basin from North to South and is strongly affected by contaminated sediments from the San Cristóbal–Perules mining site. The mine tailings are extremely rich in Pb (mean = 12,400 μg g^{-1}) and Zn (mean = 6100 μg g^{-1}), whereas As concentrations are also very high (mean = 650 μg g^{-1}). Our geochemical survey also covered anthropic soils, stream sediments and the so-called *almagres* deposits (red alum calcines). All these environmental matrices have also very high concentrations of Pb, Zn, As, and Cd compared to our local or world baseline concentrations. The calcines are rich in As (mean = 450 μg g^{-1}), and the main environmental concern relates to the wrong use of these materials as agricultural soils at discrete sites in the district. Besides, the anthropic soils of the district are very rich in Pb (mean = 2550 μg g^{-1}) and Zn (mean = 1870 μg g^{-1}). On the other hand, the seasonal river Rambla de las Moreras receives contaminated sediments from the San Cristóbal–Perules old mining site and mine wastes, which results in high concentrations of As (mean = 120 μg g^{-1}), Pb (mean = 2700 μg g^{-1}) and Zn (mean = 1090 μg g^{-1}) in the sediments. These high concentrations of dangerous contaminants in an area close to a town of 35,000 inhabitants and adjacent to significant agricultural activity may pose a risk to human health.

1. Introduction

The Mazarrón Pb–(Ag)–Zn mining district (now abandoned) is located close to the town of Mazarrón, only 4 km away from the Mediterranean coast in SE Spain (Fig. 1A, B). The mining area shares many geologic and environmental features with other districts from SE Spain such as La Unión (Robles-Arenas et al., 2006; Navarro et al., 2008) or Rodalquilar (Oyarzun et al., 2008) however, the magnitude of the environmental disturbances is much stronger. This is not surprising for an area that has been mined, although intermittently, since Roman time (200 BC to 300 AD) (Manteca Martínez et al., 2005). The district was first mined for lead in Roman time, later for the alum (aluminium sulphate: alunite) during the 15th–16th Centuries, then for the alum wastes (calcines; 1774–1953), and finally for lead, silver and zinc during the 19th–20th Centuries (until the early 1960s) (Rodríguez and Hidalgo, 1997; Manteca Martínez et al., 2005; Martínez Alcalde, 2005). The latter

corresponds to the peak period of mineral extraction. For example, 3 Mt of ore at 10% Pb and 150 gt^{-1} Ag were extracted between 1920 and 1941, whereas a decline is observed for the period 1951–1962, when only 1 Mt of ore at 3% Pb, 5% Zn and 115 gt^{-1} Ag was extracted. Despite the extent of environmental disturbances little or nothing has been done to mitigate the risk in the Mazarrón area, where most of the 35,000 inhabitants live adjacent to large abandoned mining sites and agricultural activities. Besides, water resources are exposed to contamination from waste materials. We here present a comprehensive environmental study of the Mazarrón district including geological, geochemical, mineralogical, physiographic and climatic data (Fig. 1A, B).

2. Climatic, physiographic and geologic setting
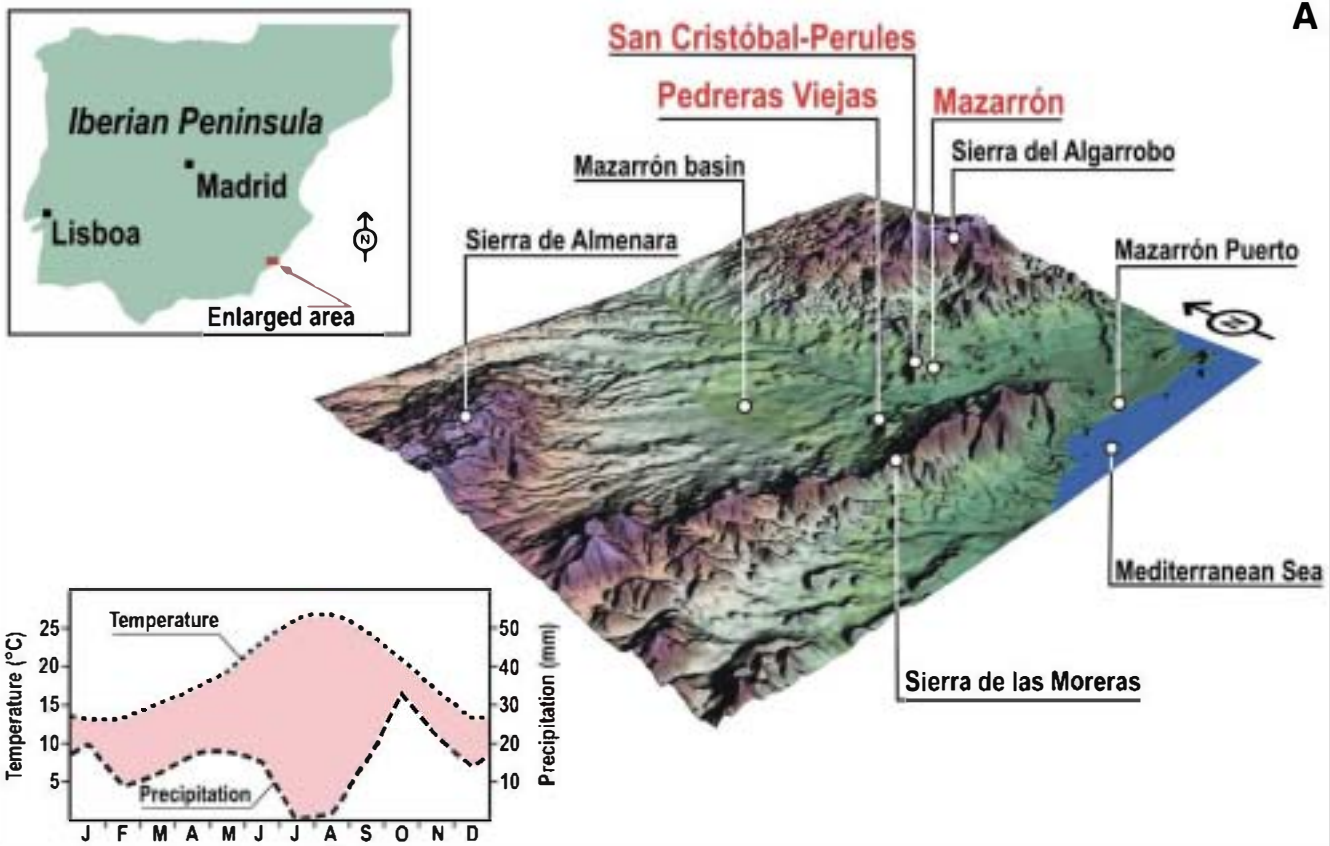
2.1. Climate and physiography

The area is characterized by a typical Mediterranean climate, with rain deprived summers and moderation of temperatures by the
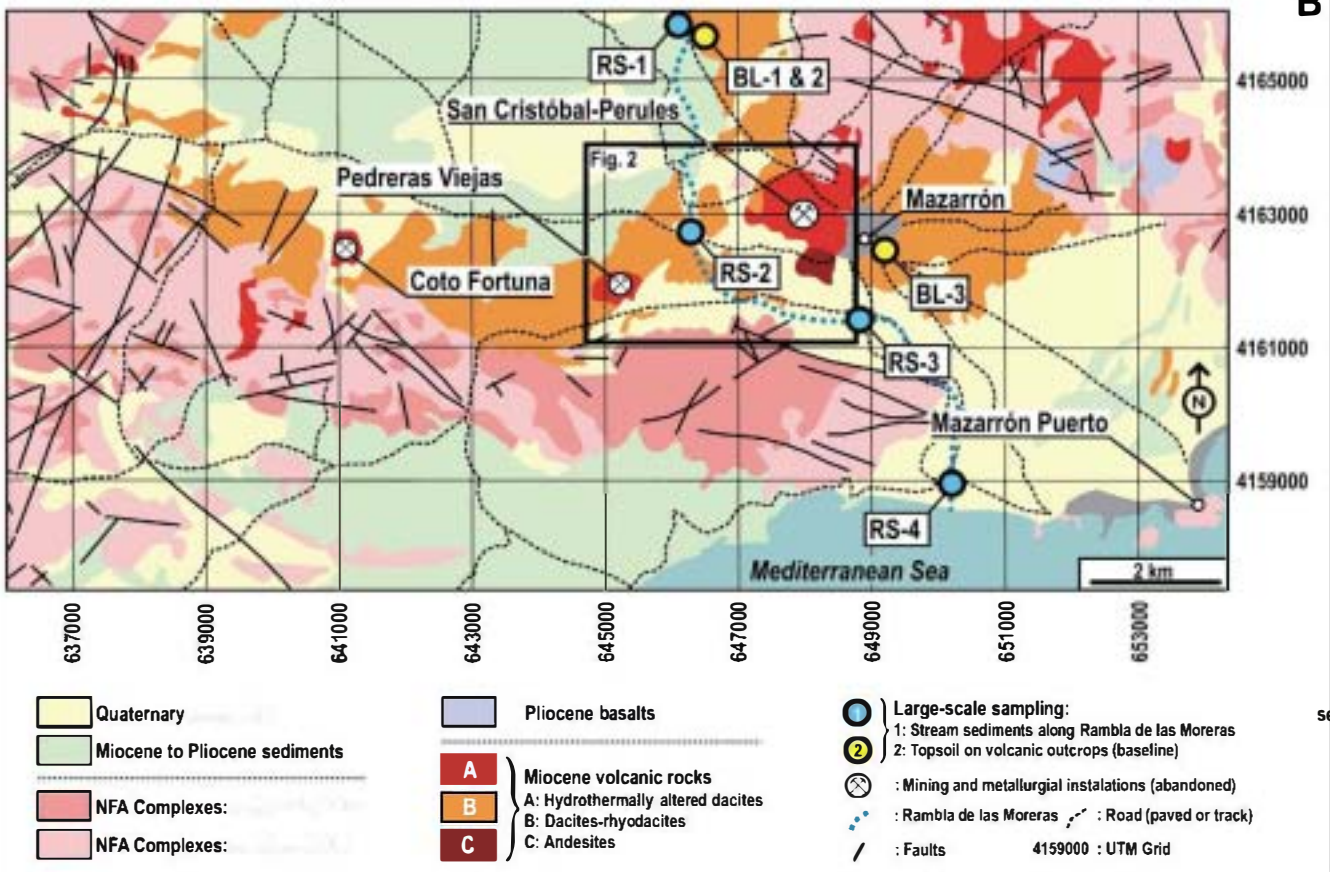
A

Iberian Peninsula
Madrid
Lisboa
Enlarged area

San Cristóbal-Perules
Pedreras Viejas
Mazarrón
Sierra del Algarrobo
Mazarrón basin
Sierra de Almenara
Mazarrón Puerto
Sierra de las Moreras
Mediterranean Sea

Temperature (°C)
Precipitation (mm)
Temperature
Precipitation
J F M A M J J A S O N D

B

RS-1
BL-1 & 2
San Cristóbal-Perules
Pedreras Viejas
Fig. 2
Mazarrón
Coto Fortuna
RS-2
BL-3
RS-3
Mazarrón Puerto
RS-4
Mediterranean Sea
2 km

4165000
4163000
4161000
4159000

637000 639000 641000 643000 645000 647000 649000 651000 653000

Quaternary		Pliocene basalts	
Miocene to Pliocene sediments			
NFA Complexes:		Miocene volcanic rocks	
NFA Complexes:		A: Hydrothermally altered dacites	
		B: Dacites-rhyodacites	
		C: Andesites	

Large-scale sampling:
1: Stream sediments along Rambla de las Moreras
2: Topsoil on volcanic outcrops (baseline)
: Mining and metallurgial instalations (abandoned)
: Rambla de las Moreras : Road (paved or track)
: Faults   4159000 : UTM Grid

sediments

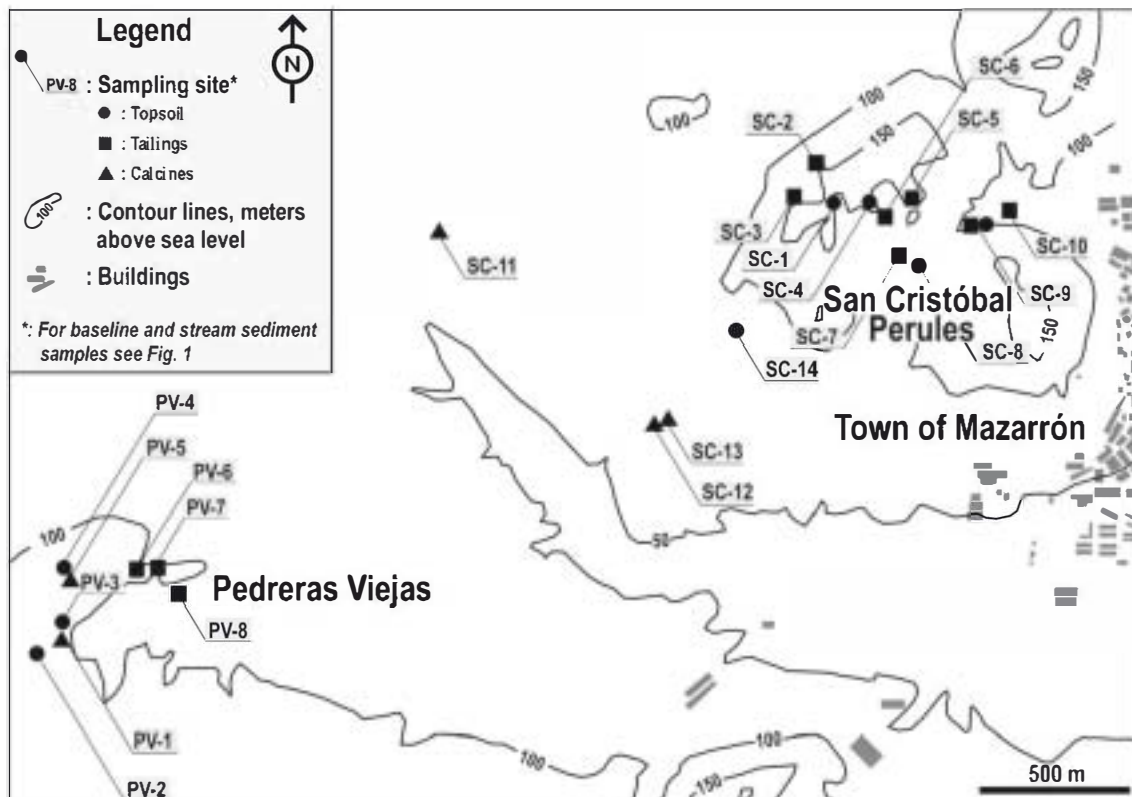carbonate fac

undiferentiate

Fig. 2. Geochemical sampling (soils, calcines, and tailings) in the San Cristóbal–Perules and Pedreras Viejas area. Location of stream sediment (RS) and local baseline (LB) samples is shown in Fig. 1.

influence of the Mediterranean Sea. Annual rainfall may strongly vary between years, and it is within the range of 185–310 mm, whereas average annual temperatures are between 16.5 and 18.8 °C (García-Rizo et al., 1999) (Fig. 1A). Although rainfall is not high, the area is subjected to annual, strong stormy episodes that can induce important flash flood phenomena. The semiarid climate of SE Spain may have started as early as ~4500 BP, with a radical transformation of the landscape that reflects in the establishment of the steppe conditions found today (Pantaleón-Cano et al., 2003), whereas Carrión et al. (2009) indicate that aridity is a feature of this realm ever since the Middle Miocene.

The most conspicuous physiographic elements of the area are three sierras, with maxima altitudes in the order of 400 to 700 m that bound the Mazarrón basin by the south (Sierra de las Moreras), west (Sierra de Almenara) and east (Sierra del Algarrobo) (Fig. 1A). The sierras define a crude horseshoe-shaped basin opened to the north and inclined to the south, at ~120–100 m of altitude. The basin is crossed by the Rambla de Las Moreras ("rambla" is a Spanish term for a ravine which is dry most of the year and turns in a high-flow torrent during short heavy rain periods) which runs straight to the Mediterranean sea. In the wet season it transports contaminated sediments from the surrounding area in its lower course (Fig. 1A, B).

2.2. Geology

Mazarrón is located within the 160 km long Almería–Cartagena Volcanic Belt (Oyarzun et al., 1995). This Miocene belt comprises a variety of volcanic series including calc-alkaline, high-K calc-alkaline,

and shoshonitic rocks. The area of Mazarrón (Espinosa Godoy et al., 1973) is also characterized by the presence of two of the most important Alpine metamorphic complexes of southern Spain: Alpujarride and Nevado Filábrides (mainly carbonates and schists) (Fig. 1B). These units were intensively folded during late Oligocene–Early Miocene, and later underwent extensional collapse through major detachment systems in Middle–Late Miocene time (e.g., Doblas and Oyarzun, 1989; Platt and Vissers, 1989). The latter episode was accompanied by volcanism throughout the belt and marine sedimentation. In Mazarrón the volcanic activity gave rise to high-K calc-alkaline andesites, dacites and rhyodacites of Tortonian to Messinian age, that were emplaced as subvolcanic domes and ashfall deposits (tuffs) (Fig. 1B). The volcanic rocks form an inner ring within the horseshoe structure bounding the Mazarrón basin. The Mazarrón basin was infilled during Tortonian–Messinian and Pliocene by marine sediments comprising marls, sandstones, conglomerates, and coquina limestones (Fig. 1B).

2.3. Ore deposits, mining and metallurgy

The southern realm of the volcanic rim hosts Pb–(Ag)–Zn epithermal ore deposits of the vein–stockwork type: Coto Fortuna, Pedreras Viejas, and San Cristóbal–Perules (Fig. 1B). These deposits are characterized by the presence of dacitic to rhyodacitic domes that underwent strong and pervasive advanced argillic hydrothermal alteration, with kaolinite, alunite and silica formation. Main ore minerals are pyrite, sphalerite, and Ag-bearing galena (up to 15–20% Ag), whereas other sulphides include chalcopyrite, tetrahedrite–tennantite,

Fig. 1. The Mazarrón district. A: Location map; digital elevation model for Mazarrón displaying major physiographic features; climatic diagram. B: Regional geology of Mazarrón, displaying major mining sites, location of towns, and large-scale sampling along the Rambla de las Moreras (stream sediments: RS samples) and local baseline samples (LB). Geology: simplified after Espinosa Godoy et al. (1973). See inlet in B for location of Fig. 2 (geochemical sampling).

Table 1

Trace element concentration in tailings, calcines, soils, stream sediments and local soil baselines from the Mazarrón mining district and neighbouring areas. LB: Mazarrón local baseline samples; RS: Sediments from rambla de las Moreras; PV: Pedreras Viejas; SC: San Cristóbal-Perules. *: calcines used as agricultural soil. **: anthrosols; ***: agricultural soil.

Element ($\mu g\ g^{-1}$)	Ag	As	Ba	Bi	Cd	Cu	Pb	Sb	Se	Sn	Te	Zn
Sample						**Tailings**						
PV-06(1)	17.8	277	417	1.09	11.8	186	7920	50.8	1.3	32	<0.1	7880
PV-06(2)	18.6	260	395	1.04	11.7	190	7910	46.0	1.9	34	<0.1	7920
PV-07	94.4	545	167	0.63	19.1	740	21,300	113.0	0.8	25	<0.1	13,100
PV-08	16.1	222	477	2.82	9.8	83	5850	48.0	0.6	21	0.5	4960
SC-02	8.6	386	171	0.37	4.2	120	4830	43.2	1.0	41	0.2	2700
SC-03	35.8	812	167	2.69	11.4	255	17,300	62.1	0.8	92	0.1	2740
SC-05	3.4	2660	237	0.24	2.6	90	1700	37.2	1.3	14	<0.1	2440
SC-06	18.2	213	285	1.84	6.5	44	11,100	63.4	0.4	42	<0.1	2410
SC-07	30.6	1000	462	2.23	24.5	219	13,100	118.0	1.0	37	<0.1	12,300
SC-09-1	84.3	551	410	1.48	26.4	264	21,600	39.6	1.5	39	<0.1	6840
SC-09-2	44.7	356	619	1.12	10.0	173	17,300	32.7	1.2	23	<0.1	2610
SC-09-3	49.0	640	537	1.04	16.7	171	15,500	35.3	1.0	27	0.1	5240
SC-10	46.1	581	473	0.87	40.7	305	15,800	44.8	1.1	26	<0.1	8180
						Calcines						
PV-01	13.0	452	1280	0.44	0.5	80	3820	56.4	0.1	9	<0.1	938
PV-05	17.7	662	1080	0.97	0.7	90	5950	87.7	0.8	16	0.1	618
SC-11*	12.4	316	149	0.40	5.4	123	2900	18.1	0.5	11	<0.1	461
SC-12*	34.5	744	1480	0.06	5.0	135	9110	80.1	1.0	11	<0.1	791
SC-13*	3.8	75	685	0.25	7.0	46	1720	27.3	0.6	6	<0.1	1060
						Soils (topsoil)						
PV-02**	0.7	58	485	0.17	1.1	27	353	10.3	1.1	4	0.1	396
PV-03-1**	4.7	154	413	0.06	0.7	40	1040	30.6	1.2	7	0.1	331
PV-03-2**	4.0	189	774	0.18	32.8	131	1330	29.6	1.2	11	0.1	624
PV-03-3**	13.3	299	490	2.44	2.9	80	2600	43.7	1.7	24	<0.1	563
PV-04**	36.0	680	6050	0.61	11.3	95	4820	174.0	2.0	12	<0.1	2090
SC-01**	6.4	288	338	<0.02	18.6	259	3950	20.1	1.4	20	0.1	3850
SC-04**	8.5	170	603	0.51	31.5	84	6010	64.1	1.8	48	<0.1	5250
SC-08-1A**	0.4	98	1100	0.06	7.6	45	235	40.5	1.2	10	<0.1	706
SC-08-1B**	0.4	83	1130	<0.02	7.6	41	243	38.6	1.1	9	0.1	712
SC-08-2**	2.5	109	1190	0.09	9.4	39	908	53.4	1.2	14	<0.1	1010
SC-09-4**	6.4	224	1390	0.22	18.0	76	3560	86.2	1.1	14	<0.1	3030
SC-14***	11.9	297	1910	0.12	12.5	109	5550	99.1	1.1	13	0.1	3890
						Stream sediments						
RS-01	0.1	15	313	<0.02	0.2	20	80	1.2	0.6	3	<0.1	73
RS-02	0.2	16	231	<0.02	0.3	15	63	1.4	2.4	3	<0.1	60
RS-03	24.8	406	594	2.54	10.5	398	10,100	70.3	1.1	33	<0.1	3400
RS-04	1.6	42	296	0.02	4.0	56	592	7.3	1.2	5	<0.1	838
						Topsoil from volcanic outcrops: local baseline concentrations						
LB-01	0.3	83	3070	1.51	0.3	103	181	1.9	0.7	12	0.1	110
LB-02	0.1	20	2650	0.15	0.1	21	97	0.9	0.5	6	<0.1	58
LB-03	0.2	15	413	0.41	0.5	42	201	3.3	0.6	3	<0.1	143

arsenopyrite, cinnabar, stibnite, and berthierite. Secondary minerals include cerusite, anglesite, smithsonite, azurite and malaquite, whereas gangue minerals include quartz, calcite, siderite, dolomite and gypsum (Arana, 2007). The ore was deposited along major vein and stockwork systems. Ore reserve estimation during the 1990s (Rodríguez and Hidalgo, 1997) indicated reserves (San Cristóbal–Perules sector) in the order of 11 Mt at 2.59% Zn, 0.57% Pb and 16.6 g t^{-1} Ag.

Given that heavy metal contamination in Mazarrón district is strongly related to the mining and metallurgical operations, it is worth a brief description of the most relevant aspects of these activities. Different from other, better documented mining districts from SE Spain, the information on Mazarrón is both scarce and scattered. We know that at San Cristóbal–Perules mining was mostly underground and that shafts and galleries reached ~ 500 m of depth (Arana, 2007), whereas for Pedreras Viejas the only available information concerns the old Roman works (pits and trenches) (Martínez Alcalde, 2005). However, the existence of a shaft collar (Mazarronera mine; Martínez Alcalde, 2005) indicates that underground mining must have taken place at Pedreras Viejas in relatively modern times (late 19th–early 20th Century). Four different mineral processing procedures were used at the district: 1. Calcination of alunite rich altered rocks to obtain alum, a potassium aluminium

sulphate ($KAl(SO_4)_2 \cdot 12H_2O$). Alum was extracted in Roman time and reached peak production during the 15th to 16th Centuries (Manteca Martínez et al., 2005). From 1774 onwards the mineral processing activity focused on the alum waste: the so-called *almagres* (Ayuntamiento de Mazarrón, 2008), a deep red coloured material rich in iron oxides, metals (Pb–Zn), and metalloids (As). 2. Gravity concentration of galena using jigs. 3. Reverberatory smelting of galena rich ore to obtain lead metal, which must have started in 1886 when two large furnaces were installed at San Cristóbal–Perules (Agüera Martínez et al., 1993). 4. It was not until 1951 (and up to 1963) that zinc was selectively extracted from the Mazarrón ores (Manteca Martínez et al., 2005), although we lack definitive information regarding 'the how and where' the ore was processed. However, it is likely that the tailings that pervade the San Cristóbal–Perules area correspond to this period. Whatever the case, if something characterizes both San Cristóbal–Perules and Pedreras Viejas is the colourful aspect of the area affected by the mining-metallurgical works. These sectors are characterized by the chaotic piling of metal and metalloid rich tailings and other mining wastes, with colours that range from purple to red and yellow, thus revealing the importance of oxidation processes, either natural or anthropically induced, or a combination of both.
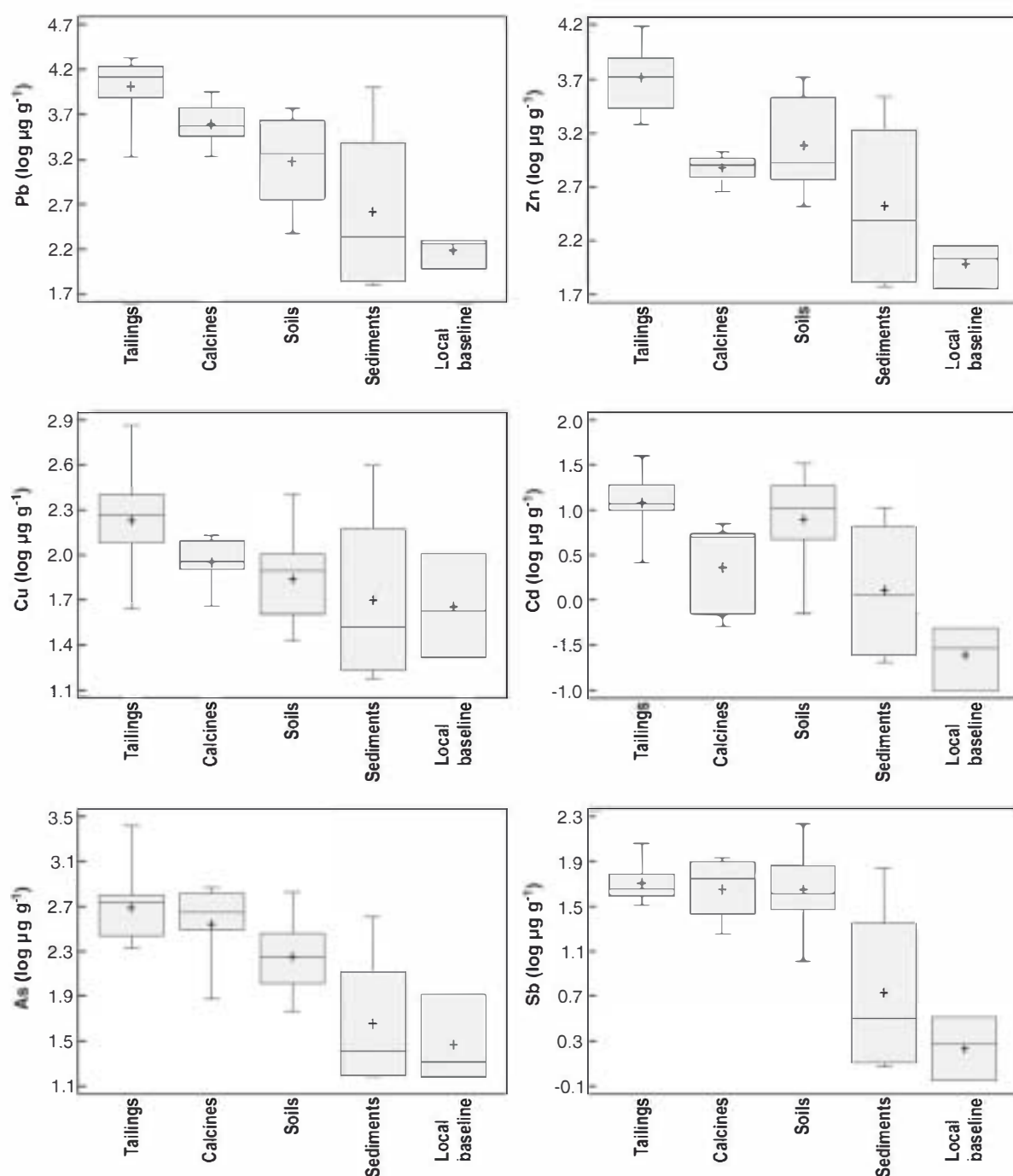
Fig. 3. Box-and-whisker plot for different data sets and elements. The central box covers the middle half of the data, extending from the lower to the upper quartile. The lines extending above and below the box (whiskers) show the location of the smallest and largest data values. The median of the data is indicated by the horizontal line within the box, whereas the plus sign (+) shows the location of the sample geometric mean. Concentration data: $\log_{10}$.

3. Materials and methods

Special consideration was given to the criteria used for the selection of sampling sites in the San Cristóbal–Perules (SC samples) and Pedreras Viejas (PV samples) area (Fig. 2). Given that the topsoil is the most important part of the soil profile for degradation control (Spaargaren and Nachtergaele, 1998), we took samples from the first 30 cm in areas that were directly or indirectly affected by mining and metallurgical activities. These are anthrosols, i.e., soils that have undergone profound modification by human activities. Other, soil-like materials in the district fall into the category of technosols (Rossiter, 2005), that is, we are dealing with relatively recent deposits of artificial origin, including

tailings and calcines. Stream sediment samples were taken along the Rambla de La Morera, up and downstream the location of the San Cristóbal–Perules (RS samples) (Fig. 1B). We also took three samples of topsoil from volcanic outcrops near to the town of Mazarrón (but away from the mining sites) to serve as a local baseline for metal and metalloid concentrations (LB samples) (Fig. 1B). The geochemical survey was carried out in May 2008 and 37 samples were taken (Figs. 1B, 2) (Table 1); 13 corresponding to tailings, 5 to calcines, 12 to soils, 4 to stream sediments, and 3 to local baselines (topsoil). Based on the mineralogy of the Mazarrón deposits and that of the mine wastes, we chose for this study the following list of chemical elements: Ag, As, Ba, Bi, Cu, Cd, Pb, Sb, Se, Sn, Te, and Zn. The samples (~2 kg) were stored in

Table 2

Arithmetic mean (above) and geometric mean (in italics, below) of trace element concentrations for the different data sets. See Figs. 1 and 2 for location of samples. For statistical calculations a concentration half of that of the detection limit (DL/2) was assigned to the elements with concentrations below DL (e.g., Singh and Nocerino 2002). Corg: organic carbon.

Element ($\mu g\,g^{-1}$)	Ag	As	Ba	Bi	Cd	Cu	Pb	Sb	Se	Sn	Te	Zn	Corg (%)	pH	Reference
Mazarrón mining district and neighbouring areas															
All samples	18.1	378.4	890.0	0.80	10.4	135.0	6124.9	48.1	1.08	20.5	0.08	2981.7	1.07	5.76	This work
	6.0	*208.3*	*585.3*	*0.33*	*4.8*	*92.7*	*2446.6*	*28.9*	*0.96*	*14.8*	*0.07*	*1338.9*			
Tailings	36.0	654.1	370.5	1.34	15.0	218.4	12,400.8	56.5	1.07	34.8	0.10	6101.5	1.09	2.97	
	26.0	*497.0*	*338.1*	*1.09*	*11.9*	*174.3*	*10,303.9*	*51.8*	*1.00*	*31.5*	*0.07*	*5119.8*			
Calcines	16.3	449.8	934.8	0.42	3.7	94.8	4700.0	53.9	0.60	10.6	0.06	773.6	0.82	5.79	
	13.0	*350.4*	*731.0*	*0.30*	*2.3*	*88.7*	*4006.9*	*45.5*	*0.47*	*10.1*	*0.06*	*741.4*			
Soils	7.9	220.8	1322.8	0.41	12.8	85.4	2549.9	57.5	1.34	15.5	0.07	1871.0	1.10	7.45	
	3.8	*177.8*	*920.0*	*0.16*	*7.9*	*69.9*	*1517.2*	*44.8*	*1.31*	*12.8*	*0.07*	*1227.0*			
Stream sediments	6.7	119.8	358.5	0.65	3.7	122.2	2708.6	20.1	1.33	11.0	0.05	1092.7	1.06	7.88	
	1.1	*45.1*	*335.8*	*0.05*	*1.3*	*50.7*	*415.5*	*5.4*	*1.17*	*6.2*	*0.05*	*333.8*			
Baseline	0.2	39.4	2044.3	0.69	0.3	55.3	159.6	2.0	0.60	7.0	0.07	103.6	1.34	8.49	
	0.2	*29.3*	*1497.7*	*0.45*	*0.2*	*44.8*	*152.1*	*1.8*	*0.59*	*6.0*	*0.06*	*96.8*			
Rodalquilar mining district (Almería, SE Spain)															
Anthropic soils		179.6		3.1	0.5	84.9	410.7	10.3	6.9	10.8	2.7	241.7			Oyarzun et al. (2008)
Cabezo Rajao (Murcia, SE Spain)															
Soils and mine wastes		315			41	332	8000					12,500			Navarro et al. (2008)
World averages for soils and stream sediments															
Selected average for soils		5.8			0.06–1.1	13–24	32		0.33						Alloway (2005)
World soils					0.06	22	30					66			Callender (2004)
Stream sediments					1.57 ±1.27	39 ±13	51 ±28					132 ±67			Callender (2004)
Suspended sediment in World rivers	36.3	522		0.85	1.55	75.9	61.1	2.19		4.57	0.54	208			Viers et al. (2009)

plastic bags, sieved at the Almadén School of Mines (ASM; Universidad de Castilla La Mancha), and sieved at the Almadén School of Mines (ASM) laboratory below Tyler mesh 80 (0.180 mm). Part of the sample was sent to Activation Laboratories Ltd. (Actlabs; Canada) to be analyzed by TD (Total Digestion) ICP-MS (Inductively Coupled Plasma-Mass Spectrometry). Quality control at the Actlabs laboratories is done by analyzing duplicate samples and blanks to check precision, whereas accuracy is obtained by using certified standards (GXR series; e.g., Gladney and Roelandts, 1990). Detection limits for the analyzed elements are (data in $\mu g\,g^{-1}$): Ag (0.05), As (0.1), Ba (1), Bi (0.02), Cd (0.1), Cu (0.2), Pb (0.5), Sb (0.1), Se (0.1), Sn (1), Te (0.1), and Zn (0.2).

The analytical procedures include the following: a 0.25 g sample is digested at 260 °C with four acids beginning with hydrofluoric, followed by a mixture of nitric and perchloric acids, heated using a precise programmer, controlled heating in several ramping, and holding cycles, which take the samples to dryness. Elements are determined by ICP-MS on the multi-acid digest solution. The samples are analyzed on a Perkin Elmer ELAN 9000 ICP-MS. Besides, an aliquot of each soil sample was kept at the ASM laboratory for the analysis of organic carbon and determination of pH following the International Soil Reference and Information Centre (ISRIC) standard procedures (Van Reeuwijk, 2002). Pb and Zn were also checked by ICP-OES (Inductively Coupled Plasma Optical Emission Spectrometry). The mineralogy and mineral chemistry of soils were studied by XRD (instrument: Philips, model PW3040/00 X'Pert MPD/MRD) and ESEM-EDX (instrument: Philips XL30; 25 kV) at the CAT facilities of Universidad Rey Juan Carlos (Madrid). Statistical data processing was done with the program Statgraphics Plus 5.1.
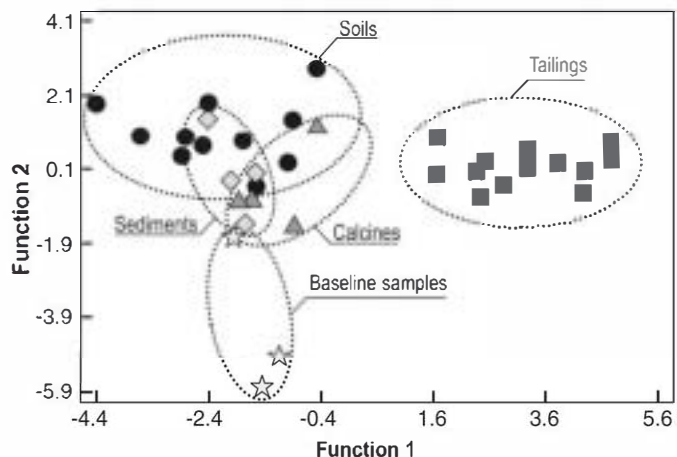

Fig. 4. Discriminant function analysis (DFA) for multiple groups of data sets from Mazarrón: baseline, calcines, soils, stream sediments and tailings. DFA is used to determine which variables discriminate between naturally occurring groups. Besides, the functions are used to classify the observations into groups. In this case, Function 1 is: $-0.160563*Ag+0.807617*As+0.133569*Ba-0.253285*Bi-0.711438*Cd-0.938409*Cu+1.47848*Pb-0.864559*Sb-0.127225*Se+0.421736*Sn+0.643715*Te+1.40769*Zn$; whereas Function 2 is: $0.309359*Ag-0.0709002*As-1.53156*Ba-0.381248*Bi+0.504243*Cd-0.290314*Cu-0.0852466*Pb+1.84778*Sb+0.478893*Se-0.130142*Sn+0.293615*Te-0.868659*Zn$. DFA coefficients are standardized.
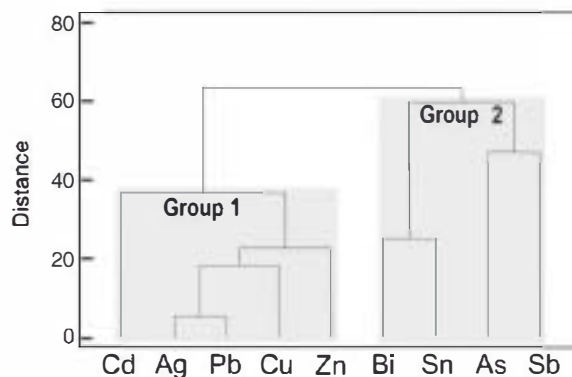

Fig. 5. Dendrogram (clusters by group average; distances: squared euclidean) for all data sets, showing the existence of two well-differentiated groups of elements. Group 1: elements that define the metallic signature of the district. Group 2: elements associated to the Group 1 but of minor importance (with the exception of As) in the mineral assemblage.

Table 3
Correlation matrix ($R>0.5$) for element concentrations ($\log_{10}$) from all data sets from Mazarrón.

	Ag	As	Cd	Cu	Pb	Sb	Sn
As	0.85						
Cd	0.69	0.58					
Cu	0.80	0.75	0.67				
Pb	0.98	0.84	0.72	0.82			
Sb	0.81	0.80	0.74	0.59	0.80		
Sn	0.75	0.72	0.67	0.73	0.82	0.65	
Zn	0.82	0.73	0.86	0.77	0.87	0.79	0.79

4. Results and discussion

4.1. General

Trace element concentrations in the samples of tailings, calcines, soils, and stream sediments are shown in Fig. 3 and Table 1, whereas mean concentrations from Mazarrón, other mining districts, and world averages are displayed in Table 2. The discriminant function analysis for multiple groups shows a clear separation of the tailings deposits whereas the soils, calcines and stream sediments sets partially overlap (Fig. 4). The dendrogram (cluster analysis) shows the existence of two main groups of elements (Fig. 5). Group 1 consists of the elements that define the metallic signature of the district (Pb-Ag, Zn–Cd, and Cu to a certain extent), whereas Group 2 hosts elements such as Bi, Sn and Sb that are found in accessory minerals from the mineral paragenesis. Several facts arise from the statistical analysis of the data sets: 1. There are important correlations between element pairs (Table 3). Two of the highest correlations are found for the pairs Pb-Ag ($R=0.98$) and Pb–Zn ($R=0.87$). The former is to be expected because as indicated above, galena is the Ag-bearing mineral phase, whereas the second one corresponds to the classic metallogenic association between these two metals. From an environmental point of view two correlations are particularly significant, those of Zn and Cd ($R=0.86$) and Cu and As ($R=0.75$). Cd is well known as being one of the most ecotoxic metals, and has a higher mobility than Zn in acid environments (Kabata-Pendias, 2001). Compared to the World soils average (Table 2) Cd concentrations in the tailings are 250 times higher, and those in anthropic soils are 213 times higher. 2. Elements such as As, Pb and Zn (among others) are extremely enriched in the Mazarrón samples respect to both our local baseline (LB) and world averages. While this fact was expected for the tailings and calcines (both being by-products of metallurgical procedures) the concentrations of metals and metalloids in either stream sediments or soils are still too high compared to the baseline and world averages, and even the local baseline is high compared to the latter (Fig. 3) (Table 2). This is not surprising for a long-lived mining-metallurgical site such as Mazarrón, because as indicated by Ownby et al. (2005), many environmental problems worldwide can be attributed to past metal mining and smelting activities. On the other hand, we must also take into account the geologic (natural) factors that induced metal dispersion in the area, such as pervading hydrothermal activity during Miocene time, and later, oxidation processes. Thus, we are dealing with a combination of factors that strongly contributed to widespread natural and anthropic dispersion of metals and metalloids throughout the district.

4.2. Environmental hazards at Mazarrón: geologic and anthropic factors

As observed elsewhere in similar settings (Oyarzun et al., 2007; Oyarzun et al., 2008), key factors controlling the environmental behaviour of epithermal mineral deposits include ore and gangue mineralogy, host rock lithology, fracturing, wall-rock alteration and climate, which influence the chemical response of mineral deposits. The Mazarrón ore deposits have a strong and extensive advanced

Fig. 6. Major potential environmental hazards in the study area. Note the change in colour (light grey to reddish) along Rambla de las Moreras from A to B as tailings and calcine materials become incorporated to the stream sediments. SCP: San Cristóbal-Perules. Agricultural Lands (AL): past or present activity.
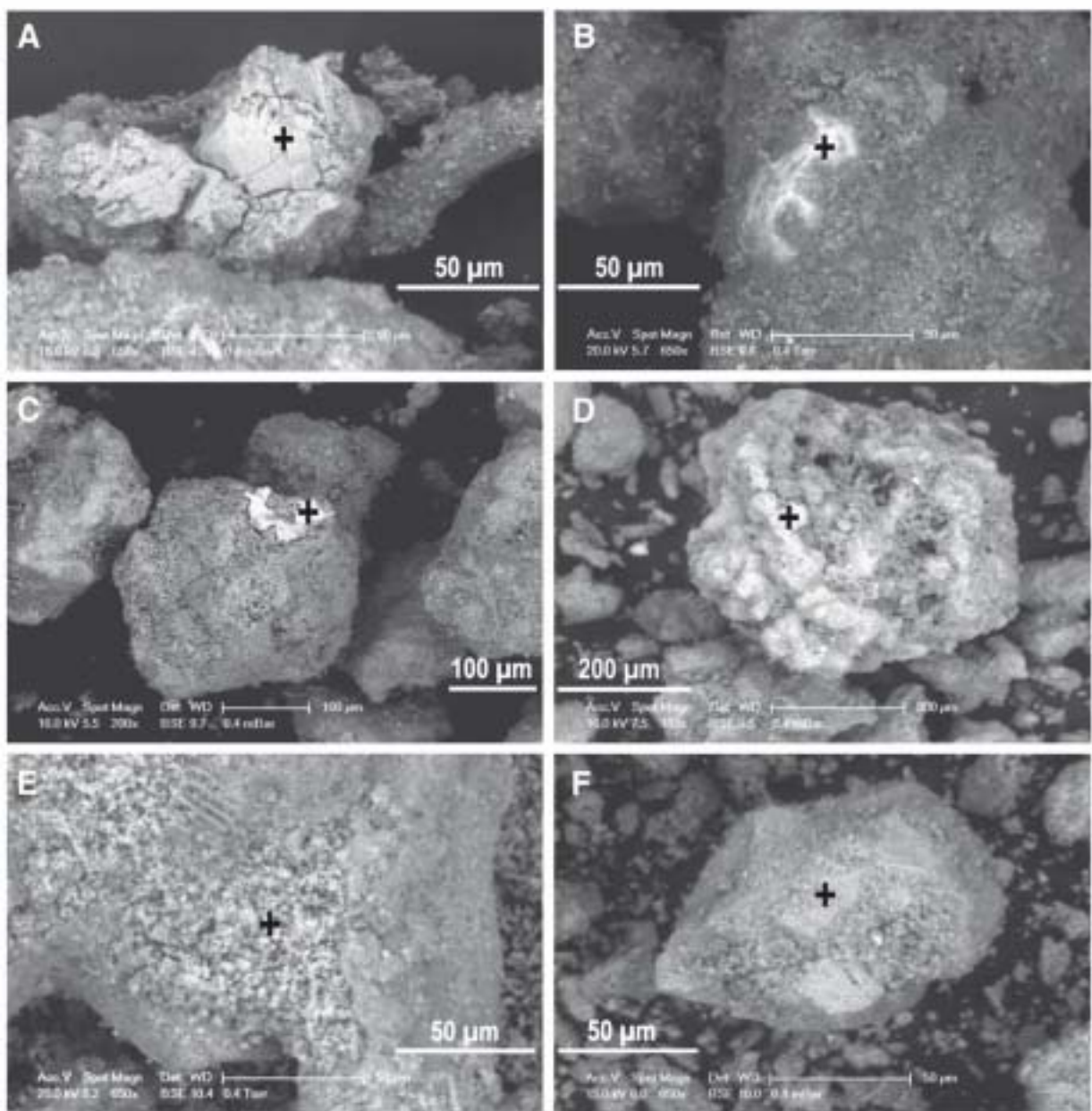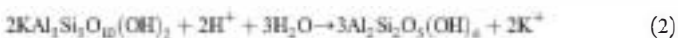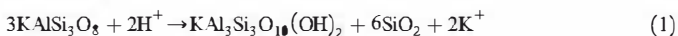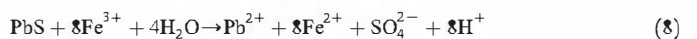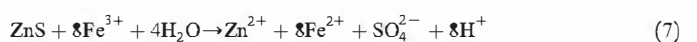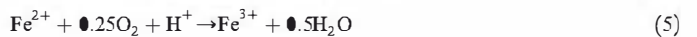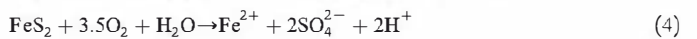
Fig. 7. BSE images of mineral grains from samples of tailings (TA) and calcines (CA). A: SC-10, pyrite (TA); Acc. V: 16 kV. B: SC-9, galena (TA); Acc. V: 20 kV. C: SC-10, sphalerite (TA); Acc V: 16 kV. D: SC-10, Zn-Fe sulphate (TA); Acc. V: 16 kV. E: SC-5, As bearing goethite-like grain (TA); Acc V: 20 kV. F: SC-12, As bearing goethite-like grain (CA); Acc V: 15 kV. The cross (+) indicates EDX point analysis.

argillic alteration zone. As shown for the Rodalquilar district (Oyarzun et al., 2008), this has profound implications regarding metal dispersion, because this type of alteration greatly decreases the acid buffering capacity of the host rocks (Plumlee, 1999; Plumlee et al., 1999; Oyarzun et al., 2007). Enhanced hydrolysis during hydrothermal activity leads to the destruction of feldspars, through subsequent formation of sericite (1), kaolinite (2), and even alunite (3) if H_2SO_4 is present in the system (Montoya and Hemley, 1975), which is common in high sulphidation (acid sulphate) systems (Heald et al., 1987). The chemistry of these processes can be summarized in the following way:

$$3KAlSi_3O_8 + 2H^+ \rightarrow KAl_3Si_3O_{10}(OH)_2 + 6SiO_2 + 2K^+ \tag{1}$$

$$2KAl_3Si_3O_{10}(OH)_2 + 2H^+ + 3H_2O \rightarrow 3Al_2Si_2O_5(OH)_4 + 2K^+ \tag{2}$$

$$KAl_3Si_3O_{10}(OH)_2 + 4H^+ + 2(SO_4)^{2-} \rightarrow KAl_3(SO_4)_2(OH)_6 + 3SiO_2 \tag{3}$$

This is particularly relevant to the case of high sulphidation epithermal deposits (such as those of San Cristóbal–Perules and

Pedreras Viejas), which are rich in pyrite and other sulphides. Thus, when oxidation of pyrite begins in an already weathered hydrothermal environment, no minerals are available to react with the acid generated during the oxidation of pyrite (4–6), which greatly increases metal mobility from other sulphides, such as sphalerite (7) and galena (8) (Seal and Hammarstrom, 2003):

$$FeS_2 + 3.5O_2 + H_2O \rightarrow Fe^{2+} + 2SO_4^{2-} + 2H^+ \tag{4}$$

$$Fe^{2+} + 0.25O_2 + H^+ \rightarrow Fe^{3+} + 0.5H_2O \tag{5}$$

$$4FeS_2 + 10H_2O + 15O_2 \rightarrow 4FeO(OH) + 16H^+ + 8SO_4^{2-} \tag{6}$$

$$ZnS + 8Fe^{3+} + 4H_2O \rightarrow Zn^{2+} + 8Fe^{2+} + SO_4^{2-} + 8H^+ \tag{7}$$

$$PbS + 8Fe^{3+} + 4H_2O \rightarrow Pb^{2+} + 8Fe^{2+} + SO_4^{2-} + 8H^+ \tag{8}$$

Zn and Pb carbonates (smithsonite and cerussite respectively) will form if enough alkalinity is present in the circulating groundwater (Blanchard, 1968).

The decrease in the acid buffering capacity of the Mazarrón host rocks (1–3) and oxidation of pyrite (4–6) results in widespread formation of acid mine drainage (AMD). Seasonal pools of deep red–orange AMD waters are usually formed on top of San Cristóbal–Perules tailings deposits (Fig. 6). In this respect, dry and rainfall events cause increases and decreases, respectively, in acid and metal concentrations. Besides, the process does not end until pyrite is fully weathered, which can take hundreds to thousands of years (Nordstrom, 2009). As noted by Nordstrom (2009), long dry spells result in gradual increases in concentrations, whereas sudden large increases are observed during initiation of rains. However, as precipitations reach their peak, the solutions become diluted. Thus, it is the initiation of the typical Mazarrón stormy episodes that can cause the highest rates of metal mobilization.

The ESEM–EDX study of samples from the tailings showed the existence of a variety of mineral oxidation states. Both pyrite and Fe oxides/hydroxides are found in the waste deposits and the same applies to sphalerite and Zn–Fe sulphates (Fig. 7A–D), whereas As is bound to Fe oxides/hydroxides (Fig. 7E). Besides, the XRD study revealed the existence of more mineral phases in the tailings, including alunite, anglesite, jarosite and Pb-jarosite, hematite, goethite, gypsum, montmorillonite, and illite.

The tailings deposits pose a series of environmental concerns. In the first place they are to be regarded as heavy metal reservoirs. Second, there is a potential for mass movement phenomena during flash flood episodes (Fig. 8A, B). A third concern relates to the agricultural activities that have taken place on top of these materials. We found evidence of past agricultural activities on thin ploughed soil (metal-rich sample SC-14) barely covering tailings deposits adjacent to San Cristóbal–Perules (Fig. 8C). Given the high metal content of the tailings these agricultural practices may have posed a risk to human health. Besides, the soils from the district and adjacent areas are also metal rich and constitute an environmental hazard by themselves. These anthrosols have a main mineralogy constituted by quartz, K feldspar, calcite, montmorillonite, illite, kaolinite, and Mn and Fe oxides.

The calcines (Figs. 6, 9A) (Table 2) form a third group of hazardous materials in the district. As explained above, there has been an important although intermittent processing industry based on the alum waste that continued until 1953 (Manteca Martínez et al., 2005). We found calcination furnaces both in Pedreras Viejas and San Cristóbal–Perules. These calcines (locally known as *almagres*) were used as pigments and at present, abandoned deposits of these materials pervade the area. The calcine piles are rich in metals and metalloids (Table 2), and one of the main environmental concerns relates to the indiscriminate present usage of these materials, which includes the use as 'agricultural soils' in almond orchards (Figs. 6, 9B). We must take into account that these materials are not only rich in Pb and Zn but also in As (Fig. 3) (Table 2). As shown by the ESEM–EDX study, at least part of the arsenic is bound to a Fe oxide/hydroxide phase (Fig. 7F). Colloidal goethite has a net positive charge in acid media (e.g. Seaman et al., 1997), which binds the negatively charged arsenic complex ions by adsorption. These complex ions may remain strongly bound to goethite up to higher pH of 8.0–8.5 (Davis and Kent, 1990; Smith, 1999; Smedley and Kinniburgh, 2002). Desorption of arsenic from goethite may occur by competition between negative charges for the positive colloid, a reduction of the iron oxide mineral phase (Meng et al., 2002), or high pH values (>8.5). Given that redox conditions in the calcines must be rather oxidative (as suggested by the very low contents of organic matter; Table 2), reduction does not

Fig. 8. Tailings deposits in the San Cristóbal–Perules area. A: Note the strong erosion in both deposits. B: Detailed view of erosion processes in the tailings. C: Thin agricultural soil on top of tailings deposits (at the base of the left tailings shown in A).
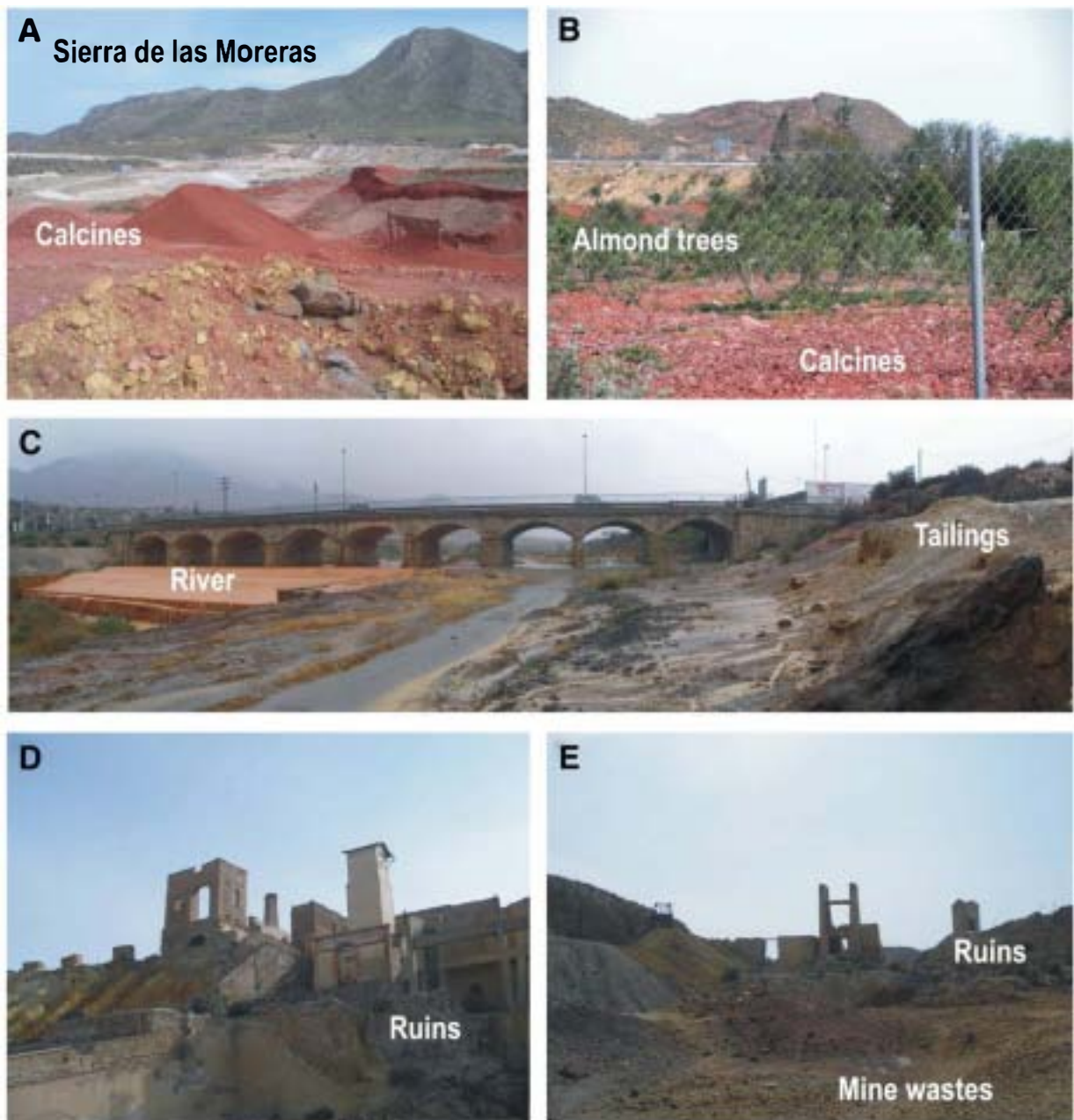
Fig. 9. A: Mechanical screening of calcines for unknown purposes near to Pedreras Viejas. B: Almond trees orchard with calcines as agricultural soil (near to San Cristóbal–Perules). C: Mechanical transport of abandoned tailings deposits to the Rambla de las Moreras outside Mazarrón. Picture taken on the 8th of May 2008, during early stages of flash flood phenomena in the Mazarrón area. Note the brown-reddish colour of the waters. D: Ruinous state of abandoned buildings in the San Cristóbal–Perules mining site. E: Ruins from the old mining operations intermingled with metal- and metalloid-rich abandoned mine wastes (San Cristóbal–Perules).

seem to be a plausible mechanism for As desorption. Besides, the mean pH (5.8) seems low enough to keep As bound to goethite (Table 2). However, as indicated above, the calcines are also used as agricultural soil, at least in two different sites in Mazarrón. If plants (in this case almond trees) are present, then we have to consider another possibility: the chemical interactions that may take place in the soil–rhizosphere–plant system. According to Fitz and Wenzel (2002), both plant-induced reductions and drastic pH decreases in the rhizosphere may dissolve Fe oxides/hydroxides. This would result in the release of As and the potential uptake by the plant of As^{3+} (enhanced bioavailability and toxicity to plants) (Fitz and Wenzel, 2002).

The sediments from the main watercourse of the area (Rambla de las Moreras) provide a fourth major environmental hazard. The river receives materials from the tailings deposits of San Cristóbal–Perules, and a conspicuous change in colour (to reddish brown) reveals the area

of influence of this southward, mechanical down slope transport (Fig. 6). The transport of these highly contaminated sediments to the river, and their incorporation to the silty-sandy sedimentary phase results in high concentrations of Pb and Zn (Table 2). The problem is aggravated by the abandoned tailings resting just outside the town of Mazarrón, which during strong rainy episodes are easily removed and transported into the river (Fig. 9C). The stream sediment sample RS-4, that was taken right in front of the river mouth (Mediterranean coast) still has very high concentrations of Pb (590 $\mu g\, g^{-1}$) and Zn (840 $\mu g\, g^{-1}$) that are well above any baseline values (Table 2).

From the visitor perspective, the abandoned mining buildings are all in very poor conservation conditions (Fig. 9D) and pose a risk to visitors. Besides, it is not only the ruinous state of the buildings, but also the widespread presence of heavy metal-rich mine wastes that poses a final risk for the visitors. Anthropic soils and wastes from the

site are not only Pb–Zn rich but also have high contents of As. There are yet two remaining major environmental concerns. As previously discussed mineral wastes and agricultural activities overlap in the district. Given the high metal and metalloid contents of these wastes, agricultural practices should be reanalyzed from an ecotoxicological perspective. The same applies to the intimate spatial relationship between the San Cristóbal–Perules mining site and the town of Mazarrón. In this respect it is important to learn from the lessons of the past, for example, the Pb poisoning incident that took place in the city of Antofagasta (Chile). Lead was gathered in bulk (Pb concentrates from Bolivia) within an urban zone of the city, which resulted in severe contamination of the surrounding schools and houses. This contamination was in turn significantly associated with high blood lead levels (Sepúlveda et al., 2000).

5. Conclusions

Mineral deposits must be regarded as hot spots for long-lived metal contamination. However, whatever the degree and extent of the natural dispersion of metals and metalloids, the mining (anthropic) factor, involving from the relatively harmless road construction works to the truly damaging metallurgical operations, strongly aggravates the environmental risks (Oyarzun et al., 2008). In this respect, the Mazarrón district is to be regarded as an extremely polluted land site. The high Pb–Zn–(As–Cd) concentrations found in the tailings, calcines, anthropic soils and stream sediments support this argument. Some of the Pb–Zn concentrations in the tailings reach economic grades, thus these deposits are not to be regarded as 'barren' but as highly enriched mine wastes. The Cd concentrations in the tailings and soils are up to 250 times larger than those of world averages for the element. Furthermore, Cd is highly correlated with Zn, a metal widely distributed in high concentrations in the tailings and soils. The high concentrations of As found in both the tailings and calcines pose an additional and important environmental hazard, particularly considering that these materials are used at discrete areas as agricultural soil. Also to be highlighted are the contaminated (Pb–Zn) sediments of the river, which discharges its suspended solids directly to the Mediterranean, only a few kilometres southward from San Cristóbal–Perules. Finally, although the mere existence of this highly polluted mining district poses a serious environmental hazard, the fact that the town of Mazarrón is juxtaposed to the mining wastes and old mining installations of San Cristóbal–Perules considerably aggravates the case. A sound policy on land reclamation is urgent for the whole area. In this respect, 'garden-like restoration' of a polluted site will not solve the many environmental hazards associated with heavy metals and metalloids, neither at Mazarrón nor anywhere else where equivalent conditions are found. We may hide the contaminated land with clean topsoil, we may even plant some flowers and trees, but the problem will not fade away. Besides if erosion is not kept at bay, the metals will eventually find their way to the water courses. Given that the region is occasionally subjected to strong flash flood phenomena, the latter is likely to happen. Finally, we must also take into account the upward migration of metal-rich solutions via capillary forces in arid, or semiarid climates (e.g., Meza-Figueroa et al., 2009) such that of Mazarrón, which results in metal enrichment of the topsoil horizon.

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