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Chapter

Geoenvironmental Characterization of Sulfide Mine Tailings

Tomás Martín-Crespo, David Gómez-Ortiz and Silvia Martín-Velázquez

Abstract

Spain has a long mining tradition dating from pre-historic times up to the present day. The cessation of mining activity has generated a large amount of mine wastes, most of which represent geochemical hazards. Mine tailings are watery sludge composed of medium-to-fine-grained material, resulting from grinding and mineral processing (e.g., galena, pyrite, sphalerite, and arsenopyrite). They entail both an accumulation and a potential subsequent emission source of trace elements (i.e. As, Cu, Fe, Pb, and Zn) with formation of acid mine drainage (AMD). Mineralogical and geochemical techniques (in combination with geophysical surveys and aerial photographs studies) have been jointly applied to selected mine areas. Seven mine deposits from the most important mine districts in Spain have been selected: Iberian Pyrite Belt, Cartagena-La Unión, Alcudia Valley, and Mazarrón. The main goal is focused on getting a geoenvironmental characterization as complete as possible by determining the geometry, evolution in time and composition of mine ponds, and the possible occurrence of AMD, for identifying related environmental hazards.

Keywords: mine tailings, mineralogy, geochemistry, geoenvironmental, Spain

1. Introduction

Sulfide ore minerals are generally concentrated by milling and flotation, which produces tailings containing gangue minerals and residual sulfides. Milling involves crushing and grinding to reduce particle size and liberate ore minerals from the rock matrix. After ore minerals have been extracted and concentrated, the resulting tailings are commonly dewatered and deposited in sub-aerial tailings, impoundments, or stockpiles [1]. They are piled up as less than 5 cm thick layers and are slightly differentiated by compositional and/or granulometric features. Although the metal content is removed in the metallurgic process, some ore sulfides (e.g. pyrite, galena, sphalerite, chalcopyrite, arsenopyrite, etc.) can be deposited, either because they were not sufficiently high-grade for use, or due to a deficient extraction technology. They entail both an accumulation and a potential emission source of trace elements (e.g., Cu, Fe, Pb, and Zn). Oxidation of the sulfide minerals accumulated in the abandoned mine tailings may cause: (a) highly contaminating acid mine drainage (AMD) from leakages and (b) mobilization of significant

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quantities of trace elements such as As, Cd, Cu, Hg, and Pb. It becomes necessary to identify and characterize these hazardous areas where large quantities of potentially toxic elements can be released into the environment. Mine ponds are, therefore, an important environmental problem, especially if they are abandoned.

Spain has a long mining tradition dating from pre-historic times up to the present day. A large amount of mine installations, galleries, and waste deposits were abandoned until the 1980s by the cessation of mining activity. Pollution from these sources can originate via mining spills, leakages, or wind-blown dust, and toxic elements with a high mobility can cause huge environmental problems: accumulation in flora and fauna, reducing the quality of streams and groundwater.

An inventory of the abandoned mine waste deposits has been prepared by the Spanish Ministry of the Economy, through the Directorate General of Energy Policy and Mining [2]. The most relevant contribution of the inventory consists in the classification of the existing mine waste deposits based on their hazard potential for infrastructure and the human population. Another significant aim is focused on providing a qualitative geotechnical and environmental assessment of the elements at risk and an associated description. Further knowledge of the current status of the highest potential risk deposits is required because of the preliminary nature of the inventory, carried out by means of visual surveys and without sampling or testing.

In summary, a complete geoenvironmental characterization of the affected areas is crucial for any proposal of effective measures that could help to minimize environmental impact and concern.

2. Study zones

Seven mine areas from the most important metallic mining district in Spain have been selected (**Figure 1**): La Naya, Monte Romero and Mina Concepción from Iberian Pyrite Belt [3, 4], Brunita from Cartagena-La Unión [5], San Quintín from Alcudia Valley [6], and San Cristóbal and Las Moreras from Mazarrón [7].

2.1 Iberian Pyrite Belt

One of the largest concentrations of massive sulfide mineralizations in the world is hosting at the volcano-sedimentary rocks of the Iberian Pyrite Belt, in the southwest (SW) of the Iberian Peninsula. The main ore mineral is pyrite, although lower quantities of sphalerite, galena, chalcopyrite, and arsenopyrite are also found. An intense mining activity in this province is related to the exploitation of S, Cu, Pb, Zn, Ag, and Au from the sulfide ore minerals. Different studies have pointed out the significant concentrations of certain trace elements in sediments and soils surrounding mining or waste sites in the Iberian Pyrite Belt district [8]. The waters of the Tinto and Odiel fluvial systems are also affected [9]. Remediation has only been conducted in a few of the mine areas, although they still display significant environmental issues [4]. In 1998, an environmental disaster occurred in the SW of Spain, when the tailing dam of one of the bigger mines from the district was ruptured. Around 2×10^6 m^3 of heavy metal-bearing sludge and ~4×10^6 m^3 of acidic waters were released [10].

Monte Romero (**Figure 1**) comprises two mine ponds located at the Cueva de la Mora mine site, where Pb- and Zn-bearing minerals were benefited [3]. La Naya (**Figure 1**) is a mine pond located to the southeast of Minas de Riotinto town, and is one of the largest deposits mined during the extensive works in this mining group. The main ores extracted were Cu-bearing minerals and pyrite. Another mine

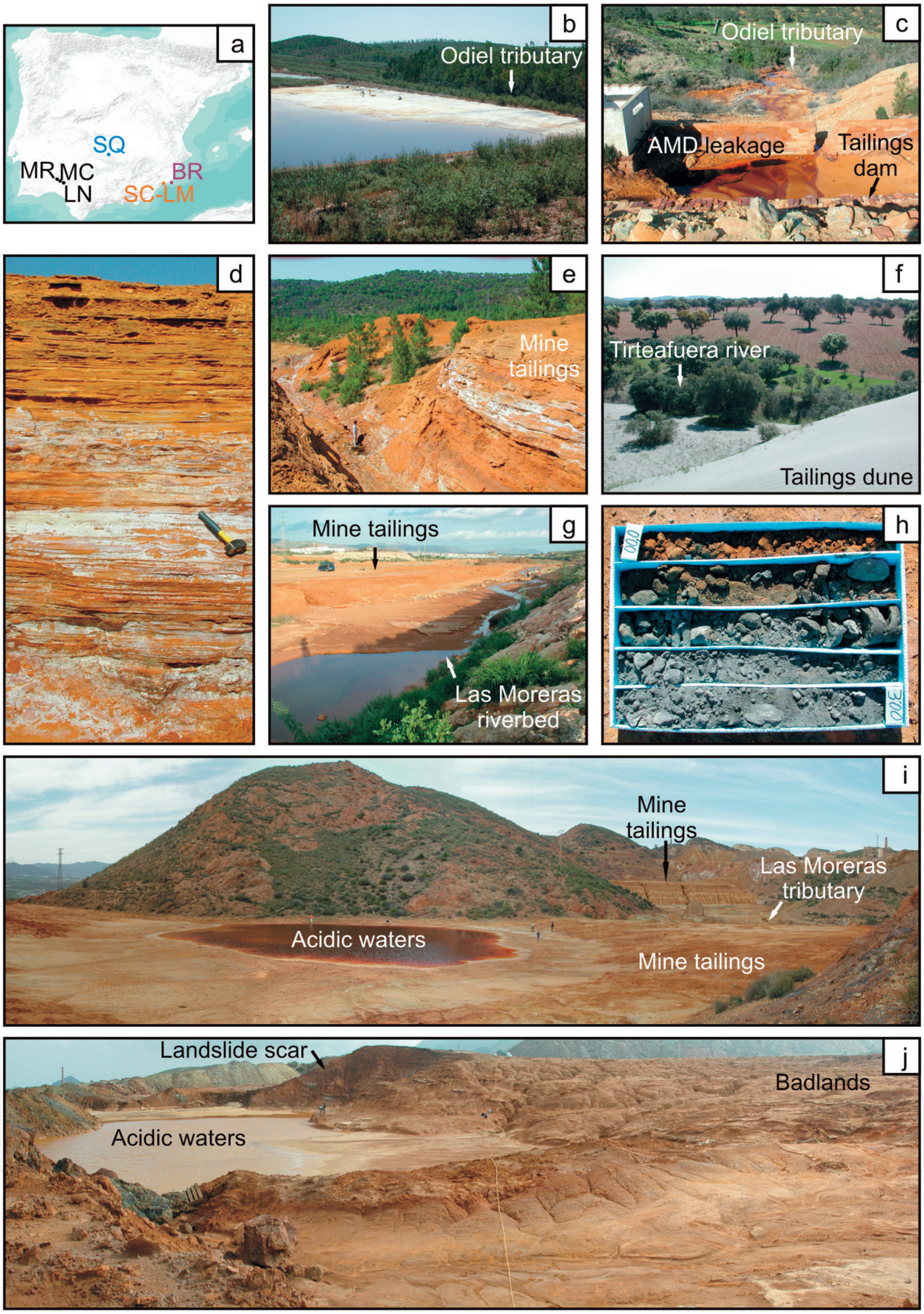

Figure 1.
Location and field photographs of the different studied mine areas: (a) location of the sulfide mine ponds in Iberian Pyrite Belt (LN—La Naya, MC—Mina Concepción, and MR—Monte Romero), Cartagena-La Unión (BR—Brunita), Alcudia Valley (SQ—San Quintín), and Mazarrón (SC—San Cristóbal and LM—Las Moreras); (b) Monte Romero; (c) acid leakage from Mina Concepción tailings; (d) detail of tailings in La Naya; (e) La Naya; (f) tailing dune in San Quintín; (g) Las Moreras; (h) borehole core samples from Brunita tailings; (i) San Cristóbal; and (j) Brunita.

site studied was Mina Concepción, a restored mine pond located on the SE of the Almonaster la Real village (**Figure 1**). Tailings from the metallurgical treatment and benefit of pyrite were piled up over metavolcanic lithologies [4]. The contention dyke retaining them is 8 m high, and three collector pipes going through the dyke controlled the drainage. The physical restoration and the landscape integration of the mine pond were achieved by sealing and reforestation with pine trees, substituting the original vegetation.

2.2 Cartagena-La Unión

One of the most significant places of geochemical pollution and geotechnical instability in Spain's abandoned mining heritage is the Cartagena-La Unión district, southeast of Spain [2]. The Brunita mine pond is one of the numerous tailing deposits in the district, affecting the surrounding watercourses that reach La Manga coastline, a major tourism location in SE Spain. Human beings, fauna, flora, groundwater, and agricultural soils are negatively stilted [5].

The mine tailings were produced from grinding and metallurgical treatment of mineral from Eloy and Brunite mines between 1952 and 1981 [2]. The main ore minerals are pyrite, sphalerite, galena, marcasite, and pyrrhotite. Other minor sulfides include arsenopyrite, minerals of the tetrahedrite-tennantite group, chalcopyrite, and stannite [11]. In October 1972, an extreme rainfall event caused damage in the Brunita mine pond (**Figure 1**). A tailing flash flood killed one person and caused serious material damage. As a result, a retaining wall of the coarse-grained tailings was built. Since 1981, when the mine was closed, no further works on restoration or reclamation have been carried out.

2.3 Alcudia Valley

The San Quintín abandoned mine area, located at the Alcudia Valley (Ciudad Real province, Spain), is crossed by the Don Quixote Route [12], a tourist set of itineraries created in 1995 to celebrate the IV Centenary of the publishing of "El ingenioso hidalgo Don Quijote de La Mancha". This route, the longest ecotourist route in Europe, was recently declared as Cultural Itinerary by the Council of Europe. It could soon reach the rank of Humanity Heritage because of its high cultural and environmental quality. These features make the San Quintín area a busy tourist route, and the environmental characterization of potential hazards is so necessary.

The ore mainly comprised Ag-bearing galena and sphalerite as major phases of a hydrothermal mineralization also including pyrite, chalcopyrite, marcasite, pyrrotine, bournonite, siderite, boulangerite, and ankerite [13]. The exploitation was performed from 1887 to 1934, date of the mining closure. In 1973, a new treatment plant was installed for re-working of approximately three million tons of tailings. Several tons of cinnabar from the Almadén mine (Ciudad Real, Spain) were experimentally treated in this new plant with successful results. At present, several mine tailings resulting from re-working together with the ruins of the mine structures are clearly visible. AMD from the tailings is recognized. Furthermore, a tailing dune, formed over one of the ponds, is migrating and toward the agricultural soils surrounding the mine area (**Figure 1**). The course of the Arroyo de la Mina stream, crossing the mining area, was altered and presently runs along the limits of the mine ponds.

2.4 Mazarrón

Mazarrón is located 4 km from the Mediterranean coast in SE Spain, and was one of the most important mining districts in the area [14]. It was exploited from Roman times to the early 1960s for Pb, Al, Ag, and Zn. Together with mining activities, the Mazarrón area is characterized by intensive farming and tourist pressure. Mining deposits caused significant water and soil pollution, and led to negative effects on both agricultural and tourism land uses. A correct geo-environmental characterization of the affected area is important for any proposal of restoration and remediation focused on minimizing environmental impacts.

The ponds are located on the hill slopes of the San Cristóbal and Los Perules hills, situated near a watercourse that drains to the Las Moreras watercourse, in turn flowing into the Mediterranean Sea (**Figure 1**). The main ore minerals were sphalerite, pyrite, and Ag-bearing galena. Other minor sulfides were arsenopyrite, chalcopyrite, the tetrahedrite-tennantite group, stibnite, cinnabar, and berthierite. The mine tailing ponds, near the Las Moreras dry watercourse, are situated on Quaternary alluvial and colluvial deposits (**Figure 1**). Although the total level amount of rainfall is not high, the area is subjected to strong stormy events each year, which can induce flash flooding phenomena.

3. Methodology

Mineralogical and geochemical techniques normally used to determine the composition of mine tailings, soils, waters, and watercourse sediments and the possible occurrence of AMD are described. In the case of high Hg contents, gaseous mercury emissions were analyzed too. Sampling features such as methods, sampling depth, analytical techniques, etc. are summarized in **Table 1** and described below.

3.1 Description of sampling

At Brunita, San Quintín, and San Cristóbal-Las Moreras areas, nondisturbed rock drill core tailing samples were collected from boreholes using a rotary drilling machine with a core bit diameter between 86 and 100 mm. Sampling was carried out by digging down below the surface of each pond, eliminating the surficial sealing to prevent falling material inside the borehole during drilling. Sampling depth of the unaltered samples varies between 0.5 and 1 m, depending on the borehole depth. All samples were air-dried for 7 days, passed through a 2-mm sieve, homogenized, and stored in plastic bags at room temperature prior to analyses. Below mine tailings, colluvial sediments (2–4 m) in San Quintín and watercourse sediments in San Cristóbal (2.5 m)—Las Moreras (4.5 m) were drilled, collected, and analyzed to obtain a complete geoenvironmental characterization of the area. Where a rotary drilling machine is not possible to place, samples were collected with an Eijkelkamp soil core manual sampler. Sampling was sequential with a centimeter vertical constant spacing and lower in depth than boreholes. This is the case of tailings studied at the Iberian Pyrite Belt district (**Table 1**). In many occasions, soils surrounding mine facilities show evident signals of contamination from different sources (tailings, ponds, open shafts, etc.) and pathways (wind erosion, water flows, etc.) affecting different receptors (agricultural soils, colluvial sediments, humans, etc.). In these scenarios, it is necessary to collect representative sample soils from the studied zone, and from a natural soil far enough of the mining area as a background sample (blank), in the case of San Quintín mine area. This is necessary to compare the potentially toxic element contents with the natural amount in the surrounding soils.

Water sampling is also necessary to check the metal amount in watercourse affected by the mining operations, as well as the possible AMD generation from the tailings. Several water samples have been collected depending on the features of the studied mine site: water sample collected at 8.5 m depth from a borehole

Mine district	Study mine	Ore mineralogy	Sample type	Sampling	Analytical techniques	Complementary techniques
Iberian Pyrite Belt	La Naya	**Py**, Sp, and Ga	Tailings	Manual sampler (2.7 m depth)	XRD, ESEM+EDX, INAA, pH	ERT (1 profile)
	Monterromero	**Sp**, **Ga**, and Py	Tailings	Manual sampler (2 m depth)	XRD, ESEM+EDX, INAA, pH	ERT (2 profiles)
	Mina Concepción	**Py**, Sp, Ga, Apy, Cpy, and Mg	Tailings	Manual sampler (1 m depth)	XRD, INAA	ERT (6 profiles)
			Water	Leakage	ICP-MS, pH, EC	
Cartagena-La Unión	Brunita	**Py**, **Sp**, **Ga**, Ma, Pyr, Te, Cpy, Apy, and St	Tailings	Borehole (24 m depth)	XRD, ICP-MS, pH, EC	ERT (6 profiles), aerial photographs
			Water	Water table	ICP-MS, pH, EC	
Alcudia Valley	San Quintín	**(Ag)-Ga**, **Sp**, Py, Ma, Cpy, and Pyr	Tailings/colluvial	Boreholes (10–12 m depth)	XRD, ICP-MS, ESEM+EDX, pH	ERT (7 profiles), aerial photographs
			Water	Borehole (8.5 m depth); watercourse; AMD	ICP-MS, pH	
			Soil	Surround; Blank		
			Air	Summer-winter	ZAAS-HFM	
Mazarrón	San Cristóbal	**Py**, **Sp**, **(Ag)-Ga**, Cpy, Apy, Te, Ci, and St	Tailings	Borehole (5.5 m depth)	XRD, ICP-MS, ESEM+EDX, pH	ERT (1 profile)
			Watercourse sediments			
			Water	Water table	ICP-MS, pH, EC	
	Las Moreras		Tailings	Borehole (6 m depth)	XRD, ICP-MS, ESEM+EDX, pH	
			Watercourse sediments			ERT (1 profile)
			Water	Watercourse	ICP-MS, pH, EC	

XRD, X-ray diffraction; ESEM, environmental scanning electron microscopy; EDS, energy dispersive X-ray; INAA, instrumental neutron activation analysis; ICP-MS, inductively coupled plasma-mass spectrometry; EC, electrical conductivity; and ZAAS-HFM, atomic absorption spectrometer with Zeeman effect.

Table 1.
Main sampling features of the studied mine district in Spain: Iberian Pyrite Belt, Alcudia Valley, Cartagena-La Unión, and Mazarrón [3–7].

(San Quintín), water samples from the tailing pond (Brunita and San Cristóbal), water sample from the watercourse crossing the mining area (San Quintín and Las Moreras), or water sample from the leakage of an abandoned (San Quintín) and a restored mine pond (Mina Concepción). All water samples were collected in 250 ml plastic bottles, were kept in a refrigerator at 4°C and, prior to analysis, and were filtered with 45 μm pore spacing. In San Quintín mine site (Alcudia Valley district), total gaseous mercury (TGM) was also measured using a 200 m sample spacing grid during both summer and winter by means of an atomic absorption spectrometer with Zeeman effect (ZAAS-HFM). The geostatistical treatment of data was performed applying block kriging to obtain interpolation maps of the study area.

3.2 Mineralogical and geochemical methods

Mineralogical characterization of borehole and soil samples was performed by X-ray diffraction (XRD) using a Philips X'Pert powder device with a Cu anticathode and standard conditions: speed 2° 2θ/min between 2° and 70° at 40 mA and 45 kV. The whole sample was examined by crystalline nonoriented powder diffraction on a side-loading sample holder. Semi-quantitative results were obtained by the normalized reference intensity ratio (RIR) method. The mineralogy of the samples was also studied by environmental scanning electron microscopy (ESEM), coupled with energy dispersive X-ray analysis (EDX), using a Philips XL30 microscope. The ESEM was operated at a low-vacuum mode, at a pressure between 0.5 and 0.6 Torr under a water vapor atmosphere and an operating voltage of 20 kV. The XRD and ESEM-EDX analyses were performed at the Centro de Apoyo Tecnológico (CAT Universidad Rey Juan Carlos, Móstoles, Spain). From the total list of major, minor, and trace elements analyzed, Ag, As, Cd, Co, Cu, Fe, Hg, Ni, Pb, S, Sb, Sn, and Zn were specially chosen because of their abundance in these types of sludges and because most of them are included in the priority contaminant list of environmental protection agencies. They were analyzed by total digestion (TD) or lithium metaborate/tetraborate fusion (FUS), inductively coupled plasma-mass spectrometry (ICP-MS), and instrumental neutron activation analysis (INAA) at the Activation Laboratories Ltd. (1428 Sandhill Drive, Ancaster, Ontario, Canada). Quality control at the Actlabs laboratories is performed by analyzing duplicate samples and blanks to check the precision, whereas accuracy is determined using Certified Reference Materials (GXR series; see [15]). Detection limits for the analyzed elements are as follows (data in $\mu g\ g^{-1}$): Ag (0.3), As (5), Cd (0.5), Co (1), Cu (1), Fe (100), Hg (0.005), Ni (1), Pb (5), S (10), Sb (0.5), Sn (1), and Zn (1). Pb content higher than 5000 $\mu g\ g^{-1}$ (above the ICP-MS maximum detection limits) was measured by ICP-OES or atomic absorption.

Water samples were analyzed by ICP-MS at Activation Laboratories Ltd. The pH was measured using an electronic pH meter (CRISON) that was calibrated using standard buffer solutions at two points: pH: 7 and pH: 4. This parameter was determined in a slurry system with an air-dried sample (10 g) mixed with distilled water (25 mL). Before reading the pH values, these solutions were vigorously stirred in a mechanical shaker for 10 min and left to stand for 30 min.

3.3 Complementary techniques

Electrical resistivity tomography (ERT) imaging is a near surface nondestructive technique designed to be widely used in many different geological applications, including the determination of the materials constituting the bedrock, unraveling the stratigraphical record of the basins and locating hidden faults, among others [16]. A resistivity profile is obtained from many different measurements using different available electrode arrays, with the data acquisition being controlled by means of a computer. These measurements provide data about the variations of apparent resistivity values at different depths, in such a manner that when the spacing between the electrodes increases, the resistivity data correspond to a greater depth of investigation. After data acquisition, the apparent resistivity values are converted to an image of true resistivity variations against depth. The resistivity meter used to obtain the data for this study was a Syscal Junior Switch 48. As mentioned before, different electrode arrays are available, with differences in relation to the depth of investigation and signal-to-noise ratio (e.g. [17]). From the different electrode arrays available, a Wenner-Schlumberger array has been selected because it provides a good penetration depth, the signal to noise ratio is good, and both vertical and horizontal resolutions are also reasonable. Moreover, different authors have previously used this array successfully in several similar studies [3–7, 18] because it shows a high contrast between the resistivity values of the vase of the mine ponds and the resistivity values of the infilling. From the field data, the information obtained about the resistance measurements between the different electrodes and distances between them is used to calculate the apparent resistivity values. Then, a plot of the apparent resistivity values vs. depth, named pseudosection, is constructed. Previously to be interpreted, the pseudosections need to be converted into profiles where true resistivity values are plotted against depth. The conversion from apparent to true resistivity values is performed by means of the RES2DINV code. As a first step of this inversion procedure, the data are filtered to remove bad data points, and then the topography information along the profile is also included. The code uses the L1 norm for the data misfit and the inversion was performed using the L1 norm (robust) for the model roughness filter [19]. The choice of the robust inversion is justified because this kind of inversion is more accurate when sharp boundaries in the model exist, and this is just the case involved in this study because of the large contrasts expected in the electrical properties of the materials. The method uses a finite element scheme for solving the 2-D forward problem and blocky inversion method for inverting the ERT data. The code RES2DINV finally provides an inverted resistivity image for each profile. The inverted profile is the one used to obtain the final interpretation about the variations of the subsurface lithology.

Aerial photographs, georeferenced and integrated into a GIS, are used to map morphologic elements and to detect the main changes in the environment through time. The evolution of mine deposits in the Brunita site was carried out to estimate anthropogenic changes in the landscape [5]. We worked with aerial photographs taken in 1929 (photogrammetric flight by Ruiz de Alda), 1946, and 1956 (flights by the Geographic Service of the Spanish Army), and 1973, 1981, 2004, and 2013 (flights by the Spanish National Geographic Institute), and anaglyphs of orthoimages from years 1946, 1956, 1981, and 2004 [20]. On the other hand, the study of a mine pond and a tailing sand dune at the San Quintín mine permitted to evidence the eolian dispersion of contaminants to the surroundings [21]. Several aerial photographs corresponding to different years were also analyzed (1957, Geographic Service of the Spanish army, 1977, 1984, Spanish National Geographic Institute, 2006, digital orthophoto IGN).

4. Geoenvironmental characterization of sulfide mine tailings

The results of the mineralogical and geochemical characterization of the samples collected from tailings, soils, air, water, and watercourse sediments are presented and discussed here. Morphological evolution over time from Brunita and San Quintín mine ponds is presented too, as well as the geophysical study concerning the structure and infilling of ponds and the possible presence of acidic water flows.

4.1 Mineralogical characterization

The mineralogical composition of tailings, colluvial, watercourse sediments, and soil samples has been inferred from the X-ray diffraction studies (**Table 2**). The following nomenclature has been used for tailing-mineral identification: primary minerals, those minerals that constitute ore and gangue assemblages originally deposited in the waste dumps, and secondary minerals, those deposited within the dumps by precipitation from metal-rich waters derived from acid mine drainage.

The nearly homogeneous mineralogical composition of mine tailings is mainly composed of primary gangue minerals from the volcanic or metamorphic host rocks: quartz (30–85 wt%), illite (5–15 wt%), feldspar (5–10 wt%), and chlorite (5–10 wt%). Minor gangue minerals appear in important amounts in some of the areas: siderite (15 wt%) in Brunita. The most important feature of the mineralogical composition of these deposits is the metallic ore mineral contents (25–40 wt%). Significant amounts of pyrite (10–35 wt%), sphalerite (5–10 wt%), and/or galena (5–10 wt%) have been identified in mine tailings (**Table 2**). These high values are probably related to

Mine district	Iberian Pyrite Belt			Cartagena-La Unión	Alcudia Valley		Mazarrón			
Study area	**LN**	**MR**	**MC**	**BR**	**SQ**	**SQ**	**SC**	**SC**	**LM**	**LM**
Sample	**Ta**	**Ta**	**Ta**	**Ta**	**Ta**	**Co**	**Ta**	**WT**	**Ta**	**WT**
Quartz	85	35	35	30	70	80	40	45	50	40
Illite	—	10	5	5	15	10	—	—	—	20
Feldspar	—	10	5	—	—	—	5	30	5	5
Chlorite	5	5	5	10	10	10	—	—	5	10
Calcite	—	—	—	—	—	—	—	—	—	20
Siderite	—	—	—	15	—	—	—	—	—	—
Pyrite	—	25	35	30	—	—	10	5	15	—
Sphalerite	—	10	5	5	—	—	5	5	10	—
Galena	—	—	—	—	—	—	10	5	5	—
Arsenopyrite	—	—	5	—	—	—	—	—	—	—
Magnetite	—	—	5	—	—	—	—	—	—	—
Jarosite	5	5	—	—	—	—	15	5	5	—
Rozenite	—	—	5	—	—	—	—	—	—	—
Goethite	5	—	—	—	—	—	—	—	—	—
Hematite	—	—	—	—	—	—	5	—	5	—
Alunite	—	—	—	—	—	—	—	5	—	—
Gypsum	—	—	5	5	5	—	10	—	—	5

La Naya (LN), Monterromero (MR), Mina Concepción (MC), Brunita (BR), San Quintín (SQ), San Cristóbal (SC), and Las Moreras (LM). Ta: tailings; Co: colluvial; and WS: watercourse sediments.

Table 2.
Semi-quantitative mineralogical composition (wt%) of the studied samples.

inefficient metallurgical processing of the benefited ore during the operational years. Because of the re-working of tailing mine areas, San Quintín area shows the lower ore mineral content. In other cases, like Brunita deposit, different ore minerals amounts are associated with the two different mines exploited and dumped: Brunita and Eloy mines. Cinnabar was identified by X-ray diffraction in one borehole sample from San Quintín. Its presence is due to the experimental metallurgical works carried out during the last period of operations in the Almadén mine (Ciudad Real, Spain). Secondary mineralogy is mainly represented by Fe-sulfates (jarosite and rozenite), Ca-sulfates (gypsum), and Al-sulfates (alunite). Fe-bearing sulfide oxidation increases the metal mobility from these materials compared to the levels mainly composed by sphalerite and galena. Significant amounts of secondary gypsum are typically found in this type of sulfide tailings. Fe-oxides and Fe-hydroxides have also been identified.

In some occasions, the ore minerals are not identified by X-ray diffraction, or are identified in low amounts. In these cases, a detailed study by environmental scanning electron microscopy (ESEM) coupled with energy dispersive X-ray analysis (EDX) is necessary. Four examples of the application of ESEM-EDX are presented in **Figure 2**. Primary sulfide minerals (e.g. galena) identified in low amounts by XRD were also recognized by ESEM-EDX in Monte Romero tailings. Galena occurred as cubic crystals commonly showing octahedron faces. Other sulfide phases such as arsenopyrite, chalcopyrite, and galena were not detected by X-ray diffraction in La Naya tailings. Secondary mineral phases recognized by ESEM-EDX were Fe-oxyhydroxides. Cryptocrystalline Fe-oxyhydroxides frequently occurred around other minerals such as quartz, completely or partially replacing primary sulfides (pyrite and sphalerite). In San Quintín mine, primary ore minerals were not identified by XRD due to the optimized mining works. Pyrite, galena, chalcopyrite, and gangue minerals (barite) were identified by ESEM-EDX (**Figure 2**). In San

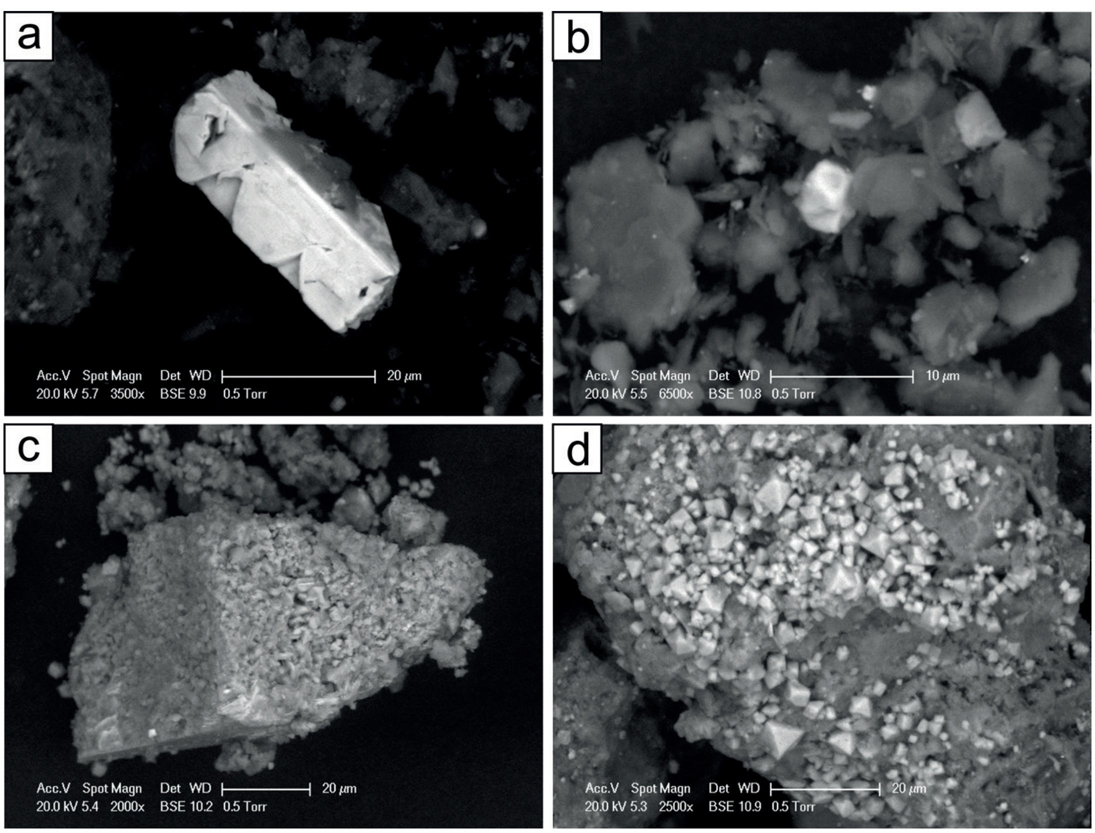

Figure 2.
Backscattered electron (BSE) images: (a) galena crystal from Monte Romero; (b) pyrite crystal from San Quintín; (c) altered faces of a pyrite crystal from San Cristóbal; (d) subidiomorphic magnetite from Las Moreras.

Cristóbal tailings, ore and gangue minerals were identified, as well as oxide minerals such as goethite. In Las Moreras samples, low quantities of Fe-oxides (hematite and magnetite) and carbonates (siderite) were identified by ESEM.

With respect to the colluvial sediments drilled at the San Quintín boreholes, the mineralogical composition was totally composed by primary silicates, as well as watercourse sediments from Las Moreras area (**Table 2**). The ore mineral content is low enough to be identified by XRD analysis. In contrast, the semi-quantitative mineralogical composition of watercourse sediment from San Cristóbal mine included ore minerals (pyrite, sphalerite, and galena) and secondary sulfates (jarosite and alunite).

4.2 Geochemical characterization

4.2.1 Mine tailings

Total ferric iron (Fe_2O_{3total}), S, and trace element (Ag, As, Au, Cd, Cu, Ni, Pb, Sb, Sn, and Zn) concentrations, and pH values from tailing samples of the four mine district are summarized in **Table 3**. All samples showed a pH range of 2.2–5.6. This value range reflects the typical acid character of stored mine tailings. The composition of all tailing samples is characterized by the high contents of ore-bearing elements in each district: As, Cu, and Pb in the Iberian Pyrite Belt, Pb and Zn in Cartagena-La Unión and Alcudia Valley, and As, Pb, and Zn in Mazarrón. The total ferric iron content is significantly high in analyzed samples from all mine districts due to the omnipresence of Fe-bearing minerals like pyrite. The significantly high contents of potentially hazardous elements like Fe, Cu, Pb, and/or Zn are due to the nature of the mined ore, which is mainly composed of pyrite, chalcopyrite, sphalerite, and galena (**Table 2**). The highest metal contents are related to the mining history of each district, and the efficiency of the metallurgical processing in the benefited ore during the operational period of time. In the case of San Quintín mine, approximately 3 million tons of minerals from the tailings were re-worked. Then, the lowest Pb and Zn contents are located at the upper levels of the ponds. High Hg content measured in the San Quintín mine tailings is related to the experimental metallurgical works previously cited (Section 2). Significant Hg values were measured in Monte Romero mine related to the formation of a replacive mineralization. Pb (up to 21,130 $\mu g\ g^{-1}$) and Zn (41,841 $\mu g\ g^{-1}$) contents in the tailings from Mazarrón district (**Table 3**) as well as the significant Ag content from San Cristóbal mine related to the exploitation of Ag-bearing galena deserve special mention.

The Mina Concepción samples were collected with a manual sampler from the first meter in depth. That is the reason for the lower metal contents to be associated with the more recent and efficient metallurgical works. Related to the Iberian Pyrite Belt district, relevant variations as a function of depth were identified in all of the analyzed element contents from Monte Romero samples. Possible explanations for these variations could be argued: (a) periods with higher mineral benefit, due to improvements in metallurgic processes or to a higher grade mineralogy and (b) a change in the exploitation targets, originally focused on galena (Pb) mining but later re-directed to pyrite (Fe) and sphalerite (Zn) mining due to environmental policies that do not recommend the use of lead in many industrial fields.

4.2.2 Sediments and soils

Total ferric iron, S and trace element concentrations, and pH values from colluvial and watercourse sediment, and soil samples of the Alcudia Valley and Mazarrón districts are summarized in **Table 4**.

Mine district	Iberian Pyrite Belt			Cartagena-La Unión	Alcudia Valley	Mazarrón	
Study area	**LN**	**MR**	**MC**	**BR**	**SQ**	**SC**	**LM**
Ag	b.d.	31–81 (48)	b.d.	2–8 (4)	5–29 (12)	20- > 100 (55)	14–26 (20)
As	191–909 (472)	1110–2740 (1650)	223–1080 (613)	39–385 (195)	16–54 (28)	400–633 (490)	181–630 (366)
Au	49–100 (70)	311–744 (558)	22–86 (53)	n.a.	n.a.	n.a.	n.a.
Cd	n.a.	n.a.	n.a.	3–67 (22)	5–22 (13)	4–833 (110)	97–373 (186)
Cu	306–4511 (998)	914–16,582 (4874)	n.a.	76–323 (179)	42–381 (171)	121–882 (406)	168–356 (230)
$Fe_2O_{3\ total}$	8.51–14.1 (11.5)	2.12–27.2 (14.57)	6.11–24.1 (14)	22.3–52.6 (38.7)	4.5–6.3 (5.6)	9.8–22.9 (19.2)	17.7–28.5 (23.7)
Ni	b.d.	b.d.	b.d.	11–40 (22)	29–61 (44)	11–41 (21)	41–59 (49)
Pb	51–222 (133)	295–12,610 (4615)	71–475 (264)	1610–5950 (3211)	1510–10,500 (3992)	5987–39,877 (21,130)	3940–5239 (4665)
S	n.a.	n.a.	n.a.	3.8–19.1 (11.8)	0.3–1.0 (0.4)	3.5–53.0 (6.6)	7.1–12.8 (9.3)
Sb	31.3–50.4 (35.2)	168–861 (338)	16.2–67.5 (40)	3–54 (30)	36–162 (79)	108- > 200 (149)	54–136 (93)
Sn	b.d.	b.d.	b.d.	14–244 (76)	3–7 (5)	8–121 (83)	24–37 (30)
Zn	50–260 (143)	0.5–6.9 (4)	200–970 (511)	2020–2112,150 (6315)	1250–4470 (2418)	2500–11,405 (4101)	12,810–41,841 (27,738)
pH	2.8–3.5 (3.2)	2.5–3.2 (3.0)	n.a.	2.4–3.7 (3.0)	n.a.	2.2–3.6 (2.5)	2.8–5.6 (4.0)

Ag, As, Au, Cd, Cu, Ni, Pb, Sb, Sn, and Zn in μg/g. Fe_2O_{3total} and S in wt%. Mean in brackets. b.d.: below detection; n.a.: not analyzed. La Naya (LN), Monterromero (MR), Mina Concepción (MC), Brunita (BR), San Quintín (SQ), San Cristóbal (SC), and Las Moreras (LM).

Table 3.
$Fe_2O_{3\ total}$, trace element content, and pH values in the studied tailings.

Mine district	Alcudia Valley			Mazarrón	
Study mine	San Quintín			San Cristóbal	Las Moreras
Sample	Colluvial	Soil	Blank	Sediment	Sediment
Ag	0–3 (2)	0–3 (1)	0.2	21–60 (38)	0–7 (3)
As	8–24 (17)	b.d.-26 (15)	11	216–312 (259)	15–131 (33)
Cd	1–7 (3)	b.d.-7 (b.d.)	b.d.	2–4 (3)	1–6 (3)
Cu	38–196 (76)	5–39 (17)	18	70–122 (96)	45–482 (177)
$Fe_2O_{3\ total}$	5.3–9.5 (6.9)	1.7–4.7 (3.5)	4.2	7.6–33.5 (18.3)	4.0–12.0 (5.9)
Ni	46–93 (59)	13–46 (34)	30	10–14 (12)	30–61 (47)
Pb	79–577 (315)	41–1110 (318)	34	9395–16,193 (12,800)	157–1880 (555)
S	0–0.2 (0.1)	0–0.3 (0.1)	0.01	2.7–4.5 (3.9)	0.1–3.0 (1.0)
Sb	5–40 (24)	2–30 (9)	2	98–124 (111)	2–48 (14)
Sn	3–5 (4)	2–3 (3)	2	5–10 (7)	2–6 (4)
Zn	186–844 (503)	34–1180 (335)	49	815–1660 (1334)	452–10,693 (2907)
pH	n.a.	5.7–6.2 (5.9)	5.1	3–3.4 (3.2)	7.0–7.7 (7.4)

Ag, As, Au, Cd, Cu, Ni, Pb, Sb, Sn, and Zn in μg/g. Fe_2O_3 and S in wt%. Mean in brackets. b.d.: below detection. n.a.: not analyzed.

Table 4.
$Fe_2O_{3\ total}$, trace element content, and pH values in the studied colluvial, soil, and watercourse sediment samples.

The highest contents were found in the pond samples, and the intermediate contents in the colluvial samples from San Quintín area. The ponds were not waterproofed, and hazardous metals from the upper ponds have percolated through the underlying colluvial sediments. Cu, Pb, and Zn contents show significant amounts. Five representative soil samples were analyzed in order to determine the importance of contamination (**Table 4**). Two mine soil samples show similar metal and As content to the upper tailing samples. The other two were agricultural soil samples, showing significantly lower metal and As content, but higher Hg and Pb contents than the local background sample (blank in **Table 4**), collected from an agricultural soil 4.5 km to the south-east. However, remarkably high As, Pb, and Zn contents were still found in this background sample, suggesting that the surrounding agricultural soils are also contaminated. In fact, Ag, Cd, Pb, and Zn contents from agricultural soil samples are higher than geochemical baselines reported by [22] for this Spanish region.

In Mazarrón district, both tailings and watercourse sediments showed high amounts of potentially toxic elements, slightly lower at the sedimentary level (3.0–5.5 m depth). The total iron content ranged between 4.0 and 33.5 wt%, Pb was 157–16,193 μg g^{-1}, and the Zn content ranged between 815 and 10,693 μg g^{-1} (**Table 4**). Other trace elements that displayed high values were: As, Cu, and Sb. The sediments mark a defined geochemical limit with the tailing unit. The upper mine tailings are significantly concentrated in Fe_2O_{3total} and heavy metals, whereas the sediments display marked lower values. This decrease is not absolutely regular, with major peaks in Cu and Zn contents, and minor increases in As, Cu, Fe_2O_{3total}, Pb, and Zn. The amount of calcite in the Las Moreras sedimentary unit (**Table 2**) controls the pH, buffering to within a small range of 7.2–7.7 (**Table 4**). In turn, the

Mine district	Iberian pyrite belt	Cartagena-La Unión	Alcudia Valley			Mazarrón	
Study mine	**MC**	**BR**	**SQ**			**SC**	**LM**
Sampling	**LK (5)**	**WT**	**BO**	**WT (6)**	**AMD (3)**	**WT**	**WC**
As	>2000	79	2.6	>1.5	2.3	>2000	b.d.
Cd	14–54	483	3.8	0.1–26.6	>3200	6470	1.5
Cu	>2000	>2000	12.3	1–12.6	>8300	>2000	52
$Fe_2O_{3\ total}$	>100,000	>100,000	90	30–100	>189,000	>100,000	100
Ni	30–143	559	80.1	1.8–22.3	>3500	5620	120
Pb	0–67	199	8.5	0.4–21.6	>2800	0.5	1
Sb	0–1	b.d.	6.1	0.1–3.0	1.3	11.8	1.4
Sn	b.d.	b.d.	b.d.	b.d.	b.d.	3	2
Zn	>2500	>2500	93.6	57–2520	>550,000	>2500	365
pH	2–2.6	2.4	5.7	6.2–7.1	2.5–4.3	1.8	8.3

Values in μg/L. b.d.: below detection. Mina Concepción (MC), Brunita (BR), San Quintín (SQ), San Cristóbal (SC), and Las Moreras (LM). LK: leakage; WT: water table; BO: borehole; AMD: acid mine drainage; and WC: watercourse.

Table 5.
$Fe_2O_{3\ total}$, trace element content, and pH values in the water samples.

upper tailing unit of Las Moreras shows much lower pH values (2.8–5.6), due to the sulfide content and the complete absence of calcite.

4.2.3 Waters

The composition of leakage sample waters of a restored mine pond (Mina Concepción) indicates that these waters represent acid mine drainage, as reflected by their very low pH (<2.6) (**Table 5**). Trace element contents are very high for Cu and Zn (>2 mg/l), both higher than the EPA's maximum recommended limits for irrigation waters (0.2 mg/l for Cu and 2 mg/l for Zn [23]). This is also the case for As in samples leaking from the dyke wall and the puddle. Lead also goes beyond the legislation limits in samples from the dyke wall and the drainage pipes. Acid mine drainage was observed in the northern part of the Brunita mine pond (pH < 2.4) (**Table 5**). The concentrations were very high for Cu, Zn, Cd, Ni, and Fe in the water sample. Results from complementary techniques (ERT), shown in Section 4.3 of this chapter, have confirmed the formation of AMD waters in Mina Concepción and Brunita mines.

One water sample was collected at 8 m depth in the borehole from San Quintín mine (**Table 5**). The high EC and acidic pH values are consistent with water from ore deposits retained in tailing ponds. Three samples showing low pH and significantly high trace element contents indicate AMD flowing from the remaining tailings. AMD was not observed in samples from the watercourse crossing the mining zone (**Table 5**). pH values in these waters are circumneutral, and EC values and metal contents are significantly lower than in samples from the tailings. Samples collected up- and downstream display the lowest trace element contents. Higher metal contents have been measured in the rest of watercourse samples, denoting that trace element contamination occurs through the mining area.

With regard to the San Cristóbal mine pond, AMD was clearly detected in the water sample: pH < 2, high redox potential, high EC, and Total dissolved salt values. Concentrations of trace elements were very high for As and Cu (>2000 μg/L), Zn

(>2500 μg/L), Cd and Ni (>5600 μg/L), and Fe (>100,000 μg/L). Water from the seasonal watercourse of Las Moreras was also analyzed. Significant contents of metallic elements (Cu, Fe, Ni, and Zn) were measured, all beyond the established limits for irrigation waters.

4.2.4 Hg in air

A singular case occurs in San Quintín mine where significantly high Hg content has been identified in the mine area. Gaseous Hg emissions were measured from the tailings and surrounding soils (**Figure 3**). The total gaseous mercury distribution in the studied area significantly changes between summer and winter. The area affected by TGM values up to 100 ng m^{-3} is restricted to the surroundings of the cinnabar stockpile in winter, but the affected area is 0.16 km^2, and extends into the Don Quixote Route in summer. TGM values are lower than the limit recommended for the general population by the World Health Organization (WHO) (1000 ng m^{-3}) for the worst scenario [24]: higher temperature and solar radiation during summer.

4.2.5 Multivariate analysis

Multivariate analysis has been carried out on the significant metal contents from samples of tailings (Brunita), tailings + colluvial sediments (San Quintín), and tailings + watercourse sediments + bedrock (San Cristóbal and Las Moreras) (**Figure 4**). Statistical data processing was carried out using Minitab® 16 software. The multivariate analysis was based on clustering (group average linkage dendrograms, Euclidean distance) of the set of samples and significant trace elements (Ag, As, Cd, Cu, Pb, Sb, Sn, and Zn). The dendrogram of the metals and As in the Brunita tailing samples shows the metallic signature of the district ores: Ag-Pb-Cd-Zn, Cu, and As-Sb-Sn, with As being mainly related to Sb (tetrahedrite-tenanntite mineral group). Ag-Pb-Cd-Zn signature is clearly defined due to the mineral source. In the case of San Quintín, the dendrogram from tailings and colluvial sediments reflects again the metallic signature of the district (Pb-Ag-Sb, Cu, and Zn-Cd to a certain extent [13]), with As mainly related to Sb (bournonite and boulangerite) and Pb-Ag (galena). Some samples display a strong affinity to the Ag-Pb-Sb-As association, whereas other samples display Cd-Zn affinity. The same

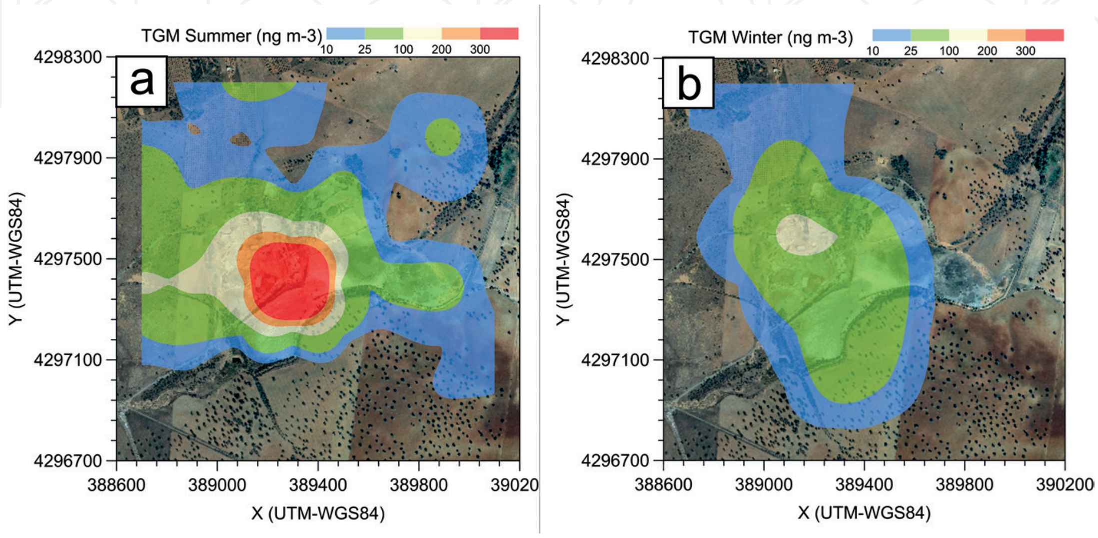

Figure 3.
Total gaseous mercury (TGM) seasonal distribution in the San Quintín area: (a) summer and (b) winter values. Modified from Martín-Crespo et al. [6].

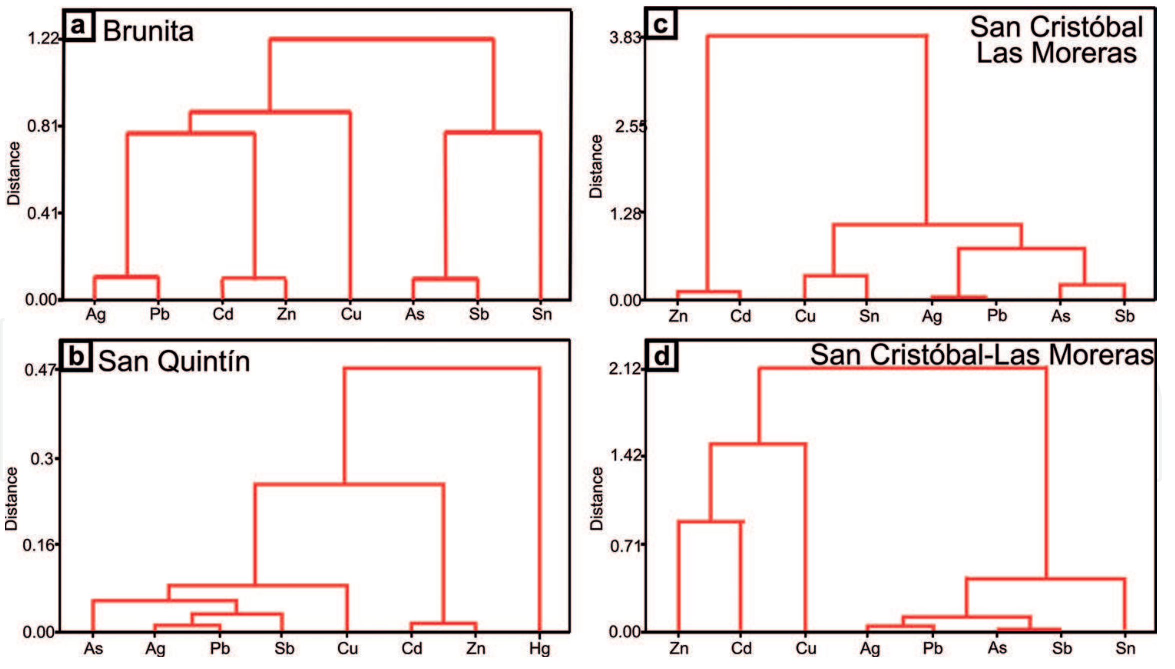

Figure 4.
Dendrograms (distance Euclidean) of metals: (a) Brunita tailings; (b) San Quintín tailings and colluvial; (c) Mazarrón tailings; and (d) Mazarrón watercourse sediments and bedrocks.

metallic signature has been obtained from tailings and colluvial sediments, reflecting the same origin for both kinds of samples. The external origin of Hg is reflected by the highest obtained distances. The same occurs for the samples from Mazarrón district, reflecting the metallic signature of the district (Pb-Ag-Sb, Zn-Cd, and Cu to a certain extent [14]) with As being mainly related to the Sb (stibnite and sulfosalts) and Pb and Ag (galena). Some slight differences are displayed in the samples from sediments and bedrocks, particularly the larger range of Cu content.

All dendrograms presented in **Figure 4** are in good agreement with field data, and mineralogical and geochemical features of tailings and watercourse deposits (**Tables 2–4** respectively). In summary, the metallic signature of the three districts is clearly defined in the samples from tailings and affected sediments.

4.3 Complementary techniques

4.3.1 Electrical resistivity tomography (ERT)

Additional information about the characteristics of the mine tailing deposits can be obtained from electrical resistivity tomography (ERT) data. The major pieces of information that this method provides are related to both the thickness of the deposits and the occurrence of AMD (both inside the mine pond as flowing out through the dyke or the base). **Figure 5** shows several examples of the type of information derived from the application of ERT to different mine ponds, resulting in a valuable tool that completes the information derived from mineralogical and geochemical techniques.

As a general rule, the materials that constitute the mine pond infilling are characterized by a medium to fine texture and high-water content. Moreover, due to oxidization of sulfide minerals, the pH of the water stored in the mine pond infilling is frequently acidic (pH < 5) in character. Opposite to this, the host rock where the mine pond is placed should be the host rock of the mineralization, typically metamorphic and/or igneous rocks of coarse texture and extremely low water content. Thus, a high resistivity contrast between the mine pond infilling (low to very low resistivity values) and the host rock (medium to high resistivity values)

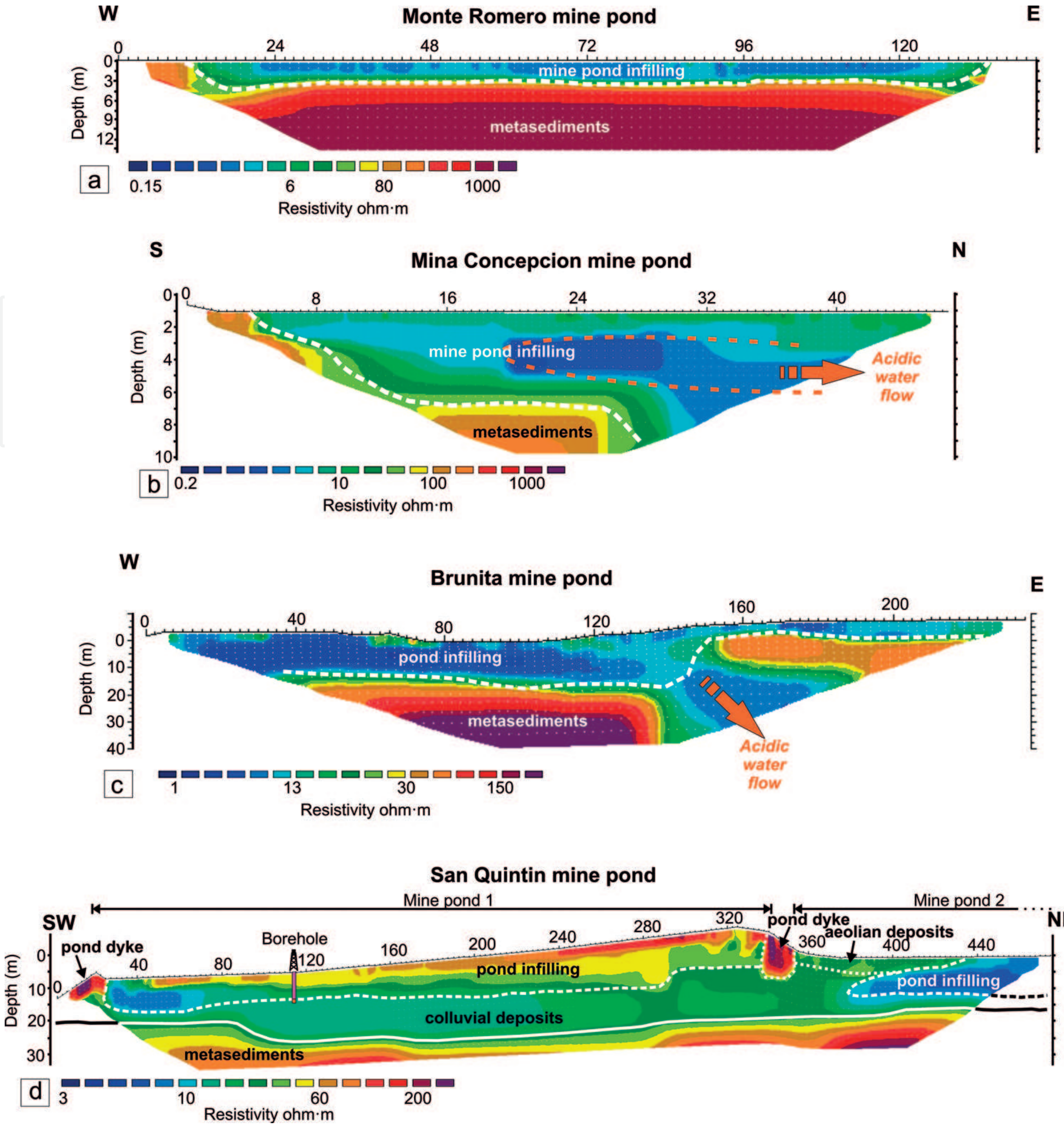

Figure 5.
ERT profiles obtained at four different mine sites. Each profile provides information about the thickness of the mine deposits and the presence or not of acidic water.

exists, allowing an accurate characterization of the boundary between both rock types and providing good estimations of the thickness of the mine pond deposits. Different mine pond thickness values and bottom geometries (dashed white lines) are imaged in **Figure 5**. Monte Romero and San Quintin mine ponds show simple bowl-shaped geometries with a thickness of ~3 and 10 m, respectively (confirmed with data from a borehole in the case of San Quintin mine pond 1), whereas Mina Concepcion and Brunite mine ponds exhibit a stepped bottom geometry with variable thickness (~6–10, and ~5–12 m, respectively). Where different rock units are present below the mine pond, instead of a homogeneous lithology, an estimation of the thickness of the different units can also be obtained. This is the case for San Quintin mine ponds, where a ~10 m thick sedimentary unit of colluvial deposits overlies the metasediments that constitute the regional basement. As mentioned before, a low pH value for the water contained in the mine pond deposits is also frequent, resulting in lower resistivity values in comparison with water with circumneutral pH. Therefore, the occurrence of acidic water inside a mine pond is revealed by extremely low resistivity values, normally lower than 1 ohm m. This is the case for Monte Romero, Mina Concepcion, and Brunita mine ponds where areas of <1 ohm m inside the mine pond correspond to the presence of water with pH ranging from 2 to 3 (see **Table 5**). On the other hand, the higher (>5 ohm m, and mainly >10 ohm m) resistivity values of the infilling of San Quintin mine ponds are associated with circumneutral pH (**Table 5**).

Finally, the strong resistivity contrast between the acidic water and the host rock results to be very useful to detect if AMD is flowing through the bottom of the mine pond. Where the sealing of the mine pond is correct, the host rock shows homogenous high resistivity values along the whole boundary with the pond infilling, such as the case of Monte Romero and San Quintin mine ponds. However, where AMD flows through the host rock, discrete areas of resistivity values much lower than the ones associated with the host rock are imaged, revealing the occurrence and sense of flow of the AMD. The latter is nicely imaged in both the cases of Mina Concepcion mine pond, where AMD flows from the inner central part of the pond toward the northern edge (confirmed during the field inspection of the dyke that exhibits AMD trough it), and Brunita mine pond, where AMD flows toward the east through the host rock.

4.3.2 Aerial photographs

Dumping of huge piles of tailings and debris since the beginning of mining operations at the Brunita area leads to a deep transformation of the landscape with the whole disappearance of the original reliefs [5] (**Figure 6**). A few studies are recognized in the 1929 and 1946 aerial photographs, but mine ponds were not yet operational. The orography consisted of smooth hills (~40 height difference) separated by NNW–SSE and WNW-ESE ravines (<500 m long). However, by 1956,

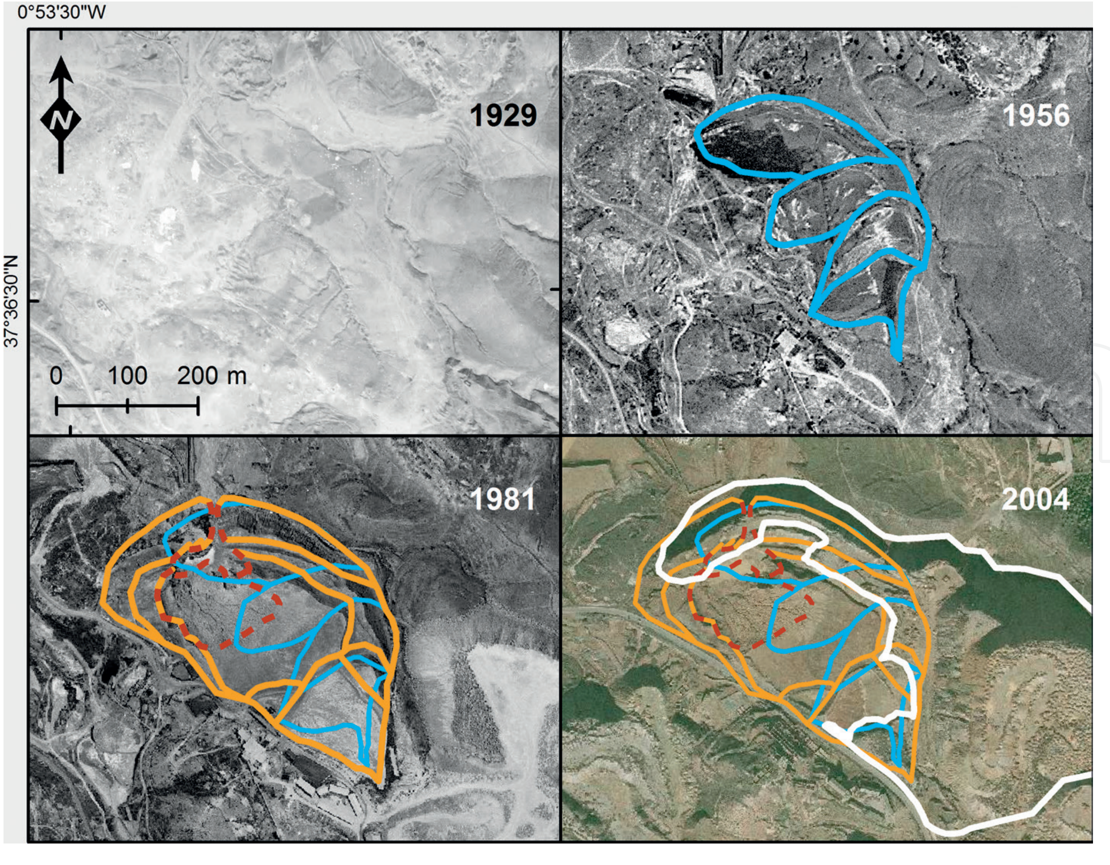

Figure 6.
Landscape evolution in the surroundings of the Brunita mine pond from aerial photographs taken in: 1929 (Ruiz de Alda photogrammetric flight); 1956 (Geographic Service of the Spanish Army); and 1981 and 2004 (Spanish National Geographic Institute). Blue lines, mine ponds in 1956; orange lines, mine ponds in 1981; brown dashed lines, badlands and landslide scar in 1981; and white line, spoil tips in 2004.

tailings from the mineral treatment plant were dumped in four stepped ponds along a NNW–SSE valley. Due to the continued mine activity, the tailings leveled the land up to the highest pond between 1973 and 1981, even burying the adjacent hills, and debris from the mine quarry began to cover the easternmost NNW–SSE ravines and hills. At this stage, there were two ponds, a large one with three stepped dikes and a small one in the highest part of the valley. The landslide scar in the dikes and the back sunken area, due to the flowage of tailings that caused the disastrous 1972 flash flood, are also visible. The sunken area was crisscrossed by gullies due to subsequent water erosion. Although the mine was closed in 1981, the reinforcement of the pond perimeter, with the sealing of the broken area, and the strong accumulation of debris to the east completely buried the ravines and hills and leveled the topography by 2004. Changes in the gully drainage pattern and the retreat of scarps indicate that tailing erosion persists.

Eolian dispersion of contaminants from a tailing sand dune (**Figure 1**) is the most important environmental concern at the San Quintín area [21]. By 1977, the mine pond was divided into three sectors through dikes. One of these dikes will be the obstacle over which the dune will be developed when the mine operations ceased. The dune has been growing and migrating by the dominant winds since 1984. As the tailings are not replaced, the dune is losing its pollutant particles by dispersion toward the nearby river and agricultural soils, so its decrease in size or disappearance is expected.

5. Environmental concern

The results obtained from the mineralogical and geochemical characterization of the samples collected from tailings, soils, air, water, and watercourse sediments allow identifying the potential environmental concerns that would affect the different mine districts. These potential environmental concerns can be classified according to three main types: (a) ecosystem risks, (b) human health risks, and (c) physical hazards. Ecosystem risks are mainly related to the negative effect of both the acidic water and metals. To properly evaluate the potential volume of metals susceptible to produce negative effects on the ecosystems, the mineralogical and geochemical characterization of the tailings is crucial. From the cartographic (area) and ERT (general geometry and thickness) studies, an infilling volume of 912,000 m^3 has been calculated for the Brunita mine pond. The maximum amounts of potential contaminants were obtained taking into account the mean content of potentially toxic elements (**Table 3**), the previously calculated volume, and the mass of the waste. A mean bulk density of 2.65 g/cm^3 was calculated from the mineral particle density and assuming a porosity of 40%, which is the value for mine ponds originating from the processing of this type of deposit. From the mean trace element content shown in **Table 3**, the Brunita impoundment contains more than 24,250 t of potentially toxic elements such as (470 t), Cd (52 t), Cu (430 t), Ni (53 t), Pb (7753 t), Sb (71 t), Sn (184 t), and Zn (15,245 t). Release of these amounts of toxic elements would be catastrophic for the environment and the community (death, serious material damage, coastal areas, and farm land). Similar studies in the Iberian Pyrite Belt district show amounts of potentially toxic elements of 5900 t in La Naya, and 2100 t in Monte Romero ponds.

In order to evaluate the contaminating degree of tailings, the geo-accumulation index (I_{geo}) was calculated. Müller [25] defined I_{geo} and enabled the assessment of sediment contamination by comparing current and pre-industrial concentrations of heavy metals. This index is mathematically expressed as $I_{geo} = \log_2 C_n/1.5B_n$, where C_n is the concentration of an element in the sample and B_n is the background concentration of the corresponding element in the Earth's crust, according to [26]. Müller [25] suggested six descriptive classes for this index: uncontaminated ($I_{geo} \leq 0$), uncontaminated to moderately contaminated ($0 < I_{geo} < 1$), moderately contaminated ($1 < I_{geo} < 2$), moderately to strongly contaminated ($2 < I_{geo} < 3$), strongly contaminated ($3 < I_{geo} < 4$), strongly to extremely contaminated

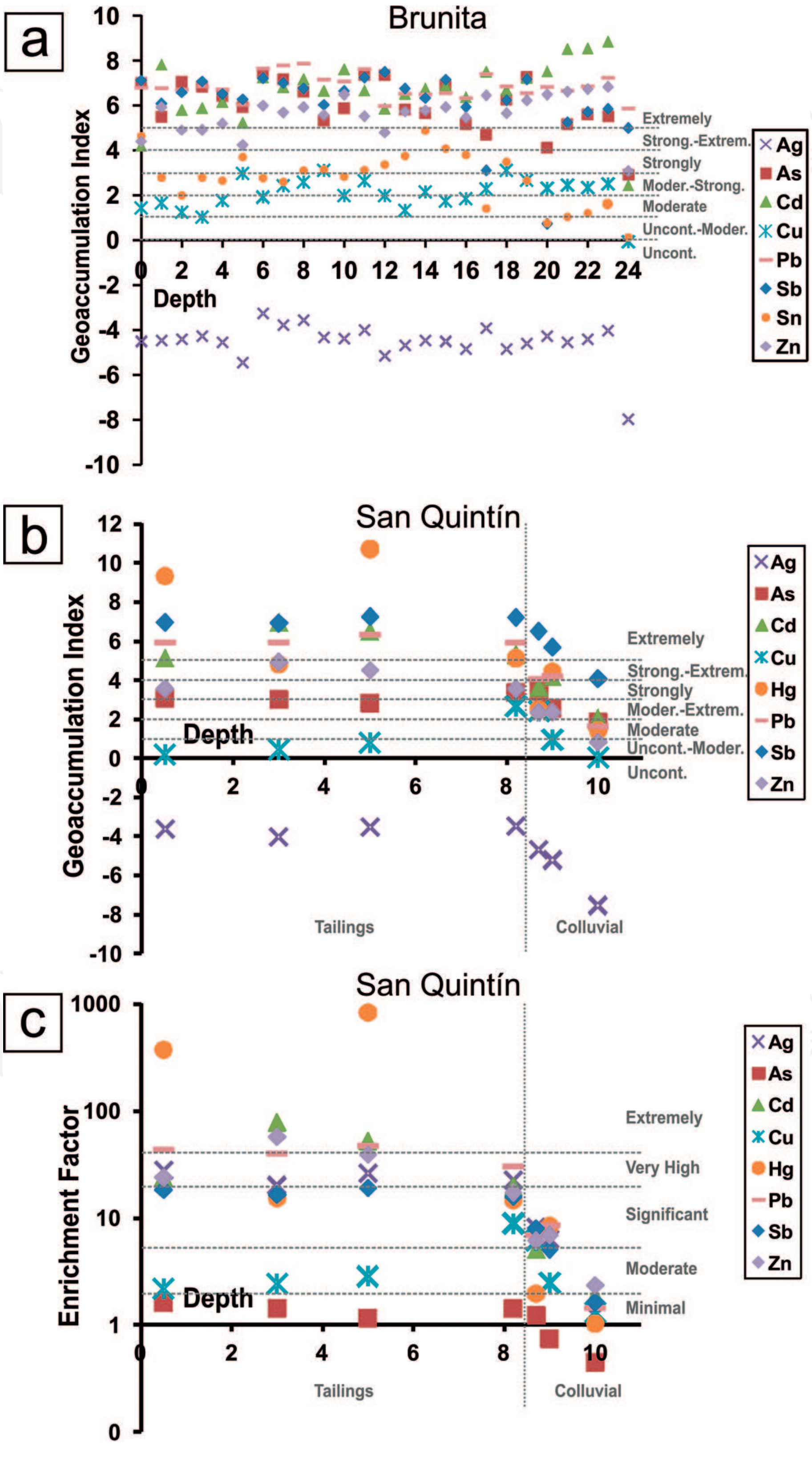

Figure 7.
(a) Geoaccumulation index for Brunita tailings, (b) geoaccumulation index for San Quintín tailings and colluvial; (c) enrichment factor for San Quintín tailings and colluvial. Modified from Martín-Crespo et al. [5, 6].

($4 < I_{geo} < 5$), and extremely contaminated ($I_{geo} > 5$). The I_{geo} index was calculated for tailings from Brunita, and tailings and colluvial from San Quintín (**Figure 7**). As, Cd, Pb, Sb, and Zn from Brunita tailings show extreme contamination ($I_{geo} > 5$), whereas Cu and Sn show moderate to strong contamination ($1 < I_{geo} < 4$). Ag is classified as a nonpollutant. The contamination classes are two levels higher than those obtained for similar tailings in Spain [6]. Cd, Hg, Pb, and Sb show extreme contamination ($I_{geo} > 5$), and As and Zn show moderate to heavy contamination ($1 < I_{geo} < 5$) in the tailings and colluvial sediment from San Quintín. Cu shows moderate to heavy contamination, and Ag is classified as unpolluted (**Figure 7**). Sutherland [27] proposed the enrichment factor (EF) to assess the level of contamination and the possible anthropogenic impact. To identify anomalous metal concentration, geochemical normalization of the heavy metal data to a conservative element, such as Fe, was employed (geochemical normalization). EF was calculated using the formula $EF = (M/Fe)_{sample}/(M/Fe)_{background}$, where $(M/Fe)_{sample}$ is the ratio of metal to Fe concentrations in the sample and $(M/Fe)_{background}$ is the ratio of metal to Fe concentrations of the background (blank; **Table 4**). Sutherland [27] proposed five contamination categories: minimal enrichment ($EF < 2$), moderate enrichment ($2 < EF < 5$), significant enrichment ($5 < EF < 20$), very high enrichment ($20 < EF < 40$), and extremely high enrichment ($EF > 40$). The San Quintín samples show very high to extremely high enrichment in Ag, Cd, Hg, Pb, Sb, and Zn. EF values for As are significantly lower than for the rest of elements, reflecting the lack of As-bearing minerals. **Figure 8** shows I_{geo} and EF for San Quintín representative soil samples. Agricultural soil samples (S-06 and S-53) and the background sample (S-00) show the same features: they are moderately contaminated by As, Cd, Pb, and Sb and not contaminated by Ag, Cu, and Zn. The I_{geo} for Hg was strong for agricultural soils and extreme for mine soils. Agricultural soil samples (S-06; S-53) and mine soil sample (S-37) show minimal or moderate EF for Ag, As, Cd, Cu, Pb, Sb, and Zn. The EF values for Hg were significant or very high for agricultural soils and extremely high for mine soils. These data highlight the significant metal contents of the mine site, which can become especially hazardous due to eolian dispersion.

The occurrence of AMD inside the tailings and its flow through the mine deposits toward the surrounding environment represents a major risk for the ecosystems. In this sense, several zones have been affected by metal mobilization though acidic water and its percolation from tailings to riverbed deposits, resulting in the affection of watercourses (Mina Concepcion) and groundwater (Brunita). Consequently, Mazarrón and Iberian Pyrite Belt districts show water metal contents beyond the EPA's maximum recommended limits in irrigation waters. Where AMD is confined inside the mine tailings (Monte Romero and San Quintín), metal mobilization also occurs but the affection to the environment is limited. However, the large volume of acidic water with high metal contents stored at these deposits

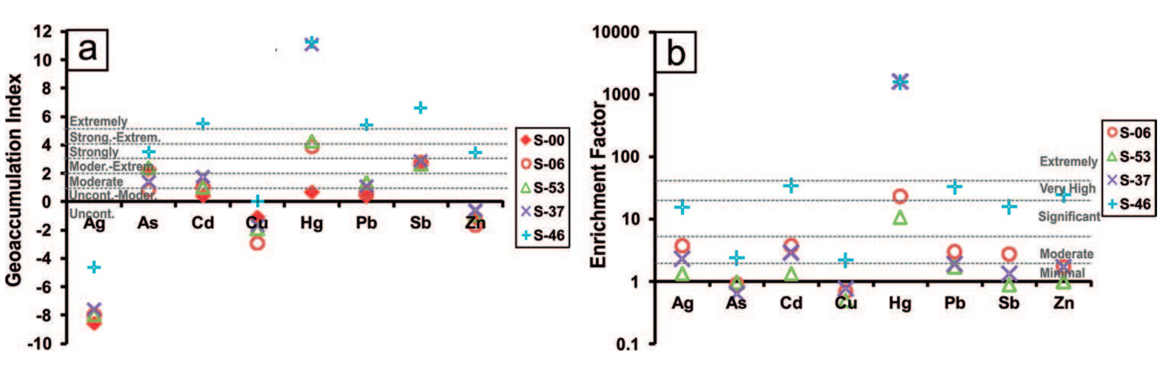

Figure 8.
Representative soils from San Quintín mine area: (a) geoaccumulation index and (b) enrichment factor. Modified from Martín-Crespo et al. [6].

represents a major potential ecosystem risk. If a failure of the dam occurs, or the sealing of the mine pond fails, the ecosystem, watercourses, and riverbed sediments would be largely affected by the release of acidic water and its dissolved hazard metals.

Regarding human health risks, they are mainly associated with the eolian dispersion of contaminants. San Quintin mine ponds represent the area with the higher risk due to the combined effect of both the eolian dispersion of metals from the dune developed on the mine tailings, affecting the surrounding agricultural soils, and the gaseous mercury emissions. As previously mentioned in Section 4.2.2, agricultural soils surrounding San Quintín mine display As, Cd, Pb, and Zn contents higher than geochemical baseline. Therefore, they are contaminated and can be considered as a potential human health risk by the metal input to the olive tree crops. Nevertheless, metal contents in water from the watercourse crossing the mining area are below recommended limits for irrigation waters, denoting not significant affection by AMD. Although this zone is not remediated and not in a condition for public transit, the San Quintín mine has been reported as one of the points to be visited on the longest Eco-tourist Itinerary in Europe, named "Don Quixote Route, a place for adventure". Section four of the route crosses the San Quintín mining area, exhibiting ruinous mine structures. This mine has become a representative example of the socio-economic and cultural benefits that its restoration could confer to this zone. Although these types of tourist initiatives are remarkable in terms of geological heritage, a previous characterization and reclamation study has not been carried out.

Physical hazards are mainly related to the presence of open shafts and unstable ponds and have also been identified in the different mine districts. Alcudia valley and Mazarrón districts contain many abandoned open shafts and tunnels. Unstable ponds have also been identified as in the case of Brunite mine pond, where a previous dam failure occurred [5]. Similar to this, the outflow of acidic water through the dam of Mina Concepcion mine pond would represent a source of instability resulting in a potential physical hazard.

6. Conclusions

This work revealed that the joint use of mineralogical, geochemical, and geophysical techniques can provide an environmental characterization of abandoned mine sites, allowing for estimations of potential pollution and the extent of affected zones.

Significant potentially hazardous element contents have been identified in all studied mine districts, not only in the mine tailings but also in the underlying colluvial and alluvial sediments and surrounding soils. Mineralogical and geochemical signatures of the ore mineralization are clearly recognized in all analyzed samples. Pyrite, sphalerite, and galena are the main ore minerals identified in the mine tailings. Gangue minerals (quartz, illite, feldspar, and chlorite) and secondary minerals (Fe-sulfates, gypsum, and Fe-sulfates) have also been identified by XRD and/or ESEM-EDX. Significantly high contents of As, Cu, Pb, and Zn have been identified in the majority of the mine tailings, reflecting the related environmental hazards associated with all of these abandoned deposits. Moreover, significant potentially toxic element content has been analyzed in tailings from restored mine pond like Mina Concepción. Agricultural soil samples show lower metal and As content but higher Hg and Pb content than in the background sample in the San Quintín area. AMD has been clearly identified not only flowing from the remaining tailings, but also from a restored mine pond, denoting that environmental hazard persists.

ERT provides valuable additional information about the mine deposits. The strong resistivity contrast between the infilling and the underlying rock allows obtaining both the thickness of the infilling as the geometry of the bottom mine pond. Moreover, if the infilling deposits contain water, the resistivity values provide information about both the acidic character of the water and the occurrence or not of AMD flow outside the mine pond. The mapping of mine deposits from time series of aerial images reveals the strong impact of mining on the landscape due to the dumping of large amounts of polluting wastes and their mobilization thereof to the surrounding areas by several geological processes (mass movement, gully erosion, and eolian dispersion).

Major environmental hazards are associated with different main pathways (wind erosion and water flows) and several receptors (bathing waters, agricultural soils, humans, and sediments) depending on the specific mine area. In summary, this type of abandoned deposits need to be characterized, monitored, and restored in order to avoid mobilization of tens thousands of tons of potentially hazardous elements.

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Conflict of interest

The authors declare no conflict of interest in this chapter.

Author details

Tomás Martín-Crespo*, David Gómez-Ortiz and Silvia Martín-Velázquez
Department of Biology and Geology, Physic and Inorganic Chemistry, University Rey Juan Carlos, Madrid, Spain

*Address all correspondence to: tomas.martin@urjc.es

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