Pb–Zn–Cd–As Pollution in Soils Affected by Mining Activities in Central and Southern Spain: A Scattered Legacy Posing Potential Environmental and Health Concerns

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Abstract In this chapter, published geochemical data for soils from several Pb–Zn mine sites and districts from Spain are reviewed. Although most of the mines have closed down, a legacy of highly polluted soils still remains throughout the sites constituting a potential hazard for the environment and human health. The fate of the studied metals and metalloids in these soils is mainly controlled by factors such as mining methods, concentration and metallurgical operations, mineralogy of the ore, gangue and host rock, fracturing of the host rocks, physiography, climate, and soil types (pedogenic evolution). It can be concluded that the most polluted soils (identified on the basis of an enrichment factor) are those of the Sierra Minera (La Unión District – SE Spain), at more than 488 (Pb), 163 (Zn), 99 (Cd), and 98 (As) times the background values from non-contaminated soils. Pb is usually related to As, which in turn is bound to Fe oxides and oxyhydroxides. Metal bearing jarosite and other soluble phases also play a relevant role in the studied soil–water

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systems, because these minerals are dissolved during intense rainy events, thus resulting in high rates of metal leaching and mobilization by runoff.

Keywords Arsenic, Environmental geochemistry, Iberian Peninsula, Metals, Mine sites, Soils

Contents

Abbreviations

A	Agricultural
AFS	Atomic fluorescence spectroscopy
AMD	Acid mine drainage
BDL	Below detection limit
EDXRF	Energy dispersive X-ray fluorescence
ETAAS	Electrothermal atomization atomic absorption spectrometry
FAAS	Flame atomic absorption spectrometry
ICP-AES	Inductively coupled plasma atomic emission spectroscopy
ICP-MS	Inductively coupled plasma mass spectrometry
INAA	Instrumental neutron activation analysis
IPB	Iberian Pyrite Belt
MCL	Maximum contaminant levels
Q1	First quartile
Q3	Third quartile
REF_{metal}	Relative enrichment factor
RPL	Residential or parkland

1 A Brief Revision of the Most Relevant Pb–Zn Ore Deposits from the Southern and Central Iberian Peninsula

Given that this chapter is focused on metal pollution and Pb–Zn mineral deposits from the Iberian Peninsula, it is worth mentioning here that metal (and metalloid) dispersion can have both a natural and industrial origin. In this regard, once a mineral deposit is in the surface or near surface environment, fracturing will result in increased permeability and, therefore, in enhanced movement of oxygen-rich meteoric solutions throughout the ore bodies. This implies higher rates of oxidation and metal leaching. This case can be understood in terms of natural (geological) metal pollution. The second case is far more obvious and relates to the mining, processing, and smelting of Pb–Zn sulfides. Thus, to fully understand the combination of natural and industrial, a concise geological revision of the studied mine sites and districts follows.

There are numerous Pb–Zn ore deposits in southern and central Spain (Fig. 1), and these formed in different geological scenarios throughout the Iberian Peninsula from Paleozoic to Cenozoic time. With the exception of a few ore deposits in the Iberian Pyrite Belt (e.g., Las Cruces in Spain, Neves Corvo in Portugal), all mining operations in the described districts have ceased. However, a legacy of tailings deposits, waste rock dumps, and highly polluted soils still remains there constituting a potential hazard for the environment and public health.

1.1 Variscan Age Ore Deposits and Districts

These ore deposits are Pb–Zn hydrothermal vein deposits of Variscan to late Variscan age emplaced along faults crosscutting metasedimentary sequences of Neoproterozoic to Silurian age:

- Alcudia Valley and the San Quintín mining group, southern–central Spain (Fig. 1, Table 1), with about 453 ore deposits (most of them are of very small size). Total Pb production from the Alcudia Valley has been estimated at 1.4 Mt, of which 1.25 Mt was produced between 1840 and 1988. Estimated Ag production was 350 t. Lack of data prevents a reliable estimation of Zn production. For more info, see the comprehensive paper of Palero et al. [1]. Environmental impact: minor and very localized [2]. However, tailings deposits and acid mine drainage (AMD) may pose an environmental hazard for surrounding agricultural lands such as at the San Quintín mining group [3].
- Py–(Cu)–Zn–Pb–(Sn) stockwork and stratiform massive sulfides of volcanogenic origin and Upper Famennian–Lower Visean age occur in southern Portugal and Spain defining the so-called Iberian Pyrite Belt (IPB) (Fig. 1, Table 1), with more than 80 known deposits containing 1,700 Mt of sulfides

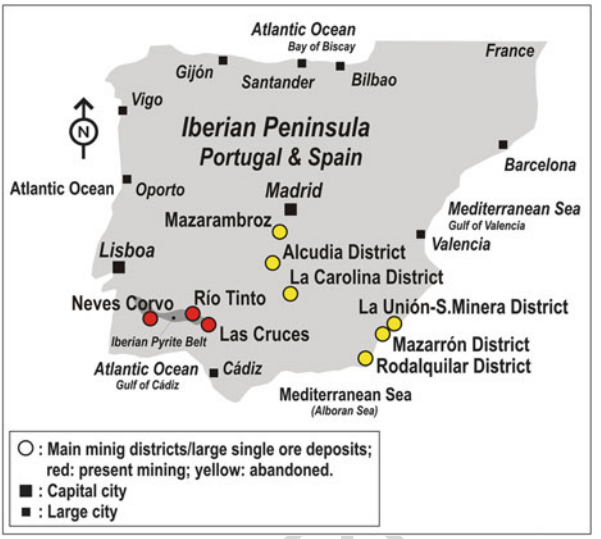

Fig. 1 Location of the Pb–Zn mining districts considered in this chapter

(250 Mt have been extracted; [25]), amounting 14.6 Mt Cu, 13 Mt Pb, 34.9 Mt Zn, 46,100 t Ag, and 880 t Au. For more info on the belt, see the comprehensive paper of Leistel et al. [9]. A few mines are currently operating along the belt, e.g., Las Cruces (Spain) and Neves Corvo (Portugal). Environmental impact: huge, including complete degradation of the River Tinto which owes its deep red color (and name) to massive AMD. The high pollution by heavy metals affecting the soils of the IPB deserved a noteworthy number of studies (e.g., [10–12]). The good news is that the red color is a tourist attraction and the river serves as a world-class natural laboratory for the study of specialized algae and bacteria (e.g., [18]).

- The Linares–La Carolina Ba–Pb–Zn–Cu–(Ag) vein deposits in central Spain (Fig. 1, Table 1) were mainly mined in the period 1875–1920 and constituted one of the most outstanding mining districts of Europe, with an average lead production of 65,000 t year^{-1} and up to 500 g/t silver obtained as a by-product. The workings were concentrated on vein-type hydrothermal mineralization hosted by granitoids and metasediments. The El Cobre vein, a cordilleran vein-type deposit, is representative of the veins in the district and is also one of the largest. The vein strikes northeast–southwest for about 5 km, has an average thickness of 2–3 m, and is hosted by monzogranitic rocks (the so-called Monzogranito de Linares) and minor Carboniferous metasediments. For more info on this district, see the paper of [5]. The soils of the district [6] are extremely rich in Pb (up to 410 times the world average for soils, [26]) whereas for Zn the enrichment is much lower (up to 7 times the world average for soils [26]).

t.1 **Table 1** Summary of basic information (ore and gangue, soils, and climate) from the districts considered in this chapter. Main references have been included

t.2 District	Metal association/ore type/main ore/gangue mineralogy	Soil uses/types/parent material	Climate	References
t.3 Alcudia, San Quíntin	Pb–Zn–(Cu)–(Ag) Vein-type deposits Sulfides, sulfosalts Quartz, ankerite, siderite, barite, calcite	*Dehesa* pastures (clear forest of evergreen oaks), Mediterranean forest Soil parent material[a]: metasediments	Mediterranean (dry season from June to September, average annual temperature is 14–15°C, average annual precipitation is 430–550 mm)	[1–4]
t.4 Linares–La Carolina	Ba–Pb–Zn–Cu–(Ag) Vein-type deposits Sulfides, sulfosalts Quartz, ankerite, barite, calcite,	*Dehesa* pastures, agriculture (olive groves, minor cereal crops) Soil parent material[a]: granites, metasediments, sedimentary rocks (sandstones, lutites, and marls)	Mediterranean (dry season from June to September, average annual temperature is 17°C, average annual precipitation is ~470 mm)	[5–8]
Iberian Pyrite Belt (IPB)	Py–(Cu)–Zn–Pb–(Sn) Stockwork and stratiform massive deposits. Gossans Sulfides Silicates (quartz, chlorite, sericite),	Degraded scrub, forest scrub, agriculture (orange plantations, horticulture), reclaimed for forest land Leptosols, Regosols, Cambisols, Fluvisols, Entisols	Semiarid Mediterranean (xeric–aridic moisture regime, dry season from April to September, average annual temperature is 15–20 °C, average annual	[9–11]: IPB2 data set [12]: IPB1 data set
t.5	carbonates, barite	Soil parent material[a]: shales, volcanic and volcanic-sedimentary rocks	precipitation is 400–700 mm)	[13]
t.6 Mazarambroz	Pb–Zn–(Ag) Vein-type deposits Sulfides, minor sulfosalts Quartz, siderite, barite	*Dehesa* pastures (clear forest of evergreen oaks), agriculture (extensive cereal crops) Cambisols, Anthrosols Soil parent material[a]: granites, migmatites, metasediments	Mediterranean (dry season from June to September, average annual temperature is ~16°C, average annual precipitation is ~370 mm)	[14–16]
t.7 Mazarrón	Pb–(Ag)–Zn–(As) Vein and stockwork type Sulfides Quartz, calcite, siderite, dolomite, and gypsum	Degraded scrub Anthrosols Soil parent material: volcanic rocks (dacites and rhyodacites)	Semiarid Mediterranean (dry season from June to August, average annual temperature is 16.5–18.8 °C, average annual precipitation is 185–310 mm)	[17]
t.8				[18–22]

(continued)

t.9 **Table 1** (continued)

t.10 District	Metal association/ore type/main ore/gangue mineralogy	Soil uses/types/parent material	Climate	References
La Unión (Sierra Minera, Cartagena)	Pb–(Ag)–Zn–(Sn)–(As) Stratabound ore deposits, disseminations in sedimentary facies, stockworks. Gossans Sulfides, sulfosalts Quartz, carbonates, clays, chlorite, sulfates	Degraded scrub, agriculture? Anthrosols Soil parent material[a]: sedimentary rocks (sands and conglomerates), subvolcanic (rhyolite, dacite, and andesite) and volcanic (alkaline basalt)	Semiarid Mediterranean (dry season from June to August, average annual temperature is 17°C, average annual precipitation is ~300 mm)	
t.9 Rodalquilar	High-sulfidation-type Au–(As)–alunite vein deposits Peripheral low-sulfidation Pb–Zn–Cu–(Au) veins Sulfides, sulfosalts Quartz, clays, alunite, chlorite	Degraded scrub, agriculture Inceptisols, Anthrosols Soil parent material[a]: ignimbrites, felsic domes	Semiarid Mediterranean (dry season from May to August, average annual temperature is 18°C, average annual precipitation is 200 mm)	[23, 24]

t.10 [a]In addition to mine wastes and modern sediments

1.2 Alpine Age Ore Deposits and Districts

- The Mazarrón district mineral deposits (SE Spain) (Fig. 1, Table 1) formed in Miocene time in relation to the emplacement of dacitic–rhyodacitic domes. The Pb–(Ag)–Zn–(As) ore deposits are of vein and stockwork type. There are three main mining sites (from east to west): San Cristóbal–Perules (adjacent to the town of Mazarrón), Pedreras Viejas, and Coto Fortuna. The area is located in the southern realm of a Miocene–Pliocene marine basin surrounded by mountains in its western, eastern, and southern flanks. The mines were exploited for lead, silver, and zinc during the nineteenth to twentieth centuries (until the early 1960s). The latter corresponds to the peak period of mineral extraction when 3 Mt of ore at 10% Pb and 150 g t^{-1} Ag was extracted between 1920 and 1941. This was followed by a decline in the period 1951–1962, when only 1 Mt of ore at 3% Pb, 5% Zn, and 115 g t^{-1} Ag was extracted. Despite strong AMD (seasonal ponds) and extremely high contents of Pb and Zn (and As) in the tailings and soils, ionic metal migration is limited by the presence of carbonate rocks (Alpujárrides Complex) and soils. The anthropic soils of the district are extremely rich in Pb (up to 200 times the world average for soils, [26]), whereas for Zn the enrichment is lower (up to 80 times the world average for soils, [26]). However, some extremely metal-rich tailings deposits reach the Las Moreras seasonal stream. For more info on this district, see Oyarzun et al. [17].
- The La Unión–Sierra Minera Pb–(Ag)–Zn–(Sn)–(As) district in Cartagena (SE Spain) (Fig. 1, Table 1) hosts ore deposits of different types, having in common a late Miocene age. These include stratabound ore deposits (the so-called mantos) (e.g., Emilia, Brunita), disseminations in the Miocene marine facies (e.g., Sultana), stockworks in felsic domes (e.g., Cabezo Rajao), and gossans. The mining district covers an area of about 10×5 km^2 that contains one of the largest densities of Pb–Zn ore deposits in Spain. Modern mining at the Sierra de Cartagena can be divided into two periods. The first one comprised traditional, underground operations that were active until the early 1950s. From 1957 onwards the Sociedad Minero Metalúrgica Peñarroya España (a French mining group) began large open pit mining operations, which led first to the generation of large volumes of tailings and mineral dumps and eventually to huge abandoned pits. The Roberto froth flotation plant disposed directly onto the Portman bay about 60 Mt of tailings during the period 1957–1990, eventually making the shoreline advance between 500 and 600 m seaward [19]. For more info on the district, see López_García et al. [18]. A myriad of tailings and waste rock deposits (nineteenth and twentieth centuries) are scattered throughout the district, although metal dispersion is restricted by the presence of carbonate rocks (Alpujárrides Complex) and soils. However, the area affected by mining activities is not small and covers about 1,000 km^2 [20]. Besides, agricultural soils surrounding old mining works (e.g., Cabezo Rajao) may have up to 2,000 mg kg^{-1} Pb and 1,200 mg kg^{-1} Zn [21].

- The Rodalquilar district in Almería (SE Spain) (Fig. 1, Table 1) is well known for its high-sulfidation-type Au–(As)–alunite vein deposits within a large volcanic caldera of Miocene age, with an ore mineralogy consisting of native gold (Au^0), pyrite, enargite (Cu_3AsS_4), tennantite ($Cu_{12}As_4S_{13}$), tetrahedrite ($Cu_{12}Sb_4S_{13}$), cinnabar (HgS), bismuthinite (Bi_2S_3), cassiterite (SnO_2), galena, and sphalerite. However, the district also hosts peripheral low-sulfidation Pb–Zn–Cu–(Au) veins. The geological setting of Rodalquilar district includes Upper Miocene felsic domes, ignimbrites, ash fall deposits, massive volcanic rocks, and a limestone complex of Messinian age. The sulfide mineralogy of the peripheral low-sulfidation deposits consists of native gold, sphalerite, galena, chalcopyrite, and pyrite. Mining initiated around 1825 for Pb, Zn, and Cu, and it was not until 1864 that the miners realized that the ore contained some gold as well. Mining operations belonging to this period are those of Consulta, María Josefa, San Diego, and Triunfo. The larger mining operation relates to the El Cinto high-sulfidation deposits and took place between 1943 and 1966, when about 1.6 Mt of ore grading 3.5 g t^{-1} Au was extracted. Most if not all of the tailings (between 900,000 and 1,250,000 m^3) around the town of Rodalquilar can be related to this mining period. For more info on the district, see the papers of Arribas et al. [23] and Oyarzun et al. [24]. Main environmental concerns relate to the high contents of As in anthropic and agricultural soils.
- The Mazarambroz Pb–Zn mineralization in the Toledo Mountains (central Spain) (Fig. 1, Table 1) is filling E–W fractures following the main direction of the so-called Mylonitic Band of Toledo. The veins are hosted by migmatites, metasediments, and granitic rocks related to the Mora Plutón [14]. Ag-rich galena and sphalerite are the main ore minerals, being accompanied by arsenopyrite (FeAsS), pyrite and marcasite (FeS_2), chalcopyrite ($CuFeS_2$), and gersdorffite (NiAsS), with quartz (SiO_2), siderite ($FeCO_3$), and barite ($BaSO_4$) as the dominant gangue minerals [15]. Mines in this area were exploited until the late 1970s [15]. The soils in this area show Pb, Zn, and As concentrations much higher than the regional averages for soils [16].

2 Understanding of the Geochemical Behavior of Pb and Zn in Natural Environments

2.1 Environmental Mineralogy and Geochemistry of Pb and Zn: A Brief Introduction

Lead and zinc are base metals that form one of the classic associations in ore deposits. Galena (PbS) and sphalerite (ZnS) are their common sulfide minerals, and they can be found together with chalcopyrite ($CuFeS_2$), pyrite (FeS_2), and arsenopyrite (FeAsS) (among others) in a variety of geological and ore-forming settings, such as skarns in limestones and dolostones (dolomites), hydrothermal veins, and

replacements in plutonic or volcanic rocks of felsic composition, volcanogenic massive sulfide deposits, and Mississippi Valley-type Pb–Zn ore deposits. Other common lead and zinc minerals are anglesite ($PbSO_4$), cerussite ($PbCO_3$), and smithsonite ($ZnCO_3$), together with the less common willemite (Zn_2SiO_4) and zincite (ZnO). The presence of silver in galena (either as mineral inclusions or solid solution) is relatively common.

The environmental legislation of most countries has progressively retired lead from common uses such as plumbing, additives for petrol, and paints, while it remains nevertheless being widely used in lead–acid batteries for cars. On the other hand, the major environmental and health concerns regarding Zn are not strictly related to the element but to its most common mineral: sphalerite, which usually hosts Cd. Cadmium and zinc belong to the same group of the periodic table (IIB) and share chemical properties such as the tetrahedral covalent bond and other crystal structures. They have similar ionic radii: Zn^{2+} (0.74 Å) and Cd^{2+} (0.97 Å), which accounts for the observation that cadmium occurs in sphalerite as an isomorphous impurity [27].

Lead and zinc ([28, 29]) can be regarded as chalcophile (i.e., those elements that combine easily with sulfur) although Zn also has lithophile affinities (i.e., those elements that concentrate in the silicate phase and combine readily with oxygen in the Earth's crust). The solubility of their ionic species (Pb^{2+}, Zn^{2+}) is controlled by the ionic potential, being extremely high in the case of Zn or extremely low in the case of Pb, which will form insoluble sulfates or carbonates ($PbSO_4$, $PbCO_3$). This is crucial to understand their geochemical behavior in the environment because while Pb will remain close to the source, Zn can move and disperse easily. This will happen even in extremely dry scenarios such as the Atacama Desert, where Zn forms vast geochemical halos surrounding the source (e.g., [30]).

Pb in freshwater systems will be complexed by carbonate species ($Pb(CO_3)_2^{2-}$) at pH 6–8, whereas stable species below and above this range will be $PbSO_4$ (or Pb^{2+} in low-sulfate waters) and $Pb(OH)_2$, respectively [26]; besides, Zn^{2+} is the most stable species of zinc below pH 8, whereas $ZnCO_3$ is stable at higher pH. Complexing of Zn with SO_4^{2-} becomes important only in sulfate-rich acidic waters [26], a geochemical scenario where important oxidation of pyrite (FeS_2) has occurred (1) leading to formation of AMD:

$$4FeS_2 + 10H_2O + 15O_2 \rightarrow 4FeO(OH) + 16H^+ + 8SO_4^{2-}. \quad (1)$$

This is also important to understand oxidation and hydrolysis of galena and sphalerite in the supergene environment of the higher sections of sulfide ore deposits (2, 3), because if pyrite is volumetrically unimportant, reaction (4) will be insignificant and no important formation of Fe^{3+} will occur [31]:

$$4FeS_2 + 14O_2 + 4H_2O \rightarrow 4FeSO_4 + 4H_2SO_4, \quad (2)$$

$$4FeSO_4 + 2H_2SO_4 + O_2 \rightarrow 2Fe_2(SO_4)_3 + 2H_2O, \quad (3)$$

$$Fe_2(SO_4)_3 \rightarrow 2Fe^{3+} + 3SO_4{}^{2-}. \quad (4)$$

The chemical evolution of the system from (2) to (4) is the main prerequisite to induce oxidation and hydrolysis of galena (5) and sphalerite (6) [31]:

$$PbS + 8Fe^{3+} + 4H_2O \rightarrow Pb^{2+} + 8Fe^{2+} + SO_4{}^{2-} + 8H^+, \quad (5)$$

$$ZnS + 8Fe^{3+} + 4H_2O \rightarrow Zn^{2+} + 8Fe^{2+} + SO_4{}^{2-} + 8H^+. \quad (6)$$

Given that sphalerite often contains Cd, the oxidation and leaching of this metal can be expressed in the following way (7):

$$Zn_{1-x}Cd_xS + 8Fe^{3+} + 4H_2O \rightarrow (1-x)Zn^{2+} + xCd^{2+} + 8Fe^{2+} + SO_4{}^{2-} + 8H^+. \quad (7)$$

Arsenopyrite is present in many Pb–Zn deposits (e.g., the Mazarrón district), and therefore it is worth showing here how the oxidation of this mineral occurs [32] (8–11):

$$FeAsS \rightarrow Fe^{2+} + \tfrac{1}{2}As_2S_2 + 2e^-, \quad (8)$$

$$As_2S_2 + 14H_2O \rightarrow 2H_3AsO_3 + 2\,SO_4{}^{-2} + 22H^+ + 18\,e^-, \quad (9)$$

$$H_3AsO_3 + H_2O \rightarrow H_3AsO_4 + 2H^+ + 2\,e^-, \quad (10)$$

$$Fe^{2+} \rightarrow Fe^{3+} + 1\,e^-. \quad (11)$$

If fO_2 conditions are high, then oxidation of As^{3+} to As^{5+} may proceed in the following way [33] (12):

$$H_3AsO_3 + \tfrac{1}{2}O_2 \rightarrow H_2AsO_4{}^- + H^+. \quad (12)$$

The concentrations of these ionic or complex ion species in water are a particularly sensitive case regarding public health; in this regard, maximum contaminant levels (MCLs) for drinking water (USA) for these elements are Pb (0.015 mg L^{-1}), Zn (5 mg L^{-1}), Cd (0.005 mg L^{-1}), and As (0.01 mg L^{-1}) [34]. MCLs have to be understood as the highest level of a contaminant that is allowed in drinking water using the best available treatment technology and taking cost into consideration [34]. However, do these MCL figures reveal the complete picture regarding metal toxicity? Not really, because toxicity does not depend on concentration but on the bioavailability of the metal species [35]. In fact, strongly complexed metals, especially those complexed by natural chelating agents such as the humic acids, appear to be completely unavailable and nontoxic [35]; thus, metal speciation studies are of paramount importance to fully understand the potential health hazards derived from the existence of high concentrations of metals in waters (surface or underground). The same applies to sediments and soils.

Regarding sediment quality guidelines for freshwater ecosystems, the following threshold effect concentrations (meaning that below these levels, no adverse effects for the biota should happen) are suggested for lead, zinc, and cadmium: Pb (35 mg kg^{-1}), Zn (121 mg kg^{-1}), Cd (0.99 mg kg^{-1}), and As (9.79 mg kg^{-1}) [36]. Nevertheless, natural systems are to be regarded for what they are, nonlinear highly complex systems in which the outcome cannot be fully predicted based only on the study of just a few variables. For example, the ultimate fate of free cadmium (Cd^{2+}) may be strongly influenced by the presence of pyrite, which is particularly important in anoxic media. In this regard, two reactions (13, 14) are to be taken into account [35]:

$$FeS_{(s)} \leftrightarrow {Fe^{2+}}_{(aq)} + {S^{2-}}_{(aq)}, \quad (13)$$

$${Cd^{2+}}_{(aq)} + {S^{2-}}_{(aq)} \leftrightarrow CdS_{(s)}. \quad (14)$$

In this regard, if the free (and therefore available) Cd^{2+} metal ion is combined with free sulfur (S^{2-}), then CdS will precipitate and become unavailable. Given that cadmium has more affinities for sulfur than iron, then the overall reaction will proceed towards the products (right-hand side) (15):

$${Cd^{2+}}_{(aq)} + FeS_{(s)} \rightarrow {Fe^{2+}}_{(aq)} + CdS_{(s)}. \quad (15)$$

A similar concern regarding these elements is observed in the Canadian Soil Quality Guidelines [37], which indicate maxima levels of (A, agricultural; RPL, residential or parkland): 70 mg kg^{-1} (A) and 140 mg kg^{-1} (RPL) for Pb, 200 mg kg^{-1} (A and RPL) for Zn, 1.4 mg kg^{-1} (A) and 10 mg kg^{-1} (RPL) for Cd, and 12 mg kg^{-1} (A and RPL) for As.

2.2 Speciation of Pb and Zn in Contaminated Soils

Speciation of metals in soils depends on the type of soil matrix, pH, Eh, colloidal activity, and climate. For example, in soils with abundant organic matter, Pb^{2+} may be complexed to salicylate- and catechol-type functional groups of humic substances [38], whereas Zn is not expected to significantly bind to organic matter [39]. Conversely, Zn^{2+} in these acidic soils can be found as franklinite ([(Zn, Mn^{2+}, Fe^{2+})(Fe^{3+},Mn^{3+})$_2O_4$]) or bound by adsorption to Fe and Mn oxyhydroxides as inner-sphere sorption complexes [39]. To understand lead speciation in carbonate-rich soils, the formation of carbonic acid has to be considered since it is a key reactant for the ultimate fate of this metal (16):

$$CO_{2(g)} + H_2O \leftrightarrow H_2CO_{3(aq)}. \quad (16)$$

Pb^{2+} in alkaline soils such as pedocals (which form in semiarid and arid regions) will first form Pb oxides (17), followed by the formation of cerussite ($PbCO_3$) (18)

at nearly neutral to slightly alkaline pH and even hydrocerussite (19) if pH is high enough:

$$Pb^{2+}{}_{(aq)} + \tfrac{1}{2}O_{2(g)} \rightarrow PbO_{(s)}, \quad (17)$$

$$PbO_{(s)} + H_2CO_{3(aq)} \rightarrow PbCO_{3(s)} + H_2O, \quad (18)$$

$$3PbO_{(s)} + 2H_2CO_{3(aq)} \rightarrow Pb_3(CO_3)_2(OH)_{2(s)}. \quad (19)$$

In the same environment, Zn^{2+} may form smithsonite ($ZnCO_3$) or hydrozincite ($Zn_5(CO_3)_2(OH)_6$).

Arsenic is usually bound to Fe oxide/hydroxide phases in soils [33] and river sediments (e.g., [40]). Colloidal goethite has a net positive charge in acid media [41], which binds by adsorption of the negatively charged arsenic complex ions of general composition $H_xAsO_y{}^{-z}$ (where $x = 1$, 2, or 3; $y = 3$ or 4; and $z = 0$, -1, or -2). These complex ions may remain strongly bound to goethite up to higher pH of 8.0–8.5 [42–44]. Desorption of arsenic from goethite may occur by competition between negative charges for the positive colloid, a reduction of the iron oxide mineral phase [45], or high pH values (>8.5). If plants are present, then the chemical interactions that take place in the soil–rhizosphere–plant system have to be considered. According to [46], 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) [46]. Alternatively, in carbonate-rich rocks and soils, the acid solutions will become neutral to alkaline, and two arsenic minerals will precipitate: first weilite ($Ca(AsO_3OH)$) and then pharmacolite ($CaHAsO_4 \cdot 2H_2O$) [33]. Besides, the same authors found remarkable redox seasonal changes for arsenic in river sediments; winter is characterized by a dominance of As^{3+} species within an environment ruled by the activity of bacteria, which leads to the formation of amorphous Fe^{3+}-As^{3+} precipitates together with nanocrystalline tooeleite ($Fe_6(AsO_3)_4SO_4(OH)_4 \cdot 4H_2O$). On the other hand, biotic oxidation of As^{3+} and Fe^{2+} leads to the precipitation of mixed Fe^{3+}-As^{5+} hydrous oxides during spring and summer [33].

3 Mining and Pb–Zn Dispersion in Soils: Some Facts and Fads

3.1 How Bad Is the Case?

Mining has indeed a bad press. Poor public relations skills of mining company officials, the action of environmental groups, and a traditional mistrust from the ordinary citizens have contributed to create an increasingly poisoned social scenario. There is no question on whether mining strongly polluted the environment

(atmosphere, soils, underground and surface waters, biota, etc.) with heavy metals and/or metalloids prior to the enforcement of environmental regulation laws (from the 1980s onwards) in most countries. However, different to popular beliefs, mining is by no means at present the evil force that many environmental lobbies claim to be. In this regard, if the Earth's land area modified by human action mostly during the last 500 years ($53.5 \pm 5.1\%$) [47] is taken into account, mining and quarrying have contributed with a mere 0.3% (there is a 67% probability that the actual value lies between 0.2% and 0.6%); for comparison, agriculture and forestry contribute with a huge $46.6 \pm 5.0\%$ [48]. This is particularly significant if it is considered that modern agriculture is the kingdom of chemicals, which are nevertheless a key prerequisite to maintain and even increase global production to sustain an ever-growing human population.

Having said all this, it must be clear on this matter that it is not suggested here that mining (and particularly the smelting of lead minerals) does not pose an important health risk. In fact, lead can affect the nervous system, kidney function, immune system, reproductive and developmental systems, and the cardiovascular system, also affecting the oxygen carrying capacity of the blood; in this regard, this metal is persistent in the environment and accumulates in soils and sediments through deposition from air sources, direct discharge of waste streams to water bodies, mining, and erosion [49]. For example, a comprehensive geochemical and epidemiologic study carried out in 1974 at Coeur d'Alene (Idaho, USA) revealed the following [50]:

- Lead levels in air, soil, and dust were highest at the smelter and decreased with distance, with peak concentrations in soils and vegetation of 9,000 and 3,478 mg kg^{-1}, respectively.
- 99% of 1- to 9-year-old children living within 1.6 km from the smelter had blood lead levels $\geq$40 μg dl^{-1}, indicating increased absorption (22% had levels $\geq$80 μg dl^{-1}).
- Lead levels $\geq$40 μg dl^{-1} decreased with distance, for example, at 72 km from the smelter, it was 1%.
- 17% of children with lead levels of $\geq$80 μg dl^{-1} were anemic.

Another example is related to the Antofagasta (Chile) incident involving lead poisoning in children. Lead was gathered in bulk (Pb mineral concentrates from Bolivia) within the 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 in children [51].

On the other hand, mining and smelting of zinc has been by far the most important contributor of this metal to the environment [26]. For a long time, Zn was not considered to be harmful for the environment, and it was thought to pose minimal health risks compared to other heavy metals; however, at present zinc is known to cause toxic effects in the aquatic biota [26]. Besides, the almost ubiquitous presence of Cd in sphalerite (ZnS) is another factor to be taken into account. Zinc is an essential element, necessary for the function of more than 300 enzymes; however, oral exposure to high levels of zinc in humans can result in several

systemic effects [52]. In this regard, the major concerns about Zn are not usually related to the element but to sphalerite, which usually hosts Cd. This toxic element causes the so-called itai-itai disease, that is, osteomalacia with various degrees of osteoporosis accompanied by severe renal tubular diseases [53]. Low-molecular-weight proteinuria has been reported among people living in contaminated areas in Japan and exposed to cadmium via food and drinking water [53]. Regarding arsenic, acute and chronic poisoning involves the respiratory, gastrointestinal, cardiovascular, nervous, and hematopoietic systems; besides arsenic is carcinogenic and may cause lung, bladder, liver, renal, and skin cancers [54]. The toxicity of this metalloid depends on its binding form. For example, the organic arsenic compounds are less toxic than inorganic species. In fact, As^{3+} is 10 times more toxic than As^{5+} and 70 times more toxic than the organic species.

Although mining and processing of Pb and Zn in the Iberian Peninsula is currently restricted to a few mines in the IPB, a myriad of abandoned mines, tailings, and waste rock dumps are scattered in the old mining districts, and some of them are in close proximity to towns. For example, Pb–Zn tailings are part of the urban landscape of Mazarrón [17].

3.2 When Should We (Really) Worry About?

This is an important question that should be addressed from a combined industrial and environmental perspective including the following factors: mining methods (underground – open pit); concentration and metallurgical operations; mineralogy of the ore, gangue, and host rock; fracturing of the host rocks; physiography (hilly vs. flat terrain); climate; and, last but not least, soil types (pedogenic evolution):

- *Mining methods*: It does not escape to anyone that the impact of open pit mining is far larger than the underground procedures. It is a matter of simple mathematics: a usual rate of waste to mineralized rock in open pit operations is 3:1 (or more), meaning that for each ton of rock that will undergo milling and mineral concentration, three will go into waste; moreover, this three tons will not be entirely "barren" because they may host subeconomic mineralization (usually rich in pyrite). In this case, the sulfides present in huge waste rock piles will be exposed to oxygen and water, which implies generation of AMD and metal leaching. Besides, once the mining operations have ceased, a huge rock surface within the pit will be also left to undergo chemical reactions, which may have disastrous consequences for the chemistry of groundwaters. On the contrary, underground mining is more selective (it has to be; otherwise it would turn out to be uneconomic), and therefore waste rock piling will be minimal. However, these galleries and stopes placed above the water table may also undergo oxidation and leaching.
- *Mineral concentration*: As any other industrial activity, mining has undergone a complete transformation since the second half of the nineteenth century.

Different to the froth flotation (introduced in the early twentieth century), mineral concentration in the nineteenth century (and well into the twentieth century) was performed by gravity using jigs (e.g., as at Mazarrón and La Unión), an inefficient procedure that contributed to generate tailings deposits extremely rich in Pb and Zn; for example, 4830–21,600 mg kg^{-1} Pb and 2410–13,100 mg kg^{-1} Zn [17].

- *Mineralogy of the ore, gangue, and host rock*: As previously discussed (1–7), key for the oxidation and leaching of Pb and Zn from galena and sphalerite is the presence of pyrite in the system. Thus, the relative abundance of pyrite among the sulfide species in one particular ore deposit will rule the rate of oxidation during weathering. Other important factors to be taken into account are the fO_2 (no oxygen–no oxidation), water (these are also hydrolytic chemical processes), and biological activity. The latter is driven by the presence of chemolithotrophic bacteria such as (among others) *Thiobacillus ferrooxidans* or *Leptospirillum* spp. [55]. In this regard, the rate of pyrite oxidation directly relates to the rate at which aqueous Fe^{3+} can be produced from Fe^{2+} by microbial catalysis [56]. In turn, abiotic and biotic oxidation of pyrite generates two powerful chemical leaching agents: sulfuric acid and ferric sulfate (2, 3). However, if the gangue minerals or the host rock includes species such as calcite ($CaCO_3$), the acid will react with the carbonate, H^+ will be consumed, and leaching will be reduced or stopped altogether (20):

$$CaCO_3 + H^+ \leftrightarrow Ca^{2+} + HCO_3^-. \quad (20)$$

The same applies to the feldspars (21) and their hydrolytic by-products (22) that can be found in volcanic or plutonic rocks [57]:

$$3KAlSi_3O_8 + 2H^+ \rightarrow KAl_3Si_3O_{10}(OH)_2 + 6SiO_2 + 2K^+, \quad (21)$$

$$2KAl_3Si_3O_{10}(OH)_2 + 2H^+ + 3H_2O \rightarrow 3Al_2Si_2O_5(OH)_4 + 2K^+. \quad (22)$$

- *Fracturing*: The intensity of fracturing also plays a major role in the oxidation leaching of sulfides. A high density of major fractures facilitates erosion and, therefore, the unroofing of mineral deposits. Once the mineral deposit is in the surface or near surface environment, fracturing will result in increased permeability and, therefore, in enhanced movement of oxygen-rich meteoric waters throughout the ore bodies. This implies higher rates of oxidation and metal leaching [57].
- *Climate and physiography*: They do play a major role in metal dispersion. Given that leaching of metals is an essentially chemical process, temperature will play a crucial role: warmer conditions will enhance the process, whereas cold conditions will slow it down. Total rain precipitation is also important [17]. For example, rainfall and dry events cause increases and decreases, respectively, in acid and metal concentrations. The process does not end until pyrite is fully weathered, which can take hundreds to thousands of years [58]. As noted by

[58], long dry spells result in gradual increases in metal concentrations, whereas sudden large increases are observed during initiation of rains. However, as precipitations reach their peak, the solutions become diluted. On top of this, the flash floods generated during stormy episodes must be added as they have the capacity to remove contaminated soils and tailings deposits. If this occurs, massive transport of contaminated materials will go to the rivers and, from there, to the lowlands. This is a process that will be enhanced by the high-altitude environment. In this regard, the rule of thumb is: the higher a mining operation is located, the greater the risk of mass movement of contaminated materials. This is well exemplified by cases in Chile (Pascua – Lama, El Indio Belt) and New Guinea (OK Tedi, Grasberg, Porgera) (e.g., [2, 40, 57], of this chapter).

- *Soil types (pedogenic evolution)*: The retention and accumulation of metals in the soil depends on various soil characteristics such as solid phase components (organic matter, sulfates, carbonates and clay minerals, oxides, etc.), texture, structure, pH, and ion exchange capacity (e.g., [13, 17]). These soil characteristics are intimately related to the climate and physiography in terms of soil evolution. Organic matter plays a key role as they may form very stable organic-mineral complexes and they have a very high ion exchange capacity. Alternatively, soluble humic substances as fulvic acids may form quelates that facilitate the metal leaching from the soil. Soil mineralogy is crucial because of the importance of adsorption processes and ion exchange capacity in clays and oxides, hydroxides, and oxyhydroxides and metal coprecipitation in sulfates and carbonates. The presence of soluble salts may affect the pH and the ion (cation) exchange of metals. Texture and structure control the water–rock interaction and solid phase reactivity through specific surface and hydraulic conductivity. The pH in terms of active and potential acidity plays a dual role, firstly because it controls the ion exchange capacity (especially in organic matter) and secondly because metal solubility depends on pH.

AU5

These reasons explain why risk assessment of metal leaching from ore deposits, tailings, and waste rock dumps is so complex. In fact, it involves complex nonlinear systems in which the measurements of the pollutant phase(s) (and other variables: see above) alone cannot provide a complete picture of the state of the system, because they are limited in space and time. However, at least a partial answer may be provided to the initial question on when we should be worried regarding metal leaching. In this process nothing is as decisive as: (1) the proportion of pyrite in the sulfide mineral assemblage and (2) the reactivity of the gangue and host rock minerals. This puts the IPB deposits in the worst possible case scenario (extremely rich in pyrite).

4 Pb, Zn, Cd, and As in Soils from the Studied Iberian Mining Sites and Districts

To study the Pb, Zn, Cd, and As distribution in soils from the revised mining sites and districts (Fig. 1, Table 1), published data from soils subjected to different uses (agricultural, natural, and anthropic) have been considered (Table 2). The more polluted soils were identified on the basis of a relative enrichment factor (REF_{metal}), defined by the ratio ([metal concentration in polluted soil – metal background concentration in soil]/[metal background concentration in soil]). By using the REF value, it is assumed that soils may have high background metal concentrations in natural, nonpolluted conditions as they are in areas that host ore deposits. Indeed, ore deposits induce the generation of geochemical dispersion halos, which can be regarded as a "natural contamination process" different to these of industrial origin generated by mining, processing, and smelting of sulfide ores. The relationships between metals and As (arsenic is a metalloid) were studied by correlation matrices, and cluster and factor analyses were also used to investigate whether different geological and industrial scenarios resulted in the formation of differentiated clusters of mineral deposits. Below detection limit (BDL) data were set to a value of half the BDL concentration for each element [59]. Besides, given that a sizeable proportion of data with identical value can seriously influence any multivariate analysis [4, 60], the sets with BDL data >10% of the population were excluded. Log transformation was applied to data to get more symmetrical (Gaussian) distributions. In this regard, many trace element distributions show important skewness, which may disappear if the logarithm of the values (log x) is considered. If this is the case, it can be said that log x has a normal distribution, or simpler, that the distribution is lognormal [61].

Although there are significant differences in size among the data sets, the following facts can be highlighted in terms of mean concentrations and enrichment factors.

4.1 Mean Concentrations

- The highest Pb and Zn mean concentrations are found in soils located in the Sierra Minera (La Unión District) with values of 6,241 and 9,111 mg kg^{-1}, respectively (Fig. 2, Table 2). However, the data population shows a large dispersion with some outliers of very high concentrations that displace the mean outside the first quartile (Q1) and third quartile (Q3) range (Fig. 2, Table 2). The lowest Pb and Zn mean concentrations are found in soils located in Rodalquilar (226.3 and 118.9 mg kg^{-1}, respectively) (Fig. 2, Table 2).
- The highest As mean concentration (1,309 mg kg^{-1}) is also found in soils from the Sierra Minera (Fig. 2, Table 2), whereas the lowest As mean concentration (26.1 mg kg^{-1}) is found in Linares (Fig. 2, Table 2).

Table 2 Descriptive basic statistics of trace element concentrations. Mean, median, minimum, maximum, first quartile (Q1), and third quartile (Q3) values are expressed in mg kg^{-1}

Variable ($n = 126$)	Analysis method	Mean	St. Dev.	Min.	Q1	Median	Q3	Max.
Linares (Source: [8]*)*								
Ag	ICP-AES	2.1	4.3	0.3	0.3	0.5	1.8	29.2
As	ICP-AES	26.1	29.2	2.5	11	17	26	175.5
Cd	ICP-AES	0.8	2.9	0.2	0.2	0.2	0.6	31.8
Cu	ICP-AES	145.4	242.5	14	32.8	53.5	128.4	1,654
Pb	ICP-AES	4077	7,016	27	267	1,279	4,867	37,356
Sb	ICP-AES	18.6	90	2.5	2.5	2.5	10	992
Zn	ICP-AES	123.9	206	26	46	71.5	133.5	1,988
Mn	ICP-AES	1,210.7	802.1	194	530.8	1,086	1,608	3,981
Va ($n = 31$)								
Rodalquilar (Source: [24]*)*								
As	ICP-MS	422	473.1	27.4	70.4	169	784	1,510
Bi	ICP-MS	8.5	13.9	0	1	2.8	10.2	73.5
Cd	ICP-MS	0.3	0.2	0.1	0.1	0.2	0.2	0.8
Cu	ICP-MS	73.6	49.5	11.2	39.8	57.5	102	178
Hg	Pyrolysis	0.4	0.6	0	0.1	0.2	0.5	2.6
Pb	ICP-MS	226.3	158.7	28.2	115	193	270	798
Sb	ICP-MS	19.4	18.8	0.6	4.6	10.7	32.2	62.6
Se	ICP-MS	15.7	14.5	1.5	3.9	8.9	27.5	49.8
Sn	ICP-MS	25.7	28.5	2	5	11	37	108
Zn	ICP-MS	118.9	103.3	1.3	42.4	77.2	160	401
Va ($n = 15$)								
Mazarrón (Source: [17]*)*								
Ag	ICP-MS	9.7	11.2	0.4	2.5	6.4	12.4	36
As	ICP-MS	252.3	206.6	58	98	189	299	744
Ba	ICP-MS	1,212	1,425	149	485	774	1,390	6,050
Bi	ICP-MS	0.3	0.6	0.01	0.1	0.2	0.4	2.4
Cd	ICP-MS	11.4	9.9	0.7	5	7.6	18	32.8
Cu	ICP-MS	88.7	59.4	27	41	80	123	259
Pb	ICP-MS	2,955	2,570	235	908	2,600	4,820	9,110
Sb	ICP-MS	54.4	42.2	10.3	27.3	40.5	80.1	174
Se	ICP-MS	1.2	0.4	0.5	1.1	1.2	1.4	2
Sn	ICP-MS	14.3	10.6	4	9	11	14	48
Zn	ICP-MS	1,651	1,584	331	563	791	3,030	5,250
Var ($n = 54$)								
Sierra Minera (Source: [22])								
As	AFS	1,309	1,123	67	453	1,020	1,597	4,429
Cd	ETAAS	37.6	22.6	2.2	22.2	33.7	44.5	123.2
Cu	ETAAS	352.1	293.4	21.5	140.5	258.4	576.2	1,335
Hg	AFS	0.3	0.5	0	0	0.1	0.4	2
Pb	ETAAS	6,241	9,390	25	2,287	3,328	4,222	47,619
Zn	FAAS	9,111	6,911	516	3,223	7,844	11,336	30,405

(continued)

Table 2 (continued) t.45

Variable ($n = 126$)	Analysis method	Mean	St. Dev.	Min.	Q1	Median	Q3	Max.	
Variable ($n = 142$)									t.46 t.47
Alcudia (Source: [2]*)*									t.48
As	EDXRF	37.4	83.16	0.5	17	22	26	792	t.49
Cd	EDXRF	10.53	51.83	0.5	0.5	0.5	2	530	t.50
Cr	EDXRF	33.84	33.39	0.5	14	26	44.25	253	t.51
Cu	EDXRF	56.6	150	1	11	15.5	31	1,283	t.52
Hg	EDXRF	71.4	342.7	0.5	0.5	0.5	0.5	2,665	t.53
Mo	EDXRF	3.067	3.702	0.5	0.5	1	5	19	t.54
Ni	EDXRF	12.3	21.63	0.5	0.5	4.5	16	137	t.55
Pb	EDXRF	1,575	5,581	69	112	169	544	52,207	t.56
Sb	EDXRF	2.98	12.37	0.5	0.5	0.5	0.5	110	t.57
Se	EDXRF	33.7	27.56	18	25	27	31	282	t.58
Zn	EDXRF	517	1,232	30	61	112	259	8,336	t.59
Variab = 50)									t.60
Mazarambroz (Source: [16])									t.61
As	EDXRF	161.8	417.5	11	30	61	140.5	2,955	t.62
Cd	EDXRF	5.69	10.02	0.5	0.5	0.5	7.25	47	t.63
Cr	EDXRF	52.11	45.45	0.5	21.75	46	75	244	t.64
Cu	EDXRF	40.78	36.22	8	17.75	32.5	50.5	232	t.65
Hg	EDXRF	0.5	0	0.5	0.5	0.5	0.5	0.5	t.66
Mo	EDXRF	9.84	3.285	3	8	10	12	19	t.67
Ni	EDXRF	22.3	23.49	0.5	6	18	29	112	t.68
Pb	EDXRF	307.9	472.8	86	97	109.5	267.3	2,867	t.69
Sb	EDXRF	0.73	1.626	0.5	0.5	0.5	0.5	12	t.70
Se	EDXRF	22.64	6.444	0.5	21	24	26	32	t.71
Zn	EDXRF	603	1,251	67	110	160	389	762	t.72
Varia = 32)									t.73
IPB1 (Source: [12])									t.74
As	INAA	562.4	441.9	51	185.5	443.5	896	1,560	t.75
Cd	ICP-AES	1.744	3.99	0.15	0.15	0.65	1	22	t.76
Cr	INAA	77.84	51.34	2.5	48.25	73	94.25	226	t.77
Cu	ICP-AES	684	678	24	238	413	992	2,874	t.78
Hg	INAA	6.78	14.5	0.5	0.5	0.5	4.75	62	t.79
Ni	ICP-AES	34.69	29.93	0.5	12	30.5	51.75	138	t.80
Pb	ICP-AES	1,705	1,839	59	239	1,165	2,637	6,500	t.81
Zn	ICP-AES	599	1,192	22	175	354	500	6,890	t.82
Varia = 15)									t.83
IPB2 (Source: [11])									t.84
As	INAA	226.8	315.8	18.8	30.2	78.7	361	994	t.85
Cd	ICP-AES	0.917	0.529	0.15	0.5	0.8	1.2	2.3	t.86
Cr	INAA	129.3	56.8	35	98	111	173	236	t.87
Cu	ICP-AES	259.7	296.8	27	90	159	253	1,160	t.88
Ni	ICP-AES	45.93	20.23	14	26	51	60	75	t.89
Pb	ICP-AES	810	1,341	41	93	197	1,270	4,890	t.90
Zn	ICP-AES	303.1	233.9	95	147	206	356	897	t.91

ICP-AES, inductively coupled plasma atomic emission spectroscopy; ICP-MS, inductively coupled plasma mass spectrometry; AFS, atomic fluorescence spectroscopy; FAAS, flame atomic absorption spectrometry; ETAAS, electrothermal atomization atomic absorption spectrometry; EDXRF, energy dispersive X-ray fluorescence; INAA, instrumental neutron activation analysis t.92

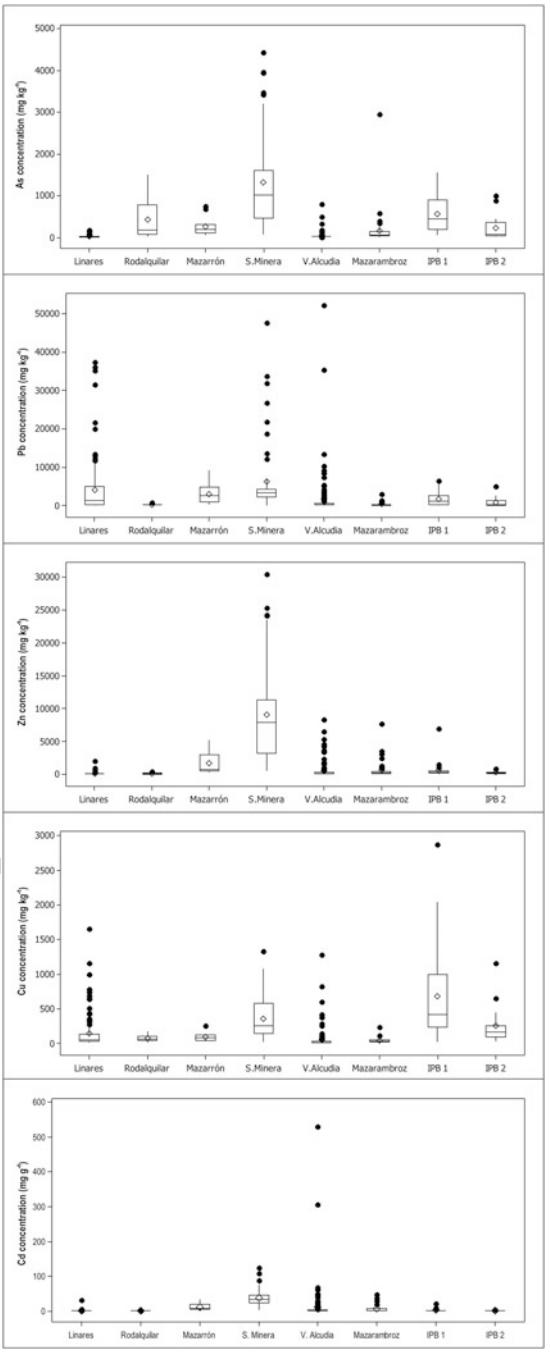

Fig. 2 Box-and-whisker plot for As, Pb, Zn, Cu, and Cd concentrations. The central box covers the middle half of the data, extending from the lower (Q1) to the upper quartile (Q3). The lines extending above and below the box (*whiskers*) show the range from which the not included data are considered as outsiders. The median of the data is indicated by the *horizontal line* within the box, whereas the *diamond sign* shows the location of the arithmetic mean

- The highest Cd mean concentration (37.6 mg kg^{-1}) is also from the Sierra Minera (Fig. 2, Table 2), whereas the lowest is found in Rodalquilar (0.2 mg kg^{-1}) (Fig. 2, Table 2).

4.2 Enrichment Factors (REFmetal)

- The most Pb–Zn polluted soils correspond to those of the Sierra Minera (Fig. 3, Table 3) with Pb and Zn at more than 488 and 163 times the background, respectively. Conversely, the least Pb–Zn polluted soils are those of Linares, with Pb at 2.5 times the background value and Zn close to the background.
- The most As polluted soils are those of the Sierra Minera (Fig. 3, Table 3) at ~98 times the background value. On the other hand, the less polluted soils correspond to those located in Linares (Fig. 3, Table 3) at less than 0.5 times the background value.
- The most Cd polluted soils are found in the Sierra Minera (Fig. 3, Table 3) at more than 99 times the background value, whereas the less polluted soils are those from IPB, close to the background values.

4.3 Correlations and Clustering of Data

- The highest correlations in soils from the Alcudia Valley are found for the Pb–Zn and Pb–Cu pairs (0.86), whereas insignificant correlations are found for As–Zn and As–Cr (0.02 and 0.07, respectively) (Table 4). Thus, the lack of relation among As and metals is remarkable (Fig. 4).
- Contrary to the results for the Alcudia Valley, the strongest correlation in the (IPB) is found for the As–Pb pair (0.80 in the data set IPB1 and 0.91 in data set IPB2) (Table 4). In this regard, As gests clustered with Pb and Cu in the two populations, whereas Zn appears to show more affinity for Cd and Cr with Ni (Fig. 4).
- The strongest correlation in Linares is found for the pair As–Pb (0.81) (Table 4), which is also indicated by the cluster analysis (Fig. 4). Besides, the lowest correlation is shown by the Pb–Zn and Cu–Zn pairs (0.65) (Table 4), a fact also shown by the cluster analysis (Fig. 4).
- The data from Mazarrón show a pattern similar on that observed for the IPB data sets, with As clustering with Pb and Cu (and also Ag in the Mazarrón case) (Fig. 4). Zn clusters with Cd, whereas Cr does it with Ni. The As–Pb is well correlated (0.81) (Table 4) although the highest correlation corresponds to the Ag–Pb pair (0.94) (Table 4). The pairs Ba–Cu and Ba–Sn display the lowest correlations (−0.06 and 0, respectively) (Table 4).
- The strongest correlation in the data from Sierra Minera is shown by the As–Cu pair (0.70) (Table 4), and the lowest corresponds to the As–Hg pair (−0.01)

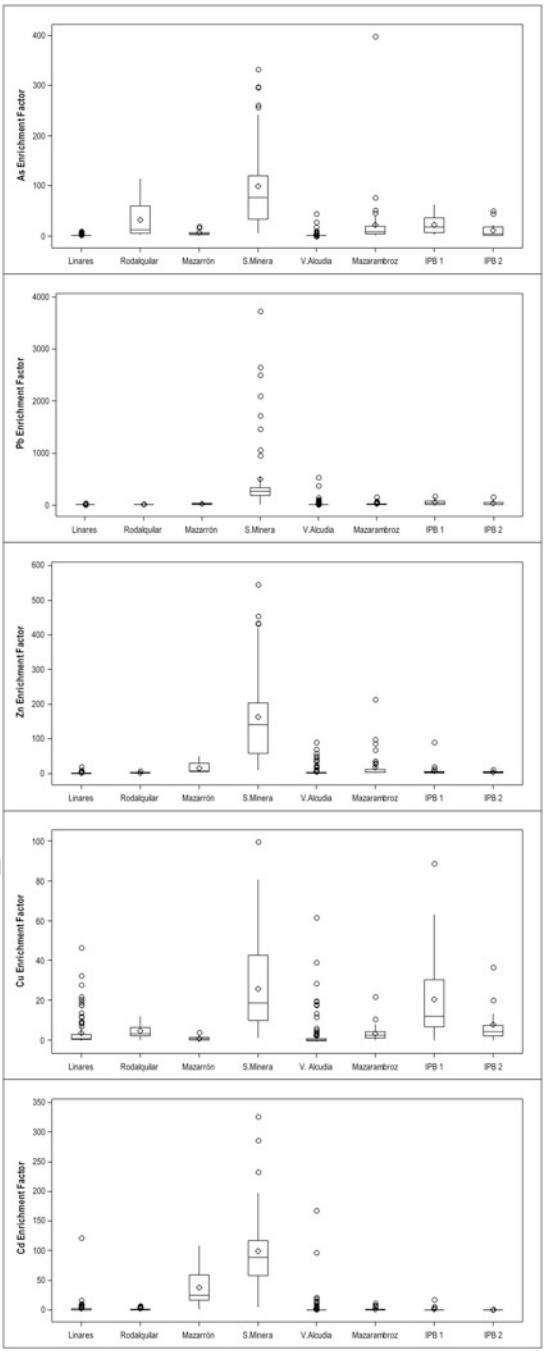

Fig. 3 Box-and-whisker plot for As, Pb, Zn, Cu, and Cd relative enrichment factors (REF_{metal} = [metal concentration in polluted soil – metal background concentration in soil]/[metal background concentration in soil]). Explanation as in Fig. 2

Table 3 Descriptive basic statistics of relative enrichment factors (REFmetal) of As, Pb, Zn, Cu, and Cd. Mean, median, minimum, maximum, first quartile (Q1), and third quartile (Q3) values are expressed in per unit of the background value

District	Backgrd	Source	N	Mean	St. Dev.	Min.	Q1	Median	Q3	Max.
As										
Linares	18.09	[7, 8]	126	0.4	1.6	−0.9	−0.4	−0.1	0.4	8.8
Rodalquilar	13.15	[24]	31	31.1	36	1.1	4.4	11.9	58.6	113.8
Mazarrón	39.33	[17]	15	5.4	5.3	0.5	1.5	3.8	6.6	17.9
S. Minera	13.25	[22]	54	97.8	84.8	4.1	33.2	76	119.6	333.2
V. Alcudia	17.5	[2]	142	1.1	4.8	−1	0	0.3	0.5	44.3
Mazarambroz	7.4	[62]	50	20.9	56.4	0.5	3.1	7.2	18	398.3
IPB1	25	[63]	32	21.5	17.7	1	6.4	16.7	34.8	61.4
IPB2	20	[11]	15	10.3	15.8	−0.1	0.5	2.9	17.1	48.7
Pb										
Linares	1,212	[7, 8]	126	2.4	5.8	−1	−0.8	0.1	3	29.8
Rodalquilar	33	[24]	31	5.9	4.8	−0.1	2.5	4.8	7.2	23.2
Mazarrón	159.67	[17]	15	17.5	16.1	0.5	4.7	15.3	29.2	56.1
S. Minera	12.75	[22]	54	488	736	1	178	260	330	3,734
V. Alcudia	96.9	[2]	142	15.3	57.6	−0.3	0.2	0.7	4.6	537.8
Mazarambroz	19.3	[62]	50	15	24.5	3.5	4	4.7	12.9	147.6
IPB1	38	[63]	32	43.9	48.4	0.6	5.3	29.7	68.4	170.1
IPB2	31	[11]	15	25.1	43.3	0.3	2	5.4	40	156.7
Zn										
Linares	100.79	[7, 8]	126	0.2	2	−0.7	−0.5	−0.3	0.3	18.7
Rodalquilar	54	[24]	31	1.2	1.9	−1	−0.2	0.4	2	6.4
Mazarrón	103.67	[17]	15	14.9	15.3	2.2	4.4	6.6	28.2	49.6
S. Minera	55.5	[22]	54	163.2	124.5	8.3	57.1	140.3	203.2	546.8
V. Alcudia	92	[2]	142	4.6	13.4	−0.7	−0.3	0.2	1.8	89.6
Mazarambroz	35.7	[62]	50	15.9	35	0.9	2.1	3.5	9.9	212.6
IPB1	76	[63]	32	6.9	15.7	-0.7	1.3	3.7	5.6	89.7
IPB2	72	[11]	15	3.2	3.2	0.3	1	1.9	3.9	11.5
Cu										
Linares	34.82	[7, 8]	126	3.2	7	−0.6	−0.1	0.5	2.7	46.5
Rodalquilar	14.1	[24]	31	4.2	3.5	−0.2	1.8	3.1	6.2	11.6
Mazarrón	55.33	[17]	15	0.6	1.1	−0.5	−0.3	0.4	1.2	3.7
S. Minera	13.25	[22]	54	25.6	22.1	0.6	9.6	18.5	42.5	99.8
V. Alcudia	20.5	[2]	142	1.8	7.3	−1	−0.5	−0.2	0.5	61.6
Mazarambroz	10.3	[62]	50	3	3.5	−0.2	0.7	2.2	3.9	21.5
IPB1	32	[63]	32	20.4	21.2	−0.3	6.4	11.9	30	88.8
IPB2	31	[11]	15	7.4	9.6	−0.1	1.9	4.1	7.2	36.4
Cd										
Linares	0.26	[7, 8]	126	2	11	−0.2	−0.2	−0.2	1.4	121.3
Rodalquilar	0.1	[24]	31	1.5	2.1	0	0	1	1	7
Mazarrón	0.3	[17]	15	37.1	33.1	1.3	15.7	24.3	59	108.3
S. Minera	0.38	[22]	54	99.2	60.3	4.8	58.3	88.9	117.5	327.4
V. Alcudia	3.14	[2]	142	2.4	16.5	−0.8	−0.8	−0.8	−0.4	168.1
Mazarambroz	3.9	[62]	50	0.5	2.6	−0.9	−0.9	−0.9	0.9	11.1
IPB1	1.2	[12]	32	0.5	3.3	−0.9	−0.9	−0.5	0.1	17.2
IPB2	1.2	[12]	15	−0.2	0.4	−0.9	−0.6	−0.3	0	0.9

Sources of the background concentrations used in this chapter are indicated in the Backgrd column. *Backgrd* background, *St. Dev.* standard deviation, *Min.* minimum, *Max.* maximum

t.1 **Table 4** Correlation index matrices for element concentrations (log10) from all data sets. For the correlation analysis, metal sets with more than 10% of all values of BDL data have been excluded from the original data sets (Linares Ag, Cd, Sb; Rodalquilar Cd; Mazarrón Bi; Alcudia Cd, Hg, Mo, Ni, Sb; Mazarambroz Cd, Cr, Hg, Ni, Sb; IPB1 Hg)

t.2		As	Cu	Pb					
t.3	*Linares*								
t.4	Cu	0.76							
t.5	Pb	0.81	0.78						
t.6	Zn		0.65	0.65					
t.7		Ag	Bi	Cu	Hg	Pb	Sb	Se	Sn
t.8	*Rodalquilar*								
t.9	Bi	0.82							
t.10	Cu	0.62	0.7						
t.11	Hg	0.26	0.33	0.2					
t.12	Pb	0.42	0.46	0.72	0.21				
t.13	Sb	0.87	0.71	0.58	0.27	0.28			
t.14	Se	0.91	0.71	0.46	0.4	0.22	0.87		
t.15	Sn	0.95	0.85	0.57	0.29	0.34	0.86	0.91	
t.16	Zn		0.33	0.58	−0.16	0.65	0.29	0.26	0.35
t.17		Ag	As	Ba	Cd	Cu	Pb	Sb	Se	Sn
t.18	*Mazarrón*									
t.19	As	0.89								
t.20	Ba	0.17	0.29							
t.21	Cd	0.18	0.23	0.30						
t.22	Cu	0.66	0.77	−0.06	0.55					
t.23	Pb	0.94	0.81	0.14	0.37	0.74				
t.24	Sb	0.51	0.58	0.83	0.41	0.21	0.50			
t.25	Se	0.13	0.23	0.45	0.19	0.09	0.12	0.46		
t.26	Sn	0.42	0.42	0.00	0.60	0.53	0.55	0.42	0.52	
t.27	Zn		0.30	0.37	0.73	0.48	0.58	0.54	0.37	0.63
t.28		Ag	Cd	Cu	Fe	Hg	Pb			
t.29	*Sierra Minera*									
t.30	Cd	0.25								
t.31	Cu	0.70	0.31							
t.32	Fe	0.57	0.50	0.55						
t.33	Hg	−0.01	0.18	0.23	0.14					
t.34	Pb	0.61	0.42	0.58	0.68	0.21				
t.35	Zn		0.46	0.56	0.42	0.31	0.43			
t.36		Ag	Cr	Cu	Pb	Se				
t.37	Alcudia Valley									
t.38	Cr	0.07								
t.39	Cu	0.15	0.22							
t.40	Pb	0.14	0.21	0.86						
t.41	Se	0.23	0.25	0.79	0.84					
t.42	Zn	0.02	0.17	0.86	0.86	0.68				

(continued)

Table 4 (continued)

	As	Cu	Pb			
	As	Cu	Mo	Pb	Se	
Mazarambroz						
Cu	0.64					
Mo	0.01	0.18				
Pb	0.56	0.49	0.27			
Se	−0.65	−0.3	0.09	−0.27		
Zn		0.62	0.33	0.89	−0.24	
	As	Cd	Cr	Cu	Ni	Pb
IPB1						
Cd	0.16					
Cr	0.06	0.09				
Cu	0.42	0.47	0.19			
Ni	0.25	0.27	0.71	0.49		
Pb	0.80	0.29	0.16	0.71	0.43	
Zn	0.25	0.68	−0.02	0.65	0.45	0.51
IPB2						
Cd	0.53	1.00				
Cr	0.16	−0.30	1.00			
Cu	0.90	0.55	0.13	1.00		
Ni	0.64	0.44	0.49	0.67	1.00	
Pb	0.91	0.57	0.00	0.87	0.46	1.00
Zn	0.80	0.61	−0.20	0.69	0.33	0.91

(Table 4). The cluster analysis allows the observation of some patterns reflecting the moderate correlation indexes among As, Cu, Pb, Zn, and Cd pairs and the low affinity of Hg with the other metals and As (Fig. 4).

- The strongest correlation in Rodalquilar is found for the pair As–Sn (0.95) (Table 4), with As being weakly related to the Pb–Zn–Cu group (Fig. 4).
- The strongest correlation from the Mazarambroz soils occurs in the Pb–Zn pair (0.89) (Table 4), whereas the most weak corresponds to the As–Mo pair (0.02) (Table 4). The cluster analysis of the Mazarambroz data is consistent with the correlation matrix, showing the Pb–Zn and As–Cu affinities (Fig. 4).

5 Conclusions

From the above results, some conclusions may be attained. The clustering of As and metals allows identification of several pollution modes, which in turn may correspond to significant differences in metal partitioning and solid phase bounding:

- The As–Pb–(Cu) + Zn–Cd mode that can be regarded as representative of the IPB, Linares, and Mazarrón. This suggests that the metals of each pair are similarly partitioned into the soil and bound to the same mineral phases, for

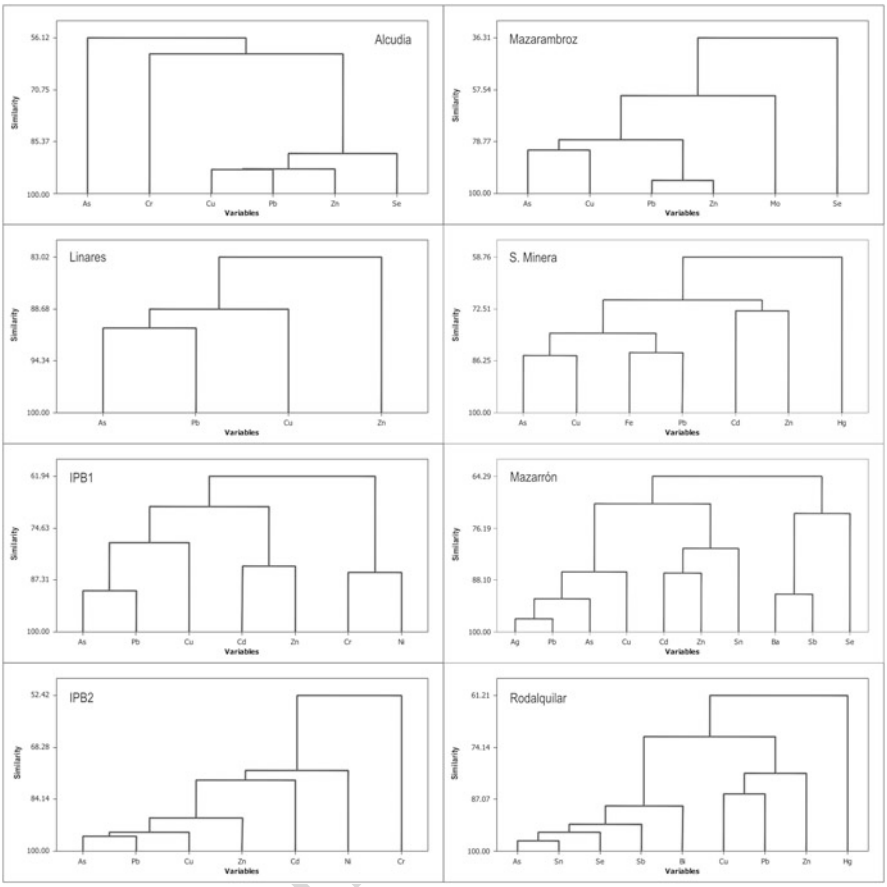

Fig. 4 Dendrogram (clusters by group average) for all data sets. Data are log-transformed, and metal sets with more than 10% of all values of BDL data have been excluded for the cluster analysis (Linares Ag, Cd, Sb; Rodalquilar Cd; Mazarrón Bi; Alcudia Cd, Hg, Mo, Ni, Sb; Mazarambroz Cd, Cr, Hg, Ni, Sb; IPB1 Hg)

example, As and Pb to iron oxyhydroxides ([12, 17]); alternatively, [11] and [13] have suggested that As, Pb, and Zn are mainly bound to Fe and Mn oxides with some Pb and Zn associated with the exchangeable fraction consisting of phyllosilicates and carbonates.

- The As–Cu mode that may be regarded as representative of: (a) the Sierra Minera with As–Cu + Pb–Zn + Cd–Zn pattern and (b) Mazarambroz with a Pb–Zn + As–Cu pattern. The As–Cu pair appears to be related to jarosite in the Sierra Minera [22]. At Mazarambroz Pb seems to be bound to supergenic carbonates and sulfates, whereas As would be bound to iron oxyhydroxides [16].
- The As–Sn + Cu–Pb–(Zn) mode is observed at Rodalquilar where Pb is bound to Mn oxide phases and As is bound to goethite [24].

- The Cu–Pb–Zn mode with As showing a weak affinity for those metals as observed at the Alcudia Valley. In the San Quintín mines, most of Pb is bound to reducible forms (Fe and Mn oxides), whereas Zn occurs mainly as a exchangeable, water- and acid-soluble form (e.g., carbonates; [4]).

A second conclusion is that these modes do not necessarily relate to the intensity of pollution in terms of absolute concentrations of metals or REF_{metal}. For example, the most As–Pb–Cd polluted district (Sierra Minera) does not show the same pattern as the IPB, Rodalquilar, or Mazarrón (Fig. 2, 3) (Tables 2, 3).

A third conclusion relates to the fact that the As–metal affinities seem to be controlled by other factors than exclusively mineral paragenesis and/or pyrite abundance. For example, Linares (a district where the ore deposits are characterized by low contents of pyrite and an important presence of carbonates that preclude a significant AMD production, [64]) displays nevertheless a similar (As–Pb–(Cu)) pattern to that of the IPB, the most representative district of AMD in the Iberian peninsula (e.g., [65]) and of the worst cases worldwide. On the other hand, the distinct pattern of metal clustering in some districts could be related to the mineral paragenesis as seen in Rodalquilar where the alteration type and minerals associated to the high-sulfidation ore-forming processes ultimately played a key role in the As and metal fate in soils (Table 1, [24]).

A fourth conclusion is that some of the most As–Pb–Zn–Cd polluted districts in terms of REF_{metal} (Sierra Minera, Rodalquilar, IPB, and Mazarrón) have a semiarid Mediterranean climate, characterized by a high evapotranspiration during the dry and hot summer. That process induces the ascent of metal-rich water in the soil by capillarity and the subsequent metal enrichment in the top soil, mostly in the form of soluble phases as sulfates and carbonates [66], which in turn will be dissolved during heavy rain stormy episodes. Thus, these rain events can produce high rates of metal leaching and mobilization by runoff (e.g., [17, 22]).

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