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METALLOGENIC AND ENVIRONMENTAL FEATURES OF THE ASTURIAN COPPER MINING DISTRICT (SPAIN): A REVIEW

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Abstract

Asturias (Northwest of Spain) is a Cu metallogenic province with abundant epithermal-type deposits, whose paragenetic sequences also include As, Co, Ni, Sb and Hg minerals. Several Cu mines have been worked in this region since prehistoric times and the six most significant ones are studied in this work. The metallogenic characteristics of each deposit were defined by means of optical and scanning-electron microscopy, X-ray diffraction and Electron Probe Micro Analysis. These characteristics were used to better interpret the environmental results, obtained from samples of mining wastes, soils and waters, which were analyzed by means of X-ray fluorescence and ICP-MS. Many of these mines are almost forgotten, but their negative effects will endure over time, since they were abandoned long before the introduction of environmental regulations to control metal release. An inheritance of derelict mine facilities and spoil heaps still remains in the sites of this district. The spoil heaps are the main pollution sources and concentrations of up to 2.1% Cu and 0.4% As, among others, were found in the surrounding soils. The potential adverse health effects of the exposure to these elements have been assessed, finding significant risks for potential receptors, such as farmers or local residents.

Keywords: copper mining; Asturian copper district; metallogenic characterization; arsenic; risk assessment

1. Introduction

Modern mining operations are efficient, thus the loss of metals to the environment is low. Nevertheless, localized impacts exist if containment has not been practiced. This occurred often in the past, allowing metals and metalloids to be released into the environment, ending up in soils and waterways (Demková *et al.*, 2017; Li *et al.*, 2014; Lottermoser, 2007; Salomons, 1995; Moore and Luoma, 1990). Abandoned underground and surface mining (and smelting) facilities, as well as untreated wastes forming spoil heaps, usually remain at old metal mine sites, which might constitute one of the most important sources of heavy metal contamination in the environment worldwide (García and Álvarez, 2008; Plumlee, 1999; Allan, 1997; Salomons, 1995). The waters drained from the mines have variable flow and quality, depending on the size and the characteristics of the mines they come from, and the geological materials involved (Álvarez *et al.*, 2018). Copper from ancient mine sites represents one of the earliest examples of anthropogenic soil metal pollution; Cu concentrations provide a unique opportunity to investigate the past and present impact of this activity, improving archaeological interpretations, however they are rarely measured (Tighe *et al.*, 2018).

Asturias (NW Spain) has a long mining tradition: i) It has the largest carboniferous outcrop in the Iberian Peninsula, having contributed 70% of total Spanish coal production in the 1990s (Ordóñez *et al.*, 2012). ii) It is a Hg metallogenic province, since it is the third highest producer of this metal in the world during the 1960-70s (Ordóñez *et al.*, 2013). iii) There are also gold, manganese, iron, cobalt, nickel, copper, lead, zinc, antimony and fluorite deposits, amongst others. The oldest extractive activity in the region is that related to Cu mining, which started in prehistoric times. There are more than 20 Cu deposits in Asturias, but the last of the mines that exploited them closed about 60 years ago. In addition to Cu, As is generally present in the mineral paragenesis of these deposits, and is an element of environmental concern in the studied sites. Factors such as the original intensity of pollution, its mobility and bioavailability, site use, soil properties and climatic conditions affect the resulting degree of contamination, however, the impacts in the long term (hundreds of years) are unknown (Tighe *et al.*, 2018; Pyatt *et al.*, 2000).

Unlike other Spanish regions, Asturias has a humid climate characterized by abundant precipitation during most of the year and mild temperatures. Annual average rainfall in the east (where most of the Cu mines are located) is above 800 mm, and average monthly temperatures range from 7 to 19°C, with an annual average value of 13°C. Thorntwaite evapotranspiration was estimated at 600 mm year⁻¹, so the average annual effective rainfall is around 200 mm. Thus, using an infiltration coefficient of 0.7 for an uncovered spoil heap, the water that infiltrates an area of e.g. 1,000 m² -responsible for leaching and erosion- is about 140 m³ year⁻¹.

The average Cu content in the earth's crust is 55 - 70 mg kg⁻¹. Excepting porphyry-type, the rest of Cu deposits generally need to be in excess of 0.5% Cu, and preferably over 2%, for profitable exploitation. Over the past years, use of metals such as Cu, Cd and Zn have increased substantially, but Cu is produced (and reaches the soil) more than any other metal (Mulligan *et al.*, 2001). The current rate of Cu production is about 13 million tons a year and the known reserves of high-grade ore in the world add up to nearly 1 billion tons. In addition, technological advances and recycling will avoid a depletion of this valuable metal (Calcutt, 2001). Worldwide average Cu background value in soils is 14 mg kg⁻¹ (5 to 70 mg kg⁻¹ Cu in the USA) (Kabata-Pendias

and Szteke, 2015; ATSDR, 2011a). Copper forms strong bonds with sulfur, creating a range of Cu sulfides such as covellite [CuS], chalcocite [Cu_2S] and bornite [Cu_5FeS_4] but when subjected to weathering, these minerals can combine with carbonate and oxygen to generate new mineral phases such as malachite [$Cu_2CO_3(OH)_2$] (Kabata-Pendias and Szteke, 2015). The few studies that have analyzed total metal concentrations at relic Cu mining and smelting sites have found them to be significantly contaminated with metals. Although associated with other elements, Cu is one of the major contaminants detected, reaching contents of hundreds and even thousands of $mg\ kg^{-1}$, e.g. concentrations up to $4,500\ mg\ kg^{-1}$ Cu in soil samples near a relic mining center dating from 3000 to 1800 BC in Jordan (Grattan *et al.*, 2013). Cu is an essential element in the human body, but it has been proven to be toxic when exceeding certain levels of exposure, usually via ingestion and inhalation; the critical targets of Cu toxicity are the gastrointestinal tract and the liver. Although an increase in cancer risk has been found in exposed receptors, the carcinogenicity of Cu has not been adequately studied (ATSDR, 2011a).

Arsenic is usually found in chemical combination with metals, especially Fe, Cu and Pb, either as arsenides or arsenide sulfides, the most common of which is arsenopyrite [$AsFeS$]. Mining is one of the main anthropogenic processes contributing to As pollution; a comprehensive description of the As mineralogy in mine sites is found in Morin and Callas (2006). Unaffected soils usually contain less than $40\ mg\ kg^{-1}$ As (typically $5-10\ mg\ kg^{-1}$) (ATSDR, 2011b; Chen *et al.*, 2002; Shacklette and Boerngen, 1984; Bowen, 1979). However, soils near sulphide deposits can far exceed those values (400 to $900\ mg\ kg^{-1}$ As; Adriano, 1986), particularly if they have been anthropically contaminated by mining-related activities (Ordóñez *et al.*, 2013; Loredó *et al.*, 2006, 2005, 2003), exceeding $9,900\ mg\ kg^{-1}$ As. Mine tailings and contaminated soils are potential sources of As exposure (WHO, 2001); its main routes of entry to the body are ingestion and inhalation, although dermal exposure may occur (US EPA, 2017a). Human long-term exposure of As increases the risk of developing skin, lung, bladder and kidney cancer (WHO, 2001), although As bioavailability in soil is variable, depending on its chemical form (ATSDR, 2011b).

The Asturian Cu metallogenic district has been studied for the last decade at the University of Oviedo. The aims of the study are to: i) characterize the main deposits from a mineralogical point of view; ii) determine the existence and extent of polluted soils and the elements of concern in each mine site; iii) accomplish a risk assessment in order to evaluate the adverse health effects that potential receptors are exposed to. Given the absence of baseline data on total metal concentrations in old Cu mines, particularly at archaeometallurgy sites, this work might provide new insights into the ancient contamination affecting past societies, studying the long term effects in terms of contemporary pollution risk that such sites still pose.

2. Area of study

The oldest known Cu mines in Iberia are located in NW Spain. The mineral was extracted in primitive galleries during the Chalcolithic and Bronze Age, shown by prehistoric findings such as skeletons and tools (picks and clubs made from the antlers of ruminants and stone), as well as vestiges of a primitive metallurgical treatment. The Texeo and El Milagro mines in Asturias (Fig. 1) date from this time and the remains found in them, such as green skulls stained by Cu carbonates, have great archaeological importance (O'Brien, 2015; De Blas and Suárez, 2010; Busk, 1868). There were also mining operations in the Roman period in western Asturias, where Cu accompanied gold ore, the latter of which was the main objective of extraction, as well as in the Delfina mine (Fig. 1). Then, there was a lapse of time without evidence of Cu extraction until the 16th century, when some mines were opened. In the 19th century, the Cu deposits in the region were investigated, especially to the east, where discoveries led to the reopening of tens of mines. The production of Cu concentrate reached a maximum of 2000 tons in 1856, but it suffered ups and downs due to export difficulties, although by 1866 there were 15 active Cu mines in Asturias, mainly in the east. In the 20th century, periods of activity and inactivity alternated; the mines employed more than 220 workers and produced $46,515\ t$ Cu in 1958 (Luque and Gutiérrez-Claverol, 2010). However, the mines were gradually abandoned up to 1961, coinciding with the discovery of vast low-grade deposits (*porphyries*) which could be exploited using open-pit methods in the USA, Chile, Peru, etc.

Fig. 1 shows the location of the Cu mines in the region. All Asturian Cu mines are located within the so-called "Cantabrian Zone", the foreland of the Variscan Chain of NW Iberia. Detailed information concerning the structural and stratigraphic characteristics of the Cantabrian Zone and its sub-domains has been summarized previously (Martínez-García, 2012, and Alonso *et al.*, 2009, among others). Most of the Cu mineralizations are found in association with Carboniferous limestones and dolostones, often karstified.

The Asturian Cu deposits cover a wide mineralogical variety with more than 30 different minerals including sulfides, sulfosalts, carbonates, arsenates, silicates, oxides and native elements. They can be classified into two types: skarn and epithermal deposits. i) In the exocontact of intrusive rocks with carbonate sedimentary sequences, the skarn type deposits are framed. Minerals with a high temperature of formation were originated by metasomatism and others of lower temperature were formed by hydrothermal alteration of the host rocks. In these Au-Cu deposits, located to the west of the region, Cu sulphides (e.g. chalcocite [Cu_2S]) and native Cu are linked to gold, among other elements, so they have been and are currently exploited to extract this metal. ii) Most of the Asturian Cu mines exploited epithermal ores developed in fractures and karst cavities. They are generally high-grade small veins and irregular mineralized bodies, hosted in carboniferous limestones. They originated from low-temperature hydrothermal fluids ($90 - 130^\circ C$) which were rich in metallic elements. The ores usually include Cu-As-Sb sulphosalts (grey copper) accompanied by Cu carbonates in the most superficial areas. In the last stages of deposition, intense processes of supergene alteration took place, giving rise to an extraordinary variety of mineral species (Luque and Gutiérrez-Claverol, 2010).

The legacy of the mining activities remains on site, in the form of old shafts, mine and metallurgical installations and significant quantities of spoil heaps. The barren rock had to be crushed to separate the sulfide minerals in order to smelt the metallic Cu in a furnace. Treatment plants of this type existed in the 19th century at the Texeo, Delfina and El Coriellu sites. In most sites where metallurgical operations (roasting) have taken place, As appears as As₂O₃ (arsenolite), or has been leached out as anionic As species, oxidized to As(V), and then sorbed onto iron-bearing minerals (O'Day, 2006). Metal bearing wastes are constituted by subeconomic ore and tailings, which are heterogeneous in terms of particle size and physico-chemical characteristics (Lottermoser, 2007). Metals entered the environment by natural dispersion by erosion and anthropogenic dispersion from wastes stored in spoil heaps, affecting local soils and water. Six sites were chosen for further study that were felt to be significant both from a mining and an environmental point of view.

2.1. Texeo mine

The Texeo mine is located in the Aramo unit (Fig. 1), at UTM coordinates (in all cases European Time Zone 30 North, Datum ETRS89): X=264498, Y=4785773. It is the oldest and the most relevant Cu (and cobalt) mine in Asturias. There are references to the prehistoric extraction of Cu at this site, dating back to 2600 BC (Dory, 1893). In the original extraction procedure, fire was used to heat the rock, followed by cooling with water, making it brittle to break it up. The extracted ore was then treated near the mine adit. It was rediscovered and reworked in the 19th century, eventually closing in 1918 although it reopened for a short time in the 1930s. Finally, the mine came back into production between 1947 and 1956, after which it was abandoned due to the decline in the price of metal. During this last period of mining about 200,000 tons of 1-20% Cu, 1-3% Co, and 1-3% Ni ore were extracted, producing up to 370 tons of Cu per year (Paniagua *et al.*, 1988). The average grade of the extracted ore was 12% Cu, reaching up to 30% in the rich oxidized zones (Luque and Gutiérrez-Claverol, 2010). Primary mining works exploited the oxidised ore and subsequently, the cementation zone was exploited until mine closure. The main mining works consisted of three adits located at different heights, as well as transversal galleries 1,750 m long. The site extends to a total area of about 300,000 m² including abandoned mine buildings, the old metallurgical plant and five uncovered spoil heaps of different ages and sizes (in which about 40,000 m³ low-grade coarse and fine-grained mine and metallurgical wastes are stored). This site is located in a steep, sparsely populated area on the northern slope of the Aramo Mountains, at heights ranging from 600 to 1,200 m a.s.l. (Loredo *et al.*, 2008), in the valley of the Llamu Stream, which runs very close to the mine buildings. The small village of Llamu is located 600 m downstream of the site (Fig. 2a), where groundwater is collected to supply the population of the capital of Asturias. This mine site was included in the Inventory of Contaminated Soils of Asturias as one of the most polluted sites in the region (Principado de Asturias, 2002).

2.2. La Sierre mine

The La Sierre mine is located in the Picos de Europa Unit (Fig. 1), at UTM coordinates: X=344520, Y=4798110, on a sloping hillside. The site covers 10,000 m² between 220 and 275 m a.s.l. close to the village of Carreña, with a population of more than 300 (Fig. 2b). It is believed that Co-Ni-Cu mineralization was exploited in the 16th century, although there is no reliable evidence until the mid-19th century. Whilst the quality of the surface material was poor – it contained quantities of Co oxide, mining intensified after 1874 and continued until the 1930s. The ore contained up to 11% Cu, 3% Co and 3% Ni, as well as up to 1 g Au per ton (Luque and Gutiérrez-Claverol, 2010). There are three spoil heaps which are located close to the mine entrances (the mine has 4 galleries), and the site as a whole is located within the basin of La Ría Stream, a tributary of the Casaño River, one of the most pristine trout rivers in the region.

2.3. Delfina mine

The Delfina mine is located in the Picos de Europa Unit (Fig. 1), at UTM coordinates: X=344419, Y=4798226, 6 km west of La Sierre mine. It is the second Asturian Cu mine in terms of economic importance (after the Texeo mine). The mine was exploited since 1827, at first with English influence, producing up to 3,000 tons per year that were exported. In the 19th century, an on-site furnace was used to produce Cu concentrates, which were rich in Fe, Zn, Sb and Ag. At the beginning of the 20th century, the extracted ore was transported to a metallurgical plant located in a village at more than 8 km. From 1956, the production increased to 100 tons of ore per year, with a grade up to 1.5% Cu, and concentrates with 70% Cu were obtained by electrolysis. The mine was closed in 1958 (Luque and Gutiérrez-Claverol, 2010). The mining works, which are located in a karst area, include 3 galleries connected by a shaft, some of which are now flooded. Six spoil heaps have been identified, with an approximate volume of 5,000 m³. The site extends to about 20,000 m² at a height of 540-550 m a.s.l. (Fig. 2c). Like the previous mine, Delfina is located within the basin of the Casaño River. The mine is located at 1.1 and 1.4 km from the villages of Canales and Ortiugero, with 70 and 90 inhabitants, respectively.

2.4. El Milagro mine

The El Milagro mine is located in the Picos de Europa Unit (Fig. 1), at UTM coordinates: X=337785, Y=4799597, 6.7 km west of the Delfina mine. The first modern workings date from 1849. The exploitation was first opencast, taking advantage of the natural caves. The high-grade part of the mineral vein was excavated, digging mostly horizontal works and reusing the old shafts when they were discovered. More than a thousand tons of ore were transported to the coast on mules and shipped to the UK. Due to the collapse of the structures because of groundwater flooding and the difficulties of extraction and transport, this production stage ceased in 1858. In 1875, a drainage gallery was constructed and new methods of extraction were applied. The extracted ore had a grade up to 26% Cu and 600 g Ag per ton. The problem of flooding forced to stop the mine again. The last stage of exploitation took place at the middle of the 20th century. Most of the extracted mineral was high-grade Cu

carbonates, with 50% Cu. The mine was definitely closed in 1959 (Luque and Gutiérrez-Claverol, 2010). The site is situated on a steep hillside, drained by the Güeña River, which is a tributary of Sella River, one of the most important and clean rivers of the region. There are two spoil heaps which extend 1,700 and 3,200 m². The site spreads about 25,000 m² with 75 m difference in elevation. Mestas de Con, with more than 200 inhabitants, is the nearest town to the mine (1.3 km). The small village Muñangu, with only a few houses, is 500 m downstream of the site (Fig. 2d).

2.5. El Coriellu mine

This mine is located within the Ponga unit (Fig. 1), at UTM coordinates: X=320777, Y=4796683. Veins and disseminated primary and secondary Cu minerals were exploited unceasingly during the 1840s and discontinuously up to the 1950s. In 1841, a small smelting furnace was placed on site, which apparently did not work efficiently due to the Sb content of the Cu ore (Luque and Gutiérrez-Claverol, 2010). The site extends over 22,000 m², between 650 and 725 m a.s.l. It is located within the basin of the Mampodre River, whose waters eventually flow into the Sella River. The old open-pit mine is connected underground to a mine adit whose entrance is just above the smallest spoil heap. Two spoil heaps, extending 1000 and 200 m², remain on site. This mine is situated 2 km south of the small village of Llerandi (60 inhabitants), but there are scattered houses near the mine (Fig. 2e).

2.6. Vegarrionda mine

The mine is located in the Ponga unit, at UTM coordinates: X=304023, Y=4796644, at a height of 400-425 m a.s.l. This is the smallest site of all those considered in this paper. The mine has two galleries, it was exploited in the 1850s and its economic importance was moderate. The grade of the extracted ore ranged between 2 and 25% Cu. This site extends about 9,500 m², mostly occupied by a spoil heap, downstream of which there is a rocky ground. Thus, no soils but only wastes were sampled in this site. It is close to La Marea River in whose basin there are many small villages, such as Las Felguerosas, with less than 10 residents, which is located 0.4 km downstream of the mine. The town Infiesto, with more than 2,100 inhabitants is 7 km from the mine.

3. Methodology

Since all of the sites had been abandoned many years previously, some are now unrecognizable and access was difficult, thus samples were taken where possible and appropriate. Firstly, samples of host rocks and ore samples were taken from the spoil heaps and the mine galleries when they were accessible. These samples were studied by optical and scanning-electron microscopy (SEM), X-ray diffraction (XRD) and electron Probe Micro Analysis (EPMA), in order to perform a metallogenic characterization of the mineralization.

The composition of the wastes helps to explain the presence of pollutants in the soils, even when they are only minor elements which form part of non-specific minerals. Thus, samples of substrate were taken from the spoil heaps of the six sites using a random sampling strategy. Between 6 and 16 samples were taken, depending on the site (see Table 1). Approximately 2 kg were collected to a maximum depth of 50 cm, using a manual auger.

Figure 2 shows the sampling strategy for the five sites where soil was sampled. In every site, a systematical soil sampling strategy was used: samples were taken at the nodes of regular grids, imposed on the potential pollution sources or hot spots such as spoil heaps and old installations, following the direction of maximum dispersion. The size of the grid was adapted to cover the expected affected area.

The Texeo site it is a bit of an exception. It is the most significant Cu mine and its site is the most extensive from all those studied. Therefore, a comprehensive soil and water sampling strategy was employed in this site. The methodology and results have been previously published (Loredo *et al.*, 2008) and they are summarized here to compare them with those of the other sites. The sampling strategy resulted in 4 phases: Phase 1) Six soil samples were taken near the lowest spoil heap and the metallurgical plant ruins and analyzed by means of a portable X-Ray Fluorescence (XRF) multielemental analyzer. Since the metals of concern were preferentially found in the finest fraction (<63 µm), this formed the focus of later phases. Phase 2) Four samples were distributed inside of each of the 14 (100 x 100) m² squares shown in Fig 2a, to be later mixed and homogenized to constitute one composite sample representative of each square unit. Phase 3) Sixteen soil samples were taken at the nodes of a new grid 50 m x 50 m, centered on the conspicuous geochemical hot spot found in Phase 2, in order to better define the anomaly. Phase 4) Six soil samples were taken downslope from the upper mine workings, following the mountain track originally used for mineral transport.

With respect to the other sites, 29, 30, 26, and 25 samples were taken at La Sierre, Delfina, El Milagro and El Coriellu sites, respectively, using grids of 50 m x 50 m, except for La Sierre, where the grid was 25 m x 25 m (Figs. 2b to 2e). It was not possible to collect a sample from some of the nodes due to access limitations. All the soil samples were collected from the upper 25 cm of the soil profile with a manual auger and transferred to a polyethylene bag for transport to the laboratory.

Waste and soil samples were oven dried at 40°C to minimize the loss of volatile elements for 72 hours. Waste samples were ground in a ring mill and soil samples were disaggregated in an agate mortar. They were homogenized and sieved to below 63 µm in the case of the Texeo mine and to below 125 µm for the other sites. Sample quartering reduction by means of a riffler resulted in a representative sample of 0.5 g for analysis. The soil samples were analyzed by XRF using a portable NITON Xl3t analyzer, since portable X-ray fluorescence spectrometry appears to be an alternative, rapid and effective tool for the

assessment of background and contaminant levels in soils affected by Cu mining and smelting (Tighe *et al.*, 2018). The Texeo waste and soil samples from sampling phases 2, 3 and 4 were subjected to multielemental analysis by ICP-MS after an aqua regia extraction at ACME Analytical Laboratories, Canada (Loredo *et al.*, 2008). The elements As, Ba, Co, Cu, Hg, Mn, Ni, Pb, Sb and Zn, related to a greater or lesser extent with the ores, were considered of particular concern.

Samples of groundwater inside the mine adits (those that were draining water), as well as surface water from the nearest watercourse downstream of the mine, were sampled where possible. At the Texeo site, groundwater was sampled from four mine entrances and the spring in Llamo village (Fig. 2a); surface water was also sampled from four points downstream of the mining and metallurgical works, in spring, summer and winter (Loredo *et al.*, 2008). During dry periods, surface water flow was notably reduced resulting in no water flowing from the mine entrances. A total of 12 surface water samples and 4 groundwater samples from Texeo were analyzed. Due to economic restrictions, only one water sample was taken in spring at 3 of the 5 other sites: inside a mine adit (Delfina), from the Güeña River (El Milagro) and in a tributary of the Mampodre River (El Coriellu) (Fig. 2). Measurements of pH and electrical conductivity were carried out in situ with a portable HANNA multiprobe. Water samples were filtered ($< 0.45 \mu\text{m}$), acidified with high quality nitric acid, and preserved in refrigerated polyethylene bottles until analysis by Inductively Coupled Plasma - Mass Spectrometry (ICP-MS). The samples from Texeo were analyzed at the ACME Analytical Laboratories in Canada; the others at the University of Oviedo.

4. Metallogenic description, microscopy, XRD and EPMA results

4.1. Texeo mine

Previous data concerning fluid inclusions studies (Paniagua *et al.*, 1988) revealed a low formation temperature (100-125 °C) and a high salinity ($\geq 20\%$ NaCl eq.) for the brines. The host rocks are limestones and dolostones and the ore deposit consists of mineralised veins. The paragenetic study of the ore reveals the presence of 29 different mineral phases in a dolomite-quartz and later calcite gangue (Loredo *et al.*, 2008). The mineral assemblages are present as three successive primary stages. The early association is formed by pyrite [FeS_2] and bravoite [$(\text{Fe,Ni,Co})\text{S}_2$], with Co-Ni arsenides and sulpharsenides and later marcasite [FeS_2]. During the intermediate primary stage, tennantite [$(\text{Cu,Ag,Fe,Zn})_{12}\text{As}_4\text{S}_{13}$] and sphalerite [ZnS] were deposited in a dolomite and/or quartz matrix. The last primary association is formed by Cu-Fe sulphides, such as chalcocite [Cu_2S], or talnakite [$\text{Cu}_3(\text{Fe,Ni})_8\text{S}_{16}$]. An extensive supergene alteration of the primary ore gave rise to an oxidation sequence, including numerous Cu-Co secondary minerals (Loredo *et al.*, 2008). From a quantitative point of view, the main constituent of the metallic mineralization is chalcocite, being also abundant bravoite, pyrite and cobaltite [CoAsS], as relicts within larger pyrite crystals (Fig. 3a). In those areas affected by supergene processes, primary sulphides are replaced by chalcocite, covellite [CuS] and, to a lesser extent, bornite [Cu_5FeS_4] and cuprite [Cu_2O]. Sulpharsenides are represented by intermediate terms in the cobaltite-gersdorffite [NiAsS] solid solution series. Main constituents of both, primary and supergene ore types, have been analysed by EPMA, in order to determine the contents of minor and trace elements. In addition to arsenides and sulpharsenides, As is also present as impurity in Cu sulphides and their weathering products: from 0.08% As in chalcocite to 0.37% As in chalcocite and 1.76 % As in covellite, as well as in iron oxides (up to 4.77% As).

4.2. La Sierre mine

The mineralization appears as irregular massive bodies from 10 cm to 3 m, filling open spaces within a limestone as host rock. The primary mineralization is epithermal, it was formed at 90-100 °C (García-Iglesias and Loredo, 1997), and it consists on chalcocite, pyrite-bravoite-cattierite [CoS_2] (Fig. 3b), and barite [BaSO_4]. The most superficial parts of the mineralization are affected by supergene alteration which results in the neoformation of malachite [$\text{Cu}_2(\text{CO}_3)(\text{OH})_2$] (predominant), azurite [$\text{Cu}_3(\text{CO}_3)_2(\text{OH})_2$], and erythrite [$\text{Cu}_3(\text{AsO}_4)_2 \cdot 8\text{H}_2\text{O}$]-annabergite [$\text{Ni}_3(\text{AsO}_4)_2 \cdot 8\text{H}_2\text{O}$], as well as Fe and Mn oxides. Light blue mineral efflorescences are common in the rock massif walls, so they were analysed by XRD, revealing gypsum as unique component. Primary sulphides have been analysed by EPMA. Regarding As, Cu arsenates are common and As can be also found in Cu sulphides as a minor element (0.44% in bravoite, 0.17% in pyrite and 0.20% in chalcocite). Although no Sb specific minerals were observed, this element has been detected in significant amounts in the crystalline lattice of other minerals (mean values of 120 mg kg⁻¹ in bravoite, 2,330 mg kg⁻¹ in pyrite and 910 mg kg⁻¹ in chalcocite). Pyrite also presents noticeable Pb contents (0.30%).

4.3. Delfina mine

The epithermal deposit occurs in subvertical veins, fissure fillings and stockworks. The host rock is the same as that of the previous mine. Predominant primary constituents of the ore are intermediate phases of the tennantite [$(\text{Cu,Ag,Fe,Zn})_{12}\text{Sb}_4\text{S}_{13}$]-tennantite solid solution series. Pyrite, chalcocite and cinnabar [HgS] appear in scarce quantities associated to the grey Cu in the mineralization primary stage. Similarly to the other mines, a great variety of secondary minerals can be found at this site, such as the Sb ochre family, which is the most abundant. Furthermore, bornite, covellite, chalcocite (Fig. 3c), and cuprite can be found in moderate quantities. Pyrolusite [MnO_2], iron oxides and Cu carbonates (Fig. 3d) are quite common. In particular, bright azurite crystals of great beauty are found in this mine (Fig. 4a). EPMA results show that Hg is present as a major element in the grey Cu (mean value of 1.42%), as well as in the Sb ochre (1.15%) and in malachite (2.69%). Additionally, significant contents of Zn were found in the grey Cu crystals (1.01%) and in the Sb ochre (0.73%), which also have valuable Ag contents (0.43% and 0.41%, respectively).

4.4. El Milagro mine

This mine shares with the Delfina mine most of the geological and mineralogical features (host rock, mineralization morphology, and mineral assemblages). The distinctive features of El Milagro mineralization are the following: i) the composition of the main Cu-bearing mineral (grey copper) is close to the tetrahedrite stoichiometry (2.33% As). ii) Sb ochres are not abundant, being Cu carbonates (Fig. 4b), bornite and chalcocite the main secondary minerals; EPMA results indicate that bornite averages a 0.27% Hg and 0.46% Ag, whilst chalcocite contains 0.76% As, 0.14% Hg and 0.22% Ag. iii) The content of Zn in grey Cu almost doubles that found in the Delfina mine minerals (up to 1.97%). Hg and Ag are also present as minor-trace elements in primary sulphides (Fig. 3e) and their weathering products.

4.5. El Coriellu mine

The Cu ore is hosted by a thick level of organic-rich limestones. The primary stage of the mineralization is constituted by scarce chalcopyrite and abundant Cu-Sb sulphosalts (zinciferous tetrahedrite). There are also inconspicuous quantities of pyrite and arsenopyrite [$FeAsS$], filling open and deformed fractures in a gangue of centimetric hydrothermal quartz crystals. Secondary minerals are represented by bornite, chalcocite, covellite and small amounts of Sb ochres (Fig. 3g). Azurite crystals and crusts are also very frequent.

4.6. Vegarrionda mine (Piloña)

This mine shares the same genetic model described for the three previous sites. The primary mineralization is similar to that described for El Coriellu mine. However, in this case there is no arsenopyrite but scarce small-size crystals of native Cu can be observed (Fig. 3h), which is distinctive of this site. Concerning the secondary minerals, Sb-ochres are more abundant than bornite-chalcocite-covellite. Cu carbonates are also very common. Average contents of 3.87% Zn and 3.88% As were found in the zinciferous tetrahedrite by means of EPMA. Concentrations of 3.27, 0.64 and 0.19% As were obtained in Sb ochres, azurite and covellite, respectively. The presence of Zn is also noticeable in the secondary compounds (1.08% in Sb ochre and 0.44% in azurite). Ag contents average 0.49% in tetrahedrite, reaching 0.80% in covellite.

5. Analytical results

5.1. Wastes

Generally, the waste materials are reasonably heterogeneous; composed of fragments of host rocks (mainly carbonates), low grade ore and, to a lesser extent, scoria from smelting processes in the three sites where metallurgical activities took place. A summary of the concentrations of some elements of concern (metals and metalloids) found in the 57 waste samples are shown in Table 1. The highest Cu contents in wastes were found in those from the Texeo site (mean of 3.43%), which is probably the richest Cu deposit in Asturias. Furthermore, some stockpiles of rock fragments seem to contain valuable ore that was missed during processing. The highest mean As concentrations were found in mine wastes from Texeo and La Sierre mines (averaging 2,569 and 1,832 mg kg⁻¹, respectively). Even though the wastes from Texeo have higher concentrations of As, Co, Ni than those from La Sierre, the soils from Texeo appear to be less polluted than those from La Sierre. This fact can be explained by the stability and occurrence of the main As compounds in both mines. Whereas As, Co and Ni in the Texeo wastes are mainly present as small crystals (<10 µm) of cobaltite and gersdorffite (always included in chalcopyrite), these elements in the wastes from La Sierre are in the form of millimetric-sized Co-Ni hydrous arsenates (annabergite-erythrite), which are more labile.

The presence of high amounts of Ba in the wastes and soils from La Sierre site is concerning. Using both optical and electronic microscopy it was found that this element is always in the form of baryte in both milieu. Baryte in soils appears as 50-100 µm, square-shaped unweathered crystals (Fig. 5). This mineral is brittle and has low solubility, in spite of being a sulphate, so when it is liberated from the waste by mechanical fragmentation, it is incorporated into the mineral fraction of the soil. Co and Ni concentrations are significant both in wastes and soils from this site, which is related to the transformation of Co-Ni arsenates to oxides/hydroxides in soils.

Although the Delfina mine was one of the last to close and it might have been expected that exploitation of the ore was more efficient, nonetheless, the waste contained an average Cu content above 1%. In mines whose main primary Cu mineral is grey copper, such as Delfina, El Milagro, El Coriellu y Vegarrionda, wastes have high concentrations of Sb (mean of 1,452 mg kg⁻¹ in Delfina) and moderate quantities of As. The Zn-bearing tetrahedrite of Delfina mine has led to an appreciable Zn content in mine wastes (mean of 798 mg kg⁻¹). The similarity between Delfina and El Milagro mineralizations from a metallogenetic point of view is reflected in their waste geochemistry, since they have a similar Cu content. The average values for Sb and As at El Milagro (2,533 and 791 mg kg⁻¹, respectively) are the highest in mineralizations with grey copper as the main Cu mineral phase. The proportion of Cu carbonates crusts (especially azurite) on the surface of the spoil heaps was visually the highest of all the studied sites.

The lowest metal(loid) content in wastes were found at El Coriellu, where only average values of Cu and Sb reached minor element threshold (7,414 and 1,088 mg kg⁻¹, respectively). Although some higher values were found, the same was true for the Vegarrionda mine, whose wastes averaged 1.30% Cu. In both cases, the main compounds of concern in wastes were azurite and tetrahedrite. The average Cu concentrations across all of the sampled waste ranged from 0.7 to 3.4% Cu and that for As varied from 238 to 2,569 mg kg⁻¹ (Fig 6).

5.2. Soils

Table 2 summarises the results of the 152 soil samples, as well as the generic reference levels (RLs) established for metals in Asturian soils developed on limestones, which considers 'other uses' including agricultural, livestock or forestry use (Principado de Asturias, 2014). In the Texeo mine, the average content of Cu, As, Co, Ni, Sb and Pb in the sampled soils were 31, 2.5, 5.2, 3.3, 1.9 and 1.8 times above this threshold, respectively. Moreover, the Cu content of 4 of the samples were more than 100 times the reference level. The highest concentrations of As, Cu and Co were found in samples collected near the spoil heap or in the mountain track used for mineral transport, which proved to be the main pollution source at this site (Loredo *et al.*, 2008). The weathering of metal(loid)-rich wastes and the leaching and subsequent adsorption and/or coprecipitation of dissolved metal(loid)s on reactive minerals have caused soil contamination downstream of the source. Although the variation in concentration of elements in the soil samples depend on their different mobilities and the variable composition of the parent ore, they all decrease in concentration with distance from the identified hot spots, with trends in Cu, Co, Ni and As being quite similar. This site had the highest Zn concentration of all the sampled soils, up to 1,120 mg kg⁻¹, which mainly originates from the sphalerite.

The highest Cu, Co, Ni and As concentrations were found at the La Sierra site, whose average values were 45, 78, 23 and 6 times above the Asturias RLs, respectively. Several samples also exceeded that limit for Cu, Co and Ni by more than 100 times, whose origin is linked to the ore minerals chalcopyrite, bravoite and Co-Ni arsenides. Their distribution is similar in the sampled soils, with maximum values found near the spoil heaps, particularly those at the lower levels.

The soils from the Delfina site show significant concentrations of Cu, Hg and Sb, whose average values exceed the Asturian RLs by 27, 41 and 148 times, respectively. Three soil samples, taken in the proximity of each of the three spoil heaps, have the highest concentrations of these elements, exceeding the RLs by nearly 200 times. The abundance of these metals is related to the mineralogy of the ore extracted from this mine (tetrahedrite-tennantite and cinnabar). The highest Hg concentrations of all the studied sites were found from this mine, exceeding 200 mg kg⁻¹.

The average contents of Cu, Hg and Sb in the soils of El Milagro site were 27, 30 and 186 times above their respective RLs. The exploited ore (tetrahedrite and Sb-ochre) is responsible for the elevated Sb content in these soils, which was up to 3,100 mg kg⁻¹ (620 times above the RL), the highest of all the studied sites. The elevated Hg content in soils is due to the presence of cinnabar and trace amounts of Hg in other sulphides.

Only the average concentrations of Cu and Sb from the El Coriellu site were significantly above their respective RLs (by 7 times). Compared to the other mines, this site had the lowest contents of all the elements of concern, although elevated concentrations were found near the spoil heaps. The abundance of Cu-Sb sulphosalts and the presence of arsenopyrite in the mineralization probably explain the high contents of Cu, Sb (and As) in the soils.

Fig. 6 shows that average Cu concentrations ranged from 458 to 2,490 mg kg⁻¹ in the sampled soils, whereas average As contents varied from 85 to 600 mg kg⁻¹. The highest concentrations (and the broadest range of values) of both elements were obtained at La Sierra site, with up to 2.1% Cu and 0.4% As. These Cu and As concentrations greatly exceed those values found in the literature for soils near Cu deposits (Kabata-Pendias and Szteke, 2015; Grattan *et al.*, 2013). Fig. 6 also shows that waste concentrations are higher than soil concentrations at every site.

5.3. Water

Table 3 shows a summary of the results of water analysis. Weathering and rain leaching the metal-bearing minerals stored in the spoil heaps might increase the dissolved metal loading to the receiving waters, depending on the amount of exposed leachable materials, their geochemistry, and the precipitation rate.

At the Texeo site, most of the analyzed metals were found in concentrations below the detection limit. However, elevated concentrations of Cu and As (up to 1,869 µg l⁻¹ Cu and 157 µg l⁻¹ As) were found in surface waters downstream of the mining area during the rainy season (spring), when leaching and runoff took place (Loredo *et al.*, 2008). Concentrations of up to 240 mg kg⁻¹ Cu and 40 mg kg⁻¹ As were obtained in the sediments accumulated in surface watercourses by Loredo *et al.* (2008), who found that these elements were carried to the watercourses not only in dissolved form but also included in mineral particles. Groundwater sampled at the spring in Llamo village in the same period did not contain As but did register more than 4,900 µg l⁻¹ Cu. This value is well above the Spanish limit for drinking water of 2 mg l⁻¹ Cu (RD 140/2003).

The Spanish limit for As in drinking water is set at 10 µg l⁻¹ (RD 140/2003), the same as the US EPA's standard (US EPA, 2017b). Background As concentrations in freshwater are typically below 1 mg l⁻¹ (WHO, 2001) and drinking water generally contains an average of 2 µg l⁻¹ As (ATDSR, 2011b). However, higher levels have been found (Rossman, 2007; WHO, 2001), such as 170 mg l⁻¹ As in surface waters downstream of Hg mine sites in Asturias (Ordóñez *et al.*, 2013). The threshold of 10 µg l⁻¹ As was exceeded in samples from the Texeo and Delfina sites, although the only catchment for drinking water supply is located downstream of the Texeo mine.

No other concentrations of concern were found for the rest of the analyzed elements. Nevertheless, it would be advisable to carry out periodic samplings of surface and groundwater downstream of the sites, over a hydrological year. The results presented here cannot be considered to conclusively rule out local impacts on groundwater or aquatic ecosystems.

All the sampled water was circumneutral-alkaline due to the scarcity of acid-generating sulphides (such as pyrite and marcasite) in mine wastes and the abundance of buffering carbonates from the host rocks.

6. Risk assessment

Risk Assessment strategies can be successfully applied in different environments such as soils polluted by mining and metallurgical activities (Ordóñez *et al.*, 2011; Wcislo *et al.*, 2002). In this case, a risk assessment was carried out following the US EPA guidelines (US EPA, 1989) to assess the potential adverse health effects of the exposure to trace elements from the soils of the studied sites. Concentrations were taken to be the upper limit of the 95% confidence interval for the mean (95% UCL; Table 2), which was calculated with ProUCL 5.1 software (US EPA, 2017c). On-site exposure of receptors to trace elements from polluted soils can occur via four main pathways: direct ingestion of soil particles, inhalation of resuspended particles through the mouth and nose, dermal absorption of trace elements in particles adhered to exposed skin, and in the case of Hg, inhalation of vapors (this last exposure pathway was discarded given the absence of elemental Hg in the samples and the negligible volatility of the mineral species of Hg found in the sampled soils). The dose received through the different pathways for each element of concern, as well as the subsequent risk, were calculated according to the procedure from the U.S. Environmental Protection Agency (US EPA, 1996; US EPA 2017d; see details in De Miguel *et al.*, 2007 and Ordóñez *et al.*, 2011). Toxicity data were obtained from the Risk Assessment Information System (RAIS) database (University of Tennessee, 2018). Most of the sites are located in rural areas. Although there are a few houses near the mines, the closest towns are located more than 500 m away, so residential exposure was not considered. An exposure frequency of 20 days per year, for an adult receptor shepherding and farming in the fields around the sites, was considered in all cases. However, this value might be higher at La Sierre site, which is located less than 100 m from a populated area. In fact, children's toys were seen at the base of a spoil heap at this site.

The results of the risk assessment are presented in Table 4. The exposure pathway that had the highest contribution to the overall risk was ingestion of soil particles followed by dermal absorption of trace elements associated with these particles. Inhalation of suspended particles was almost negligible when compared to the other routes of exposure. From the elements considered, As appears to be the largest contributors to the overall risk. Intake of As results in a value of carcinogenic risk for all the sites (excepting El Coriellu) above the critical $1 \cdot 10^{-5}$ level deemed unacceptable by most regulatory agencies, reaching $9.1 \cdot 10^{-5}$ at La Sierre. For non-cancer risk, Co had a Hazard Index (HI) above the benchmark value of 1 for the La Sierre site. If residential exposure is considered at this site (the village of Carreña is very close to the mine), values of HI above 1 are found for As (ingestion) and Co (ingestion), and the carcinogenic risk increased to $1.6 \cdot 10^{-3}$. If a child is considered as the receptor, non-cancer risk existed for As, Co, Cu, Ni and Sb (reaching a HI of 173 for Co) with the carcinogenic risk almost doubling that found for a residential adult receptor. Carcinogenic risk associated with As was found at the El Coriellu site if the exposure frequency increased to one month per year, which is not unreasonable considering that there are scattered homes near the mine.

The elevated values for HI at the La Sierre site, and carcinogenic risk in the risk analysis show that exposure to the soil at all the sites might result in adverse health effects. Despite the uncertainties involved in the quantitative assessment of exposure variables, these results probably warrant further, more detailed research and should be used to evaluate individual sites regarding categorization in terms of remedial action priority.

7. Conclusions

Asturias hosts a metallogenic Cu district, which was intensively exploited in the past. Although most mines closed 60 years ago, the past mining and metallurgical activity, as well as the stockpiling of large quantities of mine wastes, with no remediation measures, are still affecting their local environment. Elevated concentrations of the elements present in the ores remain in the spoil heaps which have been released to surrounding soils and water. The high rainfall rate in the region favours the leaching and transport of Cu and other soluble elements from their source. Concentrations of up to 2.1% Cu, 0.4% As, 1.8% Co, 0.9% Ni, 0.3% Sb and 213 mg kg^{-1} Hg were found in the soils of the six studied sites. These elements caused geochemical soil hot spots usually centered on the spoil heaps but showing downgradient dispersion. This dispersion extended further for those elements with greater mobility, such as As and Cu, but was less for less soluble elements, such as Hg.

Generally, the concentrations in the wastes were higher than those in the soils, although there were exceptions. The metallogenic characteristics help in better understanding the analytical results. For example, EPMA can find and quantify the presence of minor and trace elements, which were not optically identified as constituents in mineral paragenesis, but they can be included in the crystalline lattice of some minerals. These latter elements can be released to be found in soils and water. The crystal size (μm vs mm), its occurrence and the stability of mineral species are also decisive. For instance, an ore with As in the form of hydrous arsenates is more prone to release this metalloid than when the As is in the form of sulpharsenides. Some minerals, such as baryte are liberated from the waste and directly incorporated into the mineral fraction of the soil, without being dissolved.

The highest concentrations of elements of concern in the sampled wastes were found from the Texeo site, which is believed to be the most significant Cu deposit in the region. However, the highest contents in soils were found at La Sierre site. This might be worrying, since this site is very close to a village. Risk assessment has proven to be a useful tool for decision making, providing the information necessary to prioritize sites in terms of determining where best to undertake remediation efforts. In the sites included in this study, the estimated level of carcinogenic risk exceeds the commonly established regulatory value, driven by the high concentrations of As, the critical exposure pathway being the ingestion of soil particles. Fortunately, most of these sites are located in sparsely populated areas so the exposure frequency of potential receptors is low. This is not the case

of La Sierre mine, where the non-cancer risk due to the presence of As, Co and Hg exist for a residential exposure and the risks increase when a child receptor is considered. Remediation actions on the spoil heaps, such as isolation of the wastes to avoid the dispersion of As and metals, should be considered. In addition, the composition of waters downstream of the mines should be regularly monitored, especially if they are used for a drinking water supply (like at the Texeo site). Bioavailability assessments, which can provide a complete appraisal of environmental and human risk should be carried out.

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Table 1. Average concentrations found in samples of spoil heap wastes from the studied sites. All contents in mg kg⁻¹; LOD: Limit of Detection.

	As	Ba	Co	Cu	Hg	Mn	Ni	Pb	Sb	Zn
Texeo (n=7)										
Min.	75	29	101	8,337		99	23	20	13	52
Max.	6,522	77	5,238	69,846	<LOD	227	10,757	733	32	1,001
Mean	2,569	51	1,963	34,276		155	3,873	267	21	543
Std. Dev.	3,462	20	2,845	31,641		54	5,975	348	8	442
La Sierre (n=6)										
Min.	208	52	82	1,409	9	49	69	5	21	24
Max.	4,427	4,223	3,568	15,871	31	159	3,467	7	102	55
Mean	1,832	1,547	2,003	7,361	16	90	1,793	6	49	45
Std. Dev.	2,271	2,323	1,770	7,562	13	60	1,699	1	46	18
Delfina (n=7)										
Min.	227	52	57	7,330	10	956	73	6	577	356
Max.	1,073	367	453	24,388	66	2,540	137	16	2,888	1,675
Mean	523	157	190	13,292	32	1,554	101	9	1,452	798
Std. Dev.	477	182	228	9,618	30	860	33	6	1,254	759
El Milagro (n=7)										
Min.	260	48	42	4,496	30	375	114	5	821	250
Max.	1,368	89	621	45,113	151	598	323	35	4,028	1,209
Mean	791	66	236	13,946	91	450	207	16	2,533	589
Std. Dev.	555	21	334	20,325	61	128	106	16	1,615	538
El Coriellu (n=15)										
Min.	26	19	12	178	2	55	14	3	75	25
Max.	651	178	67	13,386	15	555	64	105	3,885	557
Mean	238	70	28	7,414	6	196	30	32	1,088	295
Std. Dev.	157	62	17	3,228	3	142	17	32	969	131
Vegarrionda (n=16)										
Min.	7	78	9	85	3	178		8	48	17
Max.	500	239	46	40,335	56	925	<LOD	752	11,659	1,343
Mean	343	130	23	13,032	15	301		198	2,160	531
Std. Dev.	131	47	10	16,520	16	183		236	2,933	394

Table 2. Elemental concentrations in the sampled soils and Asturian soil reference levels (RL) (Loredo *et al.*, 2008; Principado de Asturias, 2014, 2002). All contents in mg kg⁻¹; LOD: Limit of Detection.

	As	Ba	Co	Cu	Hg	Mn	Ni	Pb	Sb	Zn
RL	100	1540	35	55	1	6435	65	70	5	455
Texeo (n=42)										
Min.	26	6	12	37		494	25	23	1	55
Max.	1,373	1,755	742	9,921		5,869	1,040	1,191	50	1,123
Mean	254	225	180	1,735	<LOD	1,944	213	123	9	177
Std. Dev.	339	394	196	2,469		1,167	267	217	12	185
95% UCL	349	539	244	2,531		2,283	298	269	18	301
La Sierre (n=29)										
Min.	7	16	11	16	2	416	14	2	7	16
Max.	4,353	16,311	18,508	21,423	39	4,545	9,704	106	160	429
Mean	601	1,963	2,165	2,491	10	2,598	1,223	27	19	119
Std. Dev.	987	3,279	4,260	4,733	12	1,277	2,345	22	32	83
95% UCL	1,399	3,515	4,055	4,399	19	3,025	3,121	33	45	186
Delfina (n=30)										
Min.	30		27	35	2	883	13	2	8	33
Max.	1,107		506	9,876	213	21,586	901	39	1,253	617
Mean	173	<LOD	83	1,479	25	3,941	135	6	131	146
Std. Dev.	219		96	2,682	55	3,708	189	9	336	140
95% UCL	347		160	2,785	69	4,912	195	13	399	258
El Milagro (n=26)										
Min.	39		29	135	2	2,005	11	2	9	59
Max.	718		58	15,814	189	10,062	156	35	3,107	720
Mean	118	<LOD	40	1,460	17	4,654	69	9	222	147
Std. Dev.	139		9	3,296	40	1,894	37	9	650	135
95% UCL	237		43	4,277	51	5,288	81	16	778	263
El Coriellu (n=25)										
Min.	28		24	47	2	788	11	17	8	56
Max.	224		102	4,078	9	7,340	88	173	411	327
Mean	85	<LOD	41	458	3	3,005	43	91	36	116
Std. Dev.	43		22	1,011	2	1,637	21	43	96	52
95% UCL	101		49	1,339	5	3,663	51	106	120	133

Table 3. In situ parameters and concentrations of Cu, As and Sb determined in samples of groundwater (GW) and surface water (SW) downstream of the sites (Loredo *et al.*, 2008; Principado de Asturias, 2002).

	Texeo		Delfina	El Milagro	El Coriellu
	GW	SW	GW	SW	SW
pH	7.9 - 9.4	7.2 - 8.9	8.69	7.27	7.61
Elec. Cond. ($\mu\text{S cm}^{-1}$)	190 - 350	90 - 520	24.2	92.0	412
Cu ($\mu\text{g l}^{-1}$)	0.2 - 4,912	0.2 - 1,869	17.8	1.4	2.3
As ($\mu\text{g l}^{-1}$)	15 - 30	20 - 157	11.0	1.2	2.6
Sb ($\mu\text{g l}^{-1}$)	0.1 - 0.27	0.1 - 0.14	11.8	0.2	0.1

Table 4. Hazard quotient (HQ, unitless) and cancer risk (Risk, unitless) for the elements of concern and exposure route in each site; HI = Σ HQ, RISK = Σ Risk; In red bold: values of HI>1 and Risk > 10⁻⁵

		Non carcinogenic								Carcinogenic					
		As	Ba	Co	Cu	Hg	Mn	Ni	Sb	Zn	As	Co	Ni	Pb	
Texeo	HQ _{ing}	9.1E-02	2.1E-04	6.4E-02	5.0E-03		1.3E-03	2.1E-03	2.8E-03	7.9E-05	Risk _{ing}	1.8E-05			7.7E-08
	HQ _{inh}	9.4E-04	4.3E-05	1.6E-03			1.8E-03	6.0E-04			Risk _{inh}	6.0E-11	8.9E-11	3.1E-12	1.3E-13
	HQ _{der}	2.7E-02	1.2E-05	2.5E-04	6.6E-05		1.3E-04	3.1E-05	5.6E-04	1.6E-06	Risk _{der}	5.1E-06			
	HI	1.2E-01	2.7E-04	6.6E-02	5.0E-03		3.2E-03	2.7E-03	3.4E-03	8.0E-05	RISK	2.3E-05	8.9E-11	3.1E-12	7.7E-08
La Sierre	HQ _{ing}	3.7E-01	1.4E-03	1.1E+00	8.6E-03	5.1E-03	1.7E-03	2.2E-02	7.0E-03	4.9E-05	Risk _{ing}	7.0E-05			9.5E-09
	HQ _{inh}	3.8E-03	2.8E-04	2.7E-02			2.4E-03	6.3E-03			Risk _{inh}	2.4E-10	1.5E-09	3.3E-11	1.6E-14
	HQ _{der}	1.1E-01	7.8E-05	4.2E-03	1.1E-04	2.9E-04	1.7E-04	3.3E-04	1.4E-03	9.7E-07	Risk _{der}	2.1E-05			
	HI	4.8E-01	1.7E-03	1.1E+00	8.7E-03	5.4E-03	4.3E-03	2.9E-02	8.4E-03	5.0E-05	RISK	9.1E-05	1.5E-09	3.3E-11	9.5E-09
Delfina	HQ _{ing}	9.1E-02		4.2E-02	5.5E-03	1.8E-02	2.7E-03	1.4E-03	6.2E-02	6.7E-05	Risk _{ing}	1.7E-05			3.8E-09
	HQ _{inh}	9.3E-04		1.1E-03			4.0E-03	3.9E-04			Risk _{inh}	6.0E-11	5.8E-11	2.0E-12	6.4E-15
	HQ _{der}	2.6E-02		1.7E-04	7.2E-05	1.0E-03	2.7E-04	2.1E-05	1.2E-02	1.3E-06	Risk _{der}	5.1E-06			
	HI	1.2E-01		4.3E-02	5.5E-03	1.9E-02	7.0E-03	1.8E-03	7.5E-02	6.9E-05	RISK	2.3E-05	5.8E-11	2.0E-12	3.8E-09
El Milagro	HQ _{ing}	6.2E-02		1.1E-02	8.4E-03	1.3E-02	3.0E-03	5.8E-04	1.2E-01	6.9E-05	Risk _{ing}	1.2E-05			4.6E-09
	HQ _{inh}	6.4E-04		2.9E-04			4.3E-03	1.6E-04			Risk _{inh}	4.1E-11	1.6E-11	8.5E-13	7.9E-15
	HQ _{der}	1.8E-02		4.5E-05	1.1E-04	7.6E-04	2.9E-04	8.5E-06	2.4E-02	1.4E-06	Risk _{der}	3.5E-06			
	HI	8.0E-02		1.2E-02	8.5E-03	1.4E-02	7.5E-03	7.5E-04	1.5E-01	7.0E-05	RISK	1.5E-05	1.6E-11	8.5E-13	4.6E-09
El Coriellu	HQ _{ing}	2.6E-02		1.3E-02	2.6E-03	1.4E-03	2.0E-03	3.6E-04	1.9E-02	3.5E-05	Risk _{ing}	5.1E-06			3.0E-08
	HQ _{inh}	2.7E-04		3.3E-04			3.0E-03	1.0E-04			Risk _{inh}	1.7E-11	1.8E-11	5.3E-13	5.1E-14
	HQ _{der}	7.7E-03		5.1E-05	3.5E-05	7.8E-05	2.0E-04	5.3E-06	3.7E-03	6.9E-07	Risk _{der}	1.5E-06			
	HI	3.4E-02		1.3E-02	2.7E-03	1.5E-03	5.2E-03	4.7E-04	2.2E-02	3.6E-05	RISK	6.6E-06	1.8E-11	5.3E-13	3.0E-08

Fig. 1. Geological map and location of Cu deposits in Asturias (mod. from Luque and Gutiérrez-Claverol, 2010).

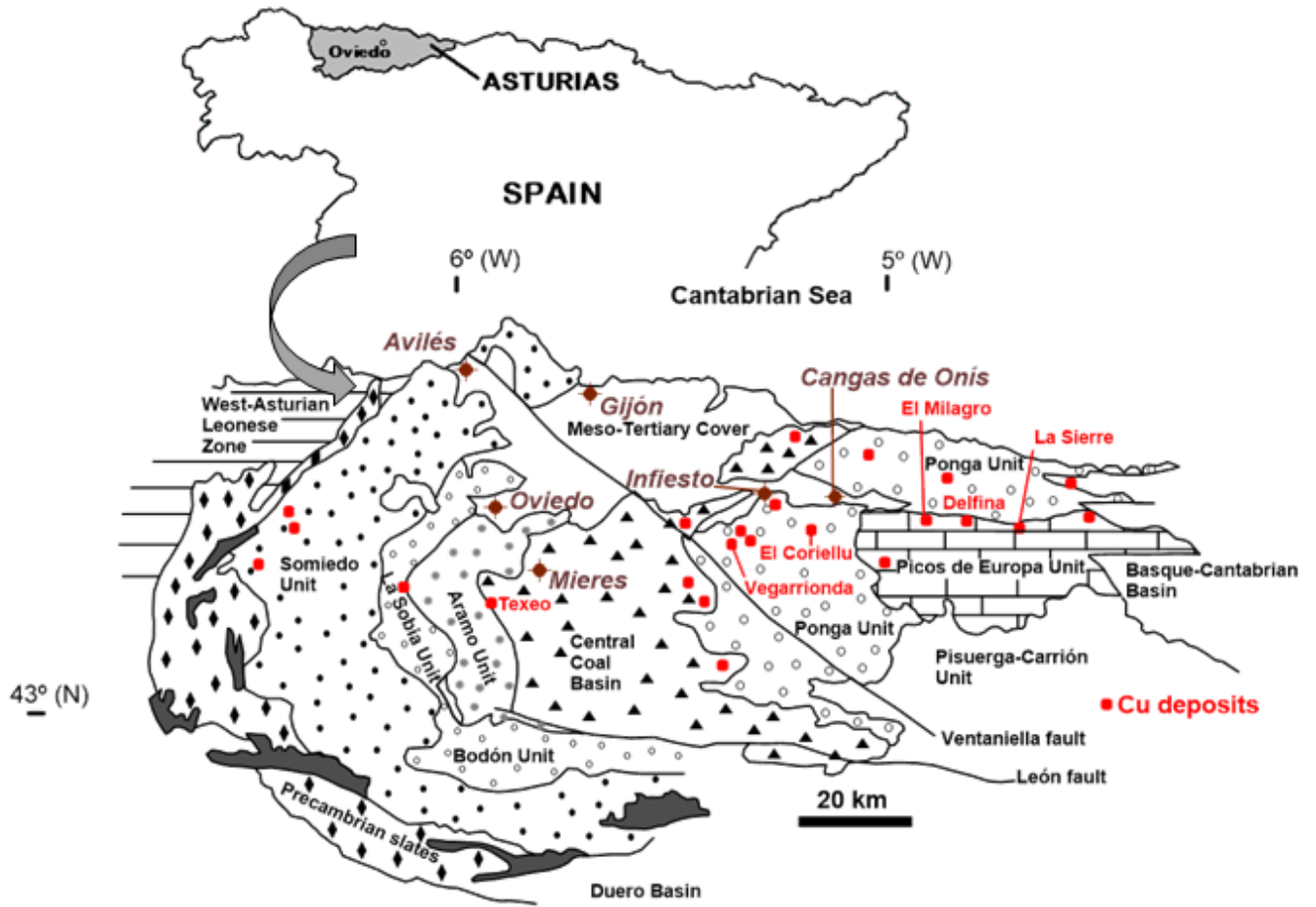


Fig. 2. Soil sampling design used at the different sites. All maps are oriented North.

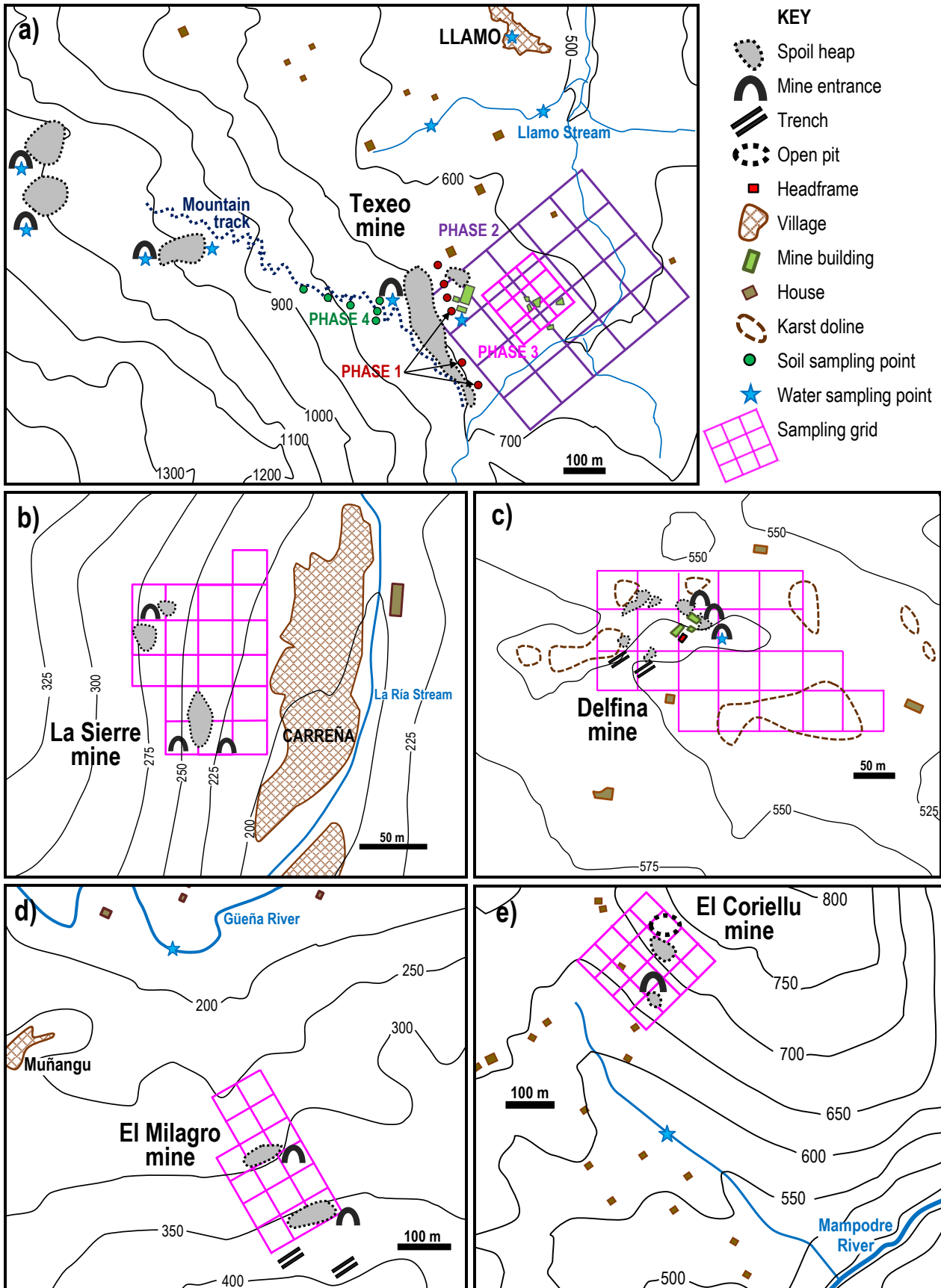


Fig. 3. Optical (a-f, h) and Scanning Electron Microscopy (g) images of selected samples. All images were taken over polished sections with plane parallel light except for d) (thin section, polarized plane light).

- a) Texeo: cobaltite (Co) crystals within chalcopyrite (Cp), which is being slightly replaced by chalcocite (Cc).
- b) La Sierre: typical sulphide association of chalcopyrite-bravoite (Bv).
- c) Delfina: supergene alteration of tetrahedrite (Tt), being transformed into bornite (Bn), chalcocite and covellite (Cov).
- d) Delfina: large crystal of azurite (Azu), accompanied with hydrothermal quartz (Qz) and crystalline calcite (Cal) from the host rock.
- e) El Milagro: irregular grain of cinnabar (Cn) with malachite (Mal) and remains of tetrahedrite.
- f) El Coriellu: moderate weathering of tetrahedrite crystals promoting Sb-ochre and covellite neoformation.
- g) El Coriellu: secondary minerals (covellite and Sb-ochre) included in azurite and quartz.
- h) Vegarrionda: small crystals of native copper.

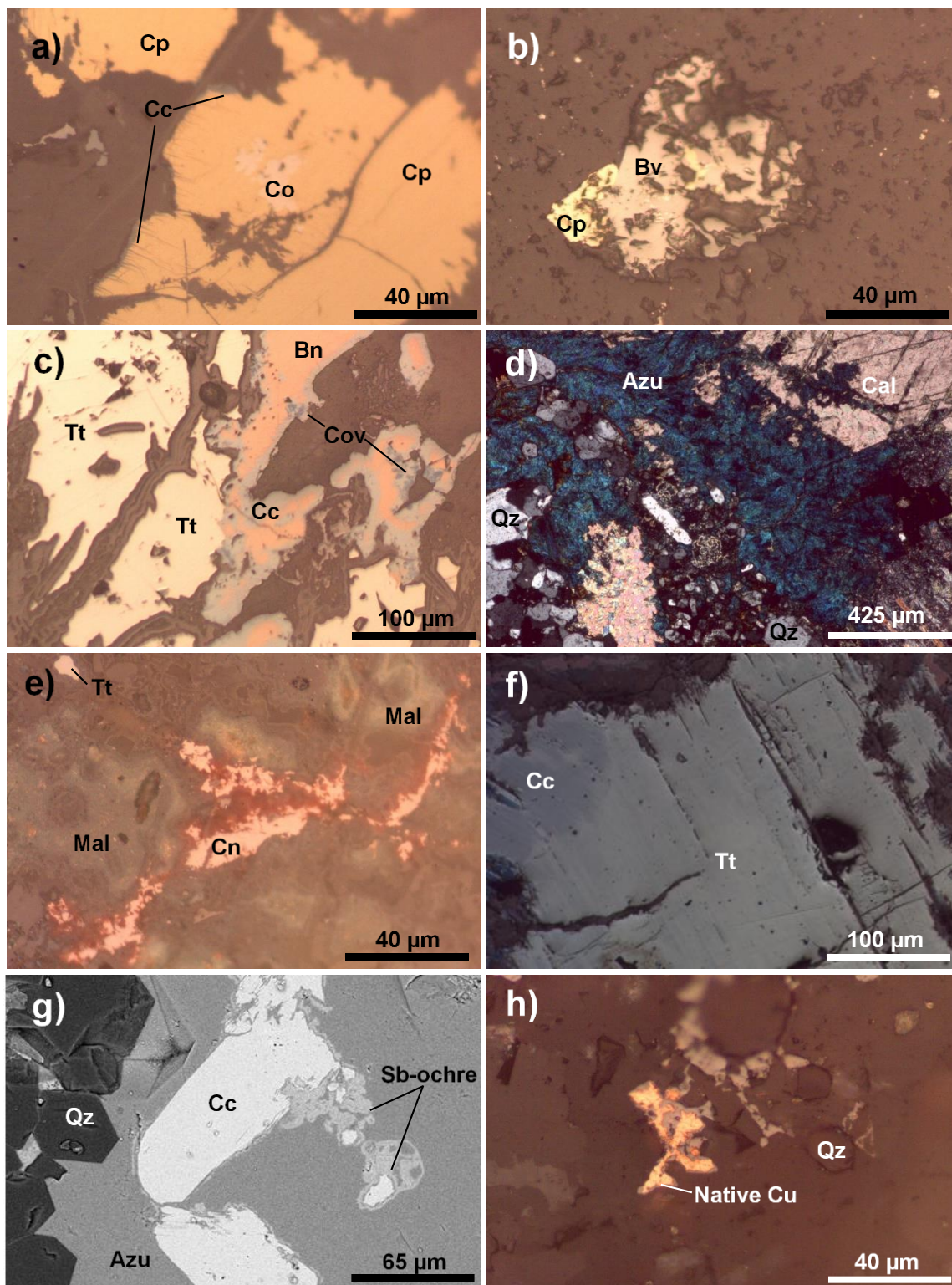


Fig. 4. a) Fibro-radial azurite crystals from Delfina mine. b) Malachite botryoid from El Milagro mine (horizontal frame: 4 mm).

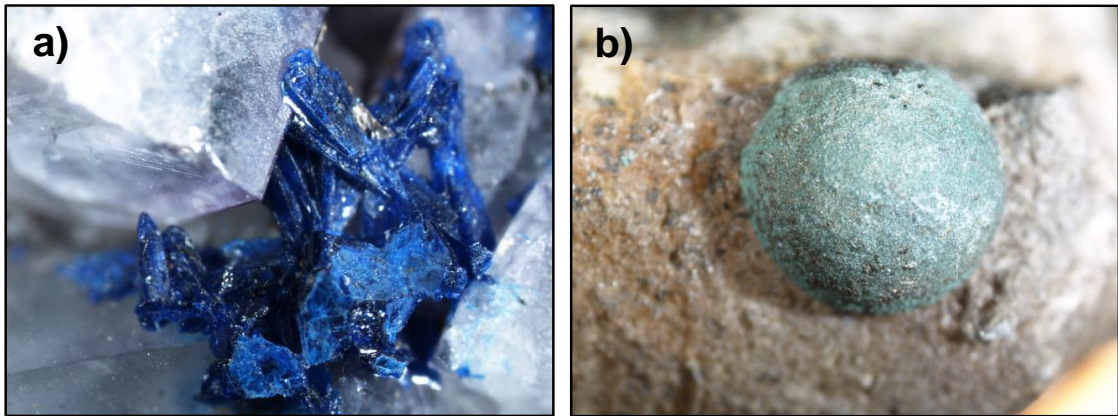


Fig. 5. SEM image of a soil sample from La Sierre mine, taken with secondary electrons detection. The three bright tabular particles in the center of the image are baryte (EDX).

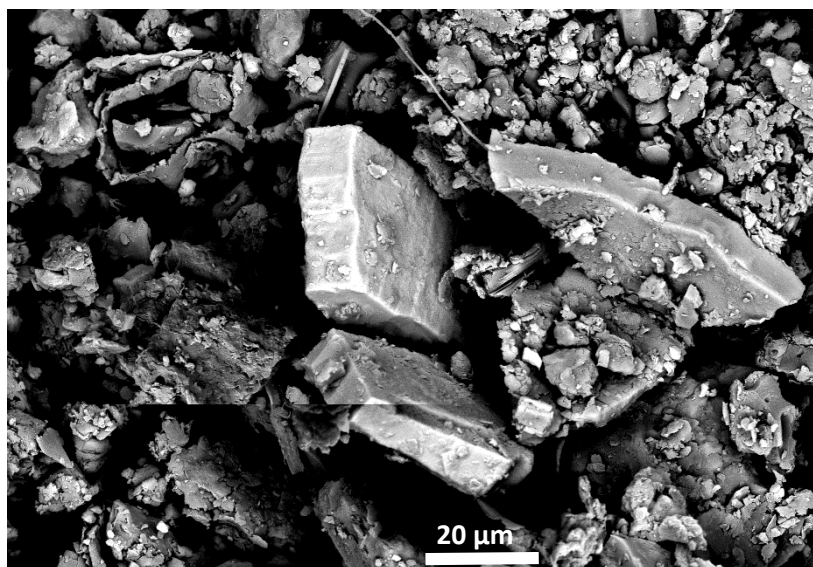


Fig. 6: Average and range of Cu and As concentrations in wastes and soils of the studied sites

