Consequences of abandoned Cu-Co mining in Northern Spain in surface watercourses

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ABSTRACT

Prehistoric tools at the Texeo Mine indicate it is one of the oldest Asturian mining sites. The ore deposit was formed by metasomatic replacement related to fracture systems in Carboniferous limestones. The mineralization comprises major Cu-Co-Ni sulphides and arsenides, with minor concentration of precious metals. The mine site has been the most important source of Cu in the region since Roman times and nowadays, approximately 40,000 m³ of wastes from mine and metallurgical operations containing average concentrations of 9,263 mg.kg¹ Cu, 1,100 mg.kg¹ As, 549 mg.kg¹ Co, and 840 mg.kg¹ Ni are accumulated on site, posing a threat to the environment, due to the potential release of toxic elements. A sequential systematic sampling has been undertaken in wastes, soils and waters, to outline anthropogenic anomalies, which have been found especially for As and Cu in soils, whereas concentrations up to 5 mg.l² Cu have been detected in surface water downstream the mine works. Computer based risk assessment for the site gives a carcinogenic risk associated to the presence of As in waters and soils, and a health index risk for long exposures mainly associated to the presence of high contents of Cu in soils.

INTRODUCTION

Mining activity is known to be a significant source of metals to the environment and subsequent transport of metals from these anthropogenic sources to surface and groundwater is of considerable concern from a contamination standpoint. In particular, pollution associated to base metal mining and smelting is abundantly reported in the literature (Davies, 1983; Salomons, 1995; Allan, 1997; Plumlee, 1999; McMartin *et al.*, 1999; Ashley *et al.*, 2003; Kelley and Kelley, 2003). The mining life cycle consists of exploration, economic feasibility evaluation, development, extractive operations, and closure. Mine sites abandoned without closure planning represent important pollution sources. This fact constitutes a major environmental problem in many historical mining districts in the world, where mine effluents and wastes have a grate deal of influence and a considerable impact on the surface watercourses. It is well known that sulphide mining poses a serious risk to water quality linked to heavy metal pollution, as a result of the oxidation of the sulphide minerals (basically S₂Fe).

In these sites, mine spoil heaps, which are usually constituted by low-grade ore and barren rocks, contain moderate to high content of metals and metalloids. These elements can be dispersed far away in the form of spoil heap leachates produced by percolation of rainwater and surface run-off through wastes. In the interaction between wastes and water, physico-chemical processes result in the pollution of surface watercourses. In general, the areas where mining activity was present for long periods, depending of the mineralogical and geochemical characteristics of the exploited ore, can potentially exhibit a wide dispersion of pollutants through surface water, affecting the environment and the ecosystems.

Mining has been an important activity in Asturias for centuries and, as a consequence, abundant abandoned mine sites form part of the mining legacy in the region. In realation to the effects on the environment of the historical metalliferous mining activity in Asturias (Loredo, 2000; Loredo et al., 1999), the historical copper-cobalt mining and smelting site at Llamo (Riosa), in the Aramo Mountains (Asturias), have been investigated. It is known that Cu is an important micronutrient, but excessive amounts in soils and waters are toxic, and although it is less toxic than other trace elements, it may lead to diarrhoea, nausea, vomiting and lesions in the gastrointestinal tract when it is ingested in significant quantities.

The study area is characterised by both former mining and metallurgical activities, resulting in spoil heaps of different age and dimensions. The basic objectives of this paper are to evaluate the effects of the mining activities, and in particular the abandoned spoil heaps, on the water quality.

THE TEXEO MINE: GEOLOGY AND MINING

The Texeo Cu-Co Mine is located in NW Spain, in an area scarcely populated on the northern slope of the Aramo Mountains, about 40 km South of Oviedo, capital city of Asturias (Figure 1). The area has a humid climate characterised by abundant precipitation during a great part of the year. According to data of the nearest meteorological station, the annual average rainfall in the last twenty years is 966 mm. The relative humidity has an average value of 78%. The annual average maximum and minimum temperatures are 22°C and 3.7°C respectively, with an annual average of 12.7°C over the aforementioned period.

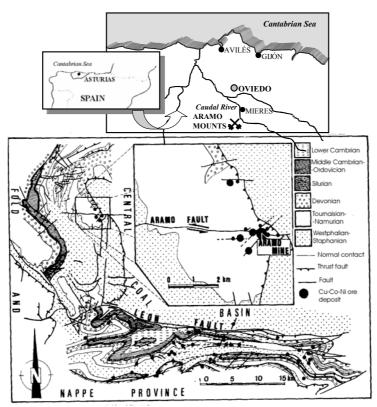


Figure 1: Location of mine site and major geological features of the area (modified from Paniagua et al.,

Geology of the area and ore deposit description

The area of study is included in the Cantabrian Zone (CZ), which is the outermost part of the Hercynian belt of the Iberian Peninsula. Post-hercynian geodynamics processes have caused little effect in the general structure of the area, contributing to keep a wide spectrum of hydrothermal deposits related to late orogenic structures. The geology of this area has been deeply studied by different authors (Oriol, 1893, Julivert, 1971, Gómez Landeta and Solans, 1981, Luque and Martínez García, 1983, Paniagua *et al.*, 1987). It is included in the Fold and Nappe Geological Province (Julivert, 1971) and constitutes the north boundary of the Asturian Central Coal Basin. It corresponds to the Aramo Unit, which comprises a sequence from Devonian to Stephanian sediments which are, from bottom to top:

- 350-400 m of shales, sandstones, limestones, and dolomites of Lower to Upper Devonian age.
- A condensed series of up to 55 m of grey and red nodular limestones of Tournaisian-Visean age.
- 700 m of black, fetid, and bituminous limestone of Namurian age, which are the host rock of the deposit as is known as "Caliza de Montaña formation"
- 2000 m of shales, interbedded with limestones and sandstones of Bashkirian-Lower Moscovian age.

The Aramo Fault lies in an E-W direction within this unit. The mineralization is located at the intersection of this important fault with the Aramo Thrust front. Important dolomitisation and minor silicification processes took place around the Aramo Fault, concerning the ore body genetics. The ore deposit consists of some sulphide mineralised veins (in all cases related to dolomite zones) with an average thickness of 25 cm and argillaceous infilled zones within the common karstic cavities.

Texeo Mine is an epigenetic carbonate-hosted Cu/Co/Ni deposit, related to the circulation of ore brines along the Late-Hercynian faults at temperatures of about 90-130°C (Paniagua *et al.*, 1987). The paragenetic study of the mineralization reveals a great number of ore minerals in a dolomite-quartz and later calcite gangue (Paniagua *et al.*, 1987). The mineral assemblages are present as three successive primary stages, with an important later supergene stage, being described in the paragenesis of the deposit up to 29 different minerals by various authors (Gómez Landeta and Solans, 1981; Paniagua *et al.*, 1987; Paniagua *et al.*, 1991). The early association is formed by pyrite and bravoite, with Co-Ni arsenides and sulphoarsenides and later marcasite. During the intermediate primary stage, major tennantite and sphalerite were deposited as idiomorphic crystals in dolomite and/or quartz matrix; this assemblage is replaced by chalcopyrite and talnakite. The last primary association is formed by Cu-Fe sulphides (chalcopyrite, talnakite, bornite). An extensive supergene alteration of the primary ore deposit gave rise to an oxidation sequence, including numerous secondary minerals such as native copper, bornite, digenite, chalcocite, covellite, cuprite, tenorite, azurite, malachite and erythrite. Sulphide reactivity apparently follows the sequence: galena, sphalerite > pyrite, arsenopyrite > chalcopyrite (Jambor, 1994). First mining works took place on the oxidised zone of the ore, which is well developed in the site of the mine. Later, a cementation zone has been exploited until the closure of the mine at the end of the 1950's. The average grade of mined ore was about

12% Cu, 2-3% Co, and 2-3% Ni (Gutiérrez Claverol and Luque, 1993). About 200.000 tons of this mineral have been extracted, and the ore reserves are estimated in 400.000 tons (Paniagua et al, 1987).

The acid-generating potential of the ore and mine wastes varies considerably from some areas of the spoil heaps to another, related to the heterogeneous distribution of types of wastes and their mineralogical characteristics. The most common transformation inferred by microscopical studies of polished sections from samples from the spoil heaps is chalcopirite—bornite—chalcocite—covellite. When the gangue is calcite and/or dolomite, a reemplacement by malachite (dominant) and azurite can be often observed.

Mining activity in the site has been documented back to the prehistorical times; there are references of Cu extraction at the site, dated to the Bronze Age (Dory, 1893; Hevia, 1959). Later, the mine was exploited during the Roman occupation of the Iberia Peninsula (1st and 2nd centuries A.D.), and it was rediscovered in the 19th century. In this period, the exploitation of the Cu-Co ore began in 1893 and continued until 1918. In the 1930s, the mine was re-opened for a short period. Finally, the mine came back to be in activity between 1947 and 1956 and it was during this period when the exploitation was more important with annual productions reaching 370 tons of copper metal (Figure 2). In 1956 the mine workings were definitively abandoned.

Past mining was developed underground. The main mining operations developed in the area consisted of three pit heads located at different heights from 715 to 1,207 m above sea level, and transversals and galleries with a total length of about 1,750 m. As occurred in other mining operations developed at that time, there was very little pollution control over the way of operation, the waste disposal arrangement, and their eventual abandonment. The most important environmental legacy of the mining and metallurgical operations, which extend in an area of about 300,000 m², is constituted by four uncovered spoil heaps of different age and size, which are subjected to strong erosion. Nowadays, these spoil heaps are covered in part by vegetation (Figure 2).

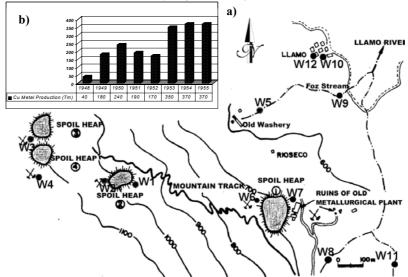


Figure 2: a) Localization of mining works, spoil heaps and ruins of metallurgical plant, as well as water sampling points (W1 to W12). B) Tonnes of Cu metal during a productive period (Gutiérrez Claverol and Luque, 1993)

Intermittent periods of mining have resulted in quite moderate volumes of mining wastes. Waste materials are heterogeneous and are composed of host rocks (carbonates), low grade ore where weathering and sulphide oxidation products are abundant, and scoriaceous materials containing sulphide and rock fragments (wastes from smelting processes). They range from coarse-grained waste rocks and low-grade ore to fine-grained materials from processing and metallurgy, and they have been disposed on the slope of the mountain, in the immediate vicinity of the mine works. The volume of wastes currently stocked in the spoil heaps is estimated at 40,000 m³ and show an important discontinuity of mineralogical composition and particle size distribution. Generally, sulphides included in mine wastes are typically in an advanced state of oxidation, where replacement is strong and iron oxides (hematite and goethite) very abundant.

CONTAMINATION FROM ABANDONED MINE WORKS AND SPOIL HEAPS

Water enters the mine by natural downward movement of rainwater, and then, by lateral movement through fissures, faults, and worked voids. The dominant lithology of the study area corresponds to carboniferous limestones ("Caliza de Montaña" Formation) which are permeable materials constituting an important aquifer at a regional level. The water that does not evaporate nor flows superficially is infiltrated through the limestones, giving rise to springs. High "secondary" porosity associated to the underground mine works and surface spoil heaps favours the infiltration of water. The flow system through the underground galleries and through the waste spoil heaps may be considered to behave as a pseudokarstic aquifer, in contrast to conventional porous media flow (characterised by slower-moving diffuse flow through the intergranular pore spaces and/or fractures in the rock). Groundwater flow in pseudokarstic aquifers is essentially characterised by multiple flow paths, extreme ranges of hydraulic conductivity, and a high degree of unpredictability. Water quality discharging from underground mines is dependent on the geochemistry of the orebody and the potential for oxygen flow into the mine. The area where

these mine works have been developed is crossed by tributaries of the Llamo river, which drains a catchment of 830,550 m². The potential of the abandoned spoil heaps to pollute the environment at this site is enhanced to various degrees by the high topographic relief and the proximity of the site to an important aguifer used by the city of Oviedo for water supply.

According to the climatological data in the area, maximum daily rainfall, calculated by adjustment to Gumbel distribution, is 97.82 mm for a return period of 100 years. The potential evapotranspiration calculated by use of the Thorntwaite expression is 691 mm.year¹, so the average annual effective rainfall is 275 mm. Finally, the maximum calculated flood flow is 561.1 l.s⁻¹. Considering an infiltration coefficient of 0.7 for a spoil heap without vegetal cover, the infiltrated water entering in contact with the wastes stocked in a total area of 4,000 m² is about 1155,000 Lyear⁻¹. The substrate of the spoil heaps is constituted by permeable carboniferous limestones.

In addition to water pollution, the weathered surface material from the spoil heaps was scattered by the wind from its uncovered storage sites, causing additional environmental pollution in soils and sediments. A typical chemical composition for wastes is 9,263 mg.kg⁻¹ Cu, 1,110 mg.kg⁻¹ As, 666 mg.kg⁻¹ Pb, 549 mg.kg⁻¹ Co, 910 mg.kg⁻¹ Zn, and 840 mg.kg⁻¹ Ni. **SAMPLING AND METHODOLOGY**

To characterise the quality of water, a sampling survey was carried out in various stages. Analysed water samples refer to springs and surface water from different streams. All samples were collected and stored following standard methods. Water samples were filtered in situ through 0.22 μm pore-size membrane filters, and collected into polyethylene bottles. Samples stabilisation was carried out in situ upon filtration using high-purity HNO₃. A total of 12 different water sampling points were chosen, covering the area of study (Figure 2).

First soil sampling stage extended in an area of 200,000 m², and it was centred on the abandoned mine works. The second one extended in an area of 22,500 m², which is included into the first one and centred on the biggest soil geochemical anomalies detected into the before mentioned area. Third stage consisted in a systematic linear sampling (400 m) along the slope of the mountain, downstream of the mine works. Figure 3 shows the location of the soil sampling points within the studied area.

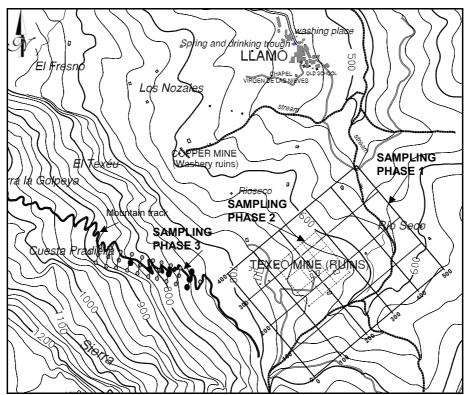


Figure 3: Soil sampling phases. On the mountain track, the filled spots are those sampling points whose samples were analysed.

Sulphide minerals in spoil heaps and mine voids, in the presence of oxidant conditions and water are subjected to a vigorous weathering process resulting in a unstabilization and dispersion of metals to the environment which is affected by particle size and moisture content. In these conditions mobile elements reach soils and waters. Weathering and oxidation of primary sulphides in ore and waste rock materials has resulted in the formation of secondary minerals such as goethite, hematite, malachite, azurite, and others, and this is accompanied by the release of waters carrying elevated amounts of Cu. This process is particularly enhanced due to the particular meteorological and geomorphologic characteristics of the site. Representative samples in different oxidation stages have been used for mineralogical studies under optical microscopy.

The geological characteristics of the site are natural geochemical sources that can give to soils and waters a "natural pollution" derived from the parent materials. Therefore, reference samples were taken in areas not affected by mining and/or metallurgical operations in order to define the local geochemical background levels. Given that pH affects all adsorption mechanisms and the speciation of metals in the soil solution, measurements of pH of soils were made "in situ" in the field by use of specially adapted portable soil pH-meter HANNA HI-9025. Water, soil and waste samples were subjected to multielemental analysis by Inductively Coupled Plasma – Atomic Emission Spectroscopy (ICP-AES) at ACME Analytical Laboratories, in Vancouver (Canada). Extraction of elements was made by partial digestion in 3 ml 3:2:1 HCl: HNO₃: H₂O (Aqua Regia) at 95°C for one hour and dilution to 10 ml with water. The total concentrations of major (Ca, Mg, K, Na, Al, Fe) and trace elements (Ag, As, Au, B, Ba, Bi, Cd, Co, Cr, Cu, La, Mn, Mo, Ni, P, Pb, Sb, Sr, Th, Ti, U, V, W and Zn) were determined. Quality control was achieved by routine analyses of standards and duplicates. Data quality was assured by introduction of internal reference samples and by duplicate analysis.

RESULTS

After the abandonment of the mine fifty years ago, Cu and other elements continue to seep into the environment from wastes stocked on the spoil heaps. On top of that, there is a naturally enriched geochemical background in some elements due to the presence of mineralised bodies, and the chemical composition of the bedrock and the ore influence the overlying soil in the same way as in the rock-water system. Then, elemental concentrations of soil samples from the mine and smelting site, show both the existence of contamination from anthropogenic activity (mining and smelting) (up to 9,921 mg.kg⁻¹ Cu and 1,373 mg.kg⁻¹ As) and a strong natural metal component related to mineralization (42 mg.kg⁻¹ Cu, 18 mg.kg⁻¹ Cu and 29 mg.kg⁻¹ As), which was estimated in undisturbed and unmineralized areas. These data are in agreement with reference values for uncontaminated soils in the world (Alloway, 1995; Bowen, 1979; Kabata-Pendias & Pendias, 1984) (Table 1). Soil pH measured "in situ" reaches values ranging from 6.9 to 7.9.

The distribution maps for As and Cu in soils in the area show that although high concentrations of these elements in mine wastes have been found, the dispersion of these elements in the soils of the area is apparently of limited extent, affecting specially to those samples adjacent to the mine ruins.

Table 1: Summary of analytical results obtained for the soil sampling campaigns, compared with local geochemical background and average world soils concentrations (*) according to various authors (Alloway, 1995; Bowen, 1979; Kabata-Pendias & Pendias, 1984; Vinogradoy, 1959).

Element	Sampl. Phase	No. of Samples	Conc. range	Mean Conc.	St. dev.	Local Background	*Range in world soils
As (mg/kg)	Phase 1	14	26 - 847	211	237		
	Phase 2	16	34 - 1,373	282	419	29	0.1 - 40
	Phase 3	6	66 – 1,211	354	399		
Cd (mg/kg)	Phase 1	14	0.4 - 1.5	0.94	0.36		
	Phase 2	16	0.26 - 1.8	1.12	0.41	0.94	0.01 - 2
	Phase 3	6	0.5 - 1.4	0.9	0.3		
Co (mg/kg)	Phase 1	14	12 - 412	123	125		
	Phase 2	16	21 - 685	137	193	18	0.5 - 65
	Phase 3	6	46 - 625	195	202		
Cu (mg/kg)	Phase 1	14	37 - 8,605	1,352	2,225		
	Phase 2	16	82 – 9,921	1,893	2,797	42	2 - 250
	Phase 3	6	438 - 7,335	2,270	2,421		
Fe (%)	Phase 1	14	0.78 - 3.02	2.18	0.66		
	Phase 2	16	1.25 - 2.99	2.42	0.47	2.18	0.5 - 3
	Phase 3	6	2.31 - 3.33	2.73	0.31		
Mn (mg/kg)	Phase 1	14	494 – 3,665	1,632	1,039		
	Phase 2	16	496 - 5,869	2,187	1,544	677	20 - 10,000
	Phase 3	6	1843 - 2406	2,081	175		
Mo (mg/kg)	Phase 1	14	1 - 8	3.14	1.85		
	Phase 2	16	1-10.3	3	2.8	3	0,1-5
	Phase 3	6	0.9 - 18.7	5	6.26		
Ni (mg/kg)	Phase 1	14	25 - 639	199	199		
	Phase 2	16	37 - 1,040	214	295	31	2 – 750
	Phase 3	6	60 - 956	246	322		
Pb (mg/kg)	Phase 1	14	23 - 690	104	166		
	Phase 2	16	37 - 641	125	305	45	2 - 300
	Phase 3	6	26 - 72	52	15		
Sb (mg/kg)	Phase 1	14	2- 28	7	7.6		
	Phase 2	16	0.6 - 50	10.7	15	3	0,1 - 4
	Phase 3	6	1.6 - 29.1	10.2	9.51		
Zn (mg/kg)	Phase 1	14	55 - 696	168	160		
	Phase 2	16	99 - 1,123	225	251	66	1 - 900
	Phase 3	6	76 - 234	118	54		

The concentrations of heavy metals and As in soils show wide variations between samples, which is indicative of their heterogeneous distribution (Table 1). These values are significantly higher than those in natural soils in the world (Vinogradov, 1959; Alloway, 1995; Bowen, 1979; Kabata-Pendias & Pendias, 1984), and also higher than the tolerable levels, which are considered as phytotoxically excessive: 100 mg.kg⁻¹ of Cu, 100 mg.kg⁻¹ of Pb, 300 mg.kg⁻¹ of Zn, and 20 mg.kg⁻¹ of As (Kabata-Pendias & Pendias, 1984). In particular, the maximum Cu concentration in soils was up to 99 times higher than that tolerable level. The ranges and descriptive statistics for As, Cd, Co, Cu, Fe, Mn, Mo, Ni, Pb, Sb and Zn contents in the sampled soils are listed in Table 1. Comparing these data to geochemical background in the mineralised area under study (Álvarez-Würtenberger, 2000), anomalous values of As, Cu, Co, Ni, Pb and Zn were found in soils affected by old mining and metallurgical operations at the site of Mina Texeo. However, excepting for Cu and As, the anomalies for the rest of the elements are only moderately high, which might be due to the dominance of carbonated bedrock and limited physical and chemical dispersion (an inverse correlation between metal Ca-Mg contents and metal concentrations was found). Some of the highest concentrations of As, Cu and Co have been found in samples collected near the spoil heaps or in the mountain track used for transport of mineral at the time of mining production, which are thought to be the most significant sources of contamination in the area. As, Cu, Co and Pb concentrations in soils decrease significantly as a function of distance from the spoil heaps. Furthermore, the collected samples display notable variations in concentrations of elements, reflecting a heterogeneous composition of the exploited ore and their different mobility. It should be noted that the morphology of the surface geochemical anomalies that were found, could have existed prior to the development of the mine, due to the weathering of outcrops of mineralised bodies.

The microscopical study of representative samples from the spoil heaps shows that chalcopyrite is very abundant, being bravoite, cobaltite and pyrite quite abundant too. Cobaltite is usually present as relicts inside pyrite crystals. Some relicts of sphalerite and galena have also been found in some cases. Some samples are typically representative of a cementation process, where copper sulphides are typically partly replaced by secondary copper sulphides (bornite, chalcocite, and covellite).

The spatial distribution of Cu and As in soils in the area are quite similar, and the highest values are detected, as would be expected, in the nearest area to the old metallurgical plant and one of the spoil heaps. The 500 mg.kg⁻¹ isoline for Cu largely follows the boundary of the mining site. Geochemical maps show differential migration pathways from the mine, as a function of the chemical mobility of the represented elements.

Surface water downstream mine works showed pH values comprised between 7.2 and 7.8 units, and electrical conductivity between 300 and 520 μ S/cm, in contrast to a background values of 8.3-9.4 units of pH and 260-380 μ S/cm of electrical conductivity, upstream of the mine works. The presence of most heavy metals in surface waters, both upstream and downstream of the mine works and spoil heaps, was not significant. Only values for Cu were found to be anomalously high, reaching maximum concentrations of 5 mg.l⁻¹ at a spring located at Llamo village (W12 sampling point), which is above the National Standard for drinking water (0.2 mg.l⁻¹). Average values of 32 μ g·l⁻¹ As, with a maximum of 157 μ g·l⁻¹ were found. Analytical results are shown in Table 2. Concentrations are usually higher at summer sampling campaigns, due to reduction of the dilution effect. Since in the village of Llamo, there is an important catchment point for drinking water supply, the presence of high Cu/As concentrations in some periods of the year can pose a potential health risk.

Table 2: Statistics of main water analytical results

	Min.	Max.	Mean	Median
pН	7.2	9.4	8.0	8.0
Electr. Conduct. (µS/cm)	260	520	378	350
Cu (μg/l)	<2	4912	740.2	248.0
As (μg/l)	15	157	32	17
Fe (mg/l)	0.01	2.74	0.53	0.36
Zn (μg/l)	<5	50	29.5	30.0
Pb (μg/l)	<10	<10	<10	<10
Ni (μg/l)	<5	<5	<5	<5
Co (μg/l)	<5	<5	<5	<5

CONCLUSIONS

The high rainfall in the area and the presence of permeable rocks (limestones) as substrate of spoil heaps, favour the leaching and transport of Cu and other easily soluble elements from the mine wastes. Transfer of contaminants from mine wastes to surface waters occurs moderately as it is evidenced by hydrogeochemical data downstream of the spoil heaps. Because of the relative scarcity of pyrite in mine wastes and the abundance of carbonates, interacting waters have neutral pH and low heavy metals concentrations.

Considering the analytical data, the extent to which an abandoned mine site become an environmental problem depends on the relation between the identified hazards and the proximity of the site to water resources and human settlements. In this case, the rests of past mining activity represent a moderate environmental problem with dispersion of toxic elements traceable up to more than one kilometre away from the pollution sources. The environmental control measurements seem unavoidable, especially taking into consideration the presence of an important catchment point (aquifer constituted by Carboniferous limestones) for drinking water supply and a drinking trough near the mine works. Rehabilitation measures to avoid the dispersion of As and heavy metals

from spoil heaps could include dry covers for the isolation of the solid wastes using impermeable liners and surface covers and revegetation, or the removal of sulphide materials, as the most feasible technologies, with a high cost/efficiency rate.

The geochemical background of some metals (Cu namely) in surface water in the area is high, as a result of the weathering of mineralised rocks and of the leaching of mining/metallurgical wastes. Impact on groundwater quality caused by mining activity is observed at the Lamo spring; however, no suitable monitoring piezometers exist to determine whether a local contamination plume exists. The potential capacity of the sampled water to transport other heavy-metal pollutants watercourses is low according the analytical data obtained.

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