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Geochemical assessment of an arsenic mine adjacent to a water reservoir (León, Spain)

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Abstract A water reservoir constructed for production of hydraulic energy and drinking water in the Riaño valley (León, northern Spain) receives leachates from polluted soils and spoil heaps from a site where small-scale As mining and smelting operations have been developed in the first half of the twentieth century. Water of the upper catchments of the Esla, Yuso and Orza Rivers is stored in this reservoir. The location of these abandoned mine works within the reservoir drainage basin suggested that the stored water could contain high As concentrations. In order to evaluate possible environmental risks, a preliminary soil and surface water geochemical survey has been carried out downstream of the Santa Águeda Mine.

Total As concentrations in soils reach 23,800 mg kg⁻¹ in soils and increase with depth, at least up to a depth of 80 cm. Total As concentrations in surface waters reach 890 µg l⁻¹. Despite the fact that there is an important As input to the water reservoir, the water flow from the mine catchment is a negligible contribution when compared with the total volume of water inside the dam (0.07%). This fact considerably decreases the environmental risk associated with the presence of untreated spoil heaps containing As-rich minerals at Santa Águeda mine site.

Keywords Former mine · Arsenic · Environmental geochemistry · Pollution assessment · Spain

Introduction

Arsenic can enter into soils and waters through various pathways including the weathering of arsenopyrite, mining and smelting of non-ferrous metals and burning of fossil fuels. Arsenic is a metalloid of environmental concern due to its toxic properties; it is one of the most dangerous inorganic pollutants for the environment and human health (Smedley and Kinniburgh 2002). Average As crustal abundance is 1.8 mg kg⁻¹ (Greenwood and Earnshaw 1984), but it can attain high concentrations in sulphide ore assemblages, where it is mainly found in sulphides and sulphosalts, such as arsenopyrite, arsenical pyrite, orpiment, realgar, enargite and tennantite, which are typically concentrated in metalliferous

deposits. Mining of these deposits derives into As pollution.

The most dangerous pollution is caused by abandoned spoil heaps where sulphide-rich wastes containing large amounts of toxic metals are subject to weathering processes. It is known that impacts of mining on water resources, both surface and groundwater, occur at various stages of the life cycle of the mine and after its closure. Mine waters are part of the water cycle, although they are rarely considered as such in regulatory frameworks. Short and long-term pollution from mines is still one of the most serious threats to the water environment in the world. In this context, the weathering and oxidation of As-bearing ore and gangue minerals has been highlighted as a main cause of As

contamination of soils, where the availability and migration of this element is largely controlled through sorption processes (Cullen and Reimer 1989; Korte and Fernando 1991).

At contaminated mine sites, As appears as arsenite [As (III)] or as arsenate [As (V)], which is less mobile than the former, and exhibits anionic behaviour in the presence of water. Hence its aqueous solubility increases with increasing pH. Under reducing conditions, arsenite is the dominant form, while arsenate is generally the stable form in oxygenated environments (Gómez-Camino et al. 2001). The toxicity of As varies depending upon its chemical state: in general, inorganic forms are more toxic than organic complexes, and soluble forms more than insoluble ones, so arsenite is more toxic than arsenate. Arsenate reduction to highly toxic trivalent arsenite may accompany its release into solution, potentially leading to widespread environmental contamination (Nickson et al. 1998; Acharyya et al. 1999; Langner and Inskeep 2000). Under oxic conditions, As is primarily found as pentavalent arsenate, which absorbs strongly to Fe hydroxides (Waychunas et al. 1993; Fendorf et al. 1997). Surface-bound As is released into solution under slightly reducing conditions through the reductive dissolution of the Fe hydroxides (Cummings et al. 1999; Nickson et al. 2000; Zobrist et al. 2000). The availability and migration of As is controlled largely through sorption processes (Cullen and Reimer 1989; Korte and Fernando 1991). Arsenic behaves as an anion in solution and in consequence does not necessarily follow the pattern of being more mobile at low pH. Arsenic sorption onto soil particles is one of the most important processes that immobilises this metalloid (Matera et al. 2003). Geochemical and biological processes occurring naturally, including adsorption by iron oxides and organic matter, play critical roles in controlling the fate and transformation of As in the environment. Adsorption and desorption reactions between arsenate and Fe-oxide surfaces are particularly important controlling reactions because Fe oxides are widespread in the geologic environment as coatings on other solids, and because arsenate adsorbs strongly to Fe-oxide surfaces in acidic and near-neutral pH water (Dzombak and Morel 1990; Waychunas et al. 1993). The adsorption capacity of soil particles is dependent on different physico-chemical parameters such as pH (Sadiq 1997), but Fe and Al hydroxides, redox potential, and type and content of clay in the soil are other parameters to which As retention in soils is related. It is well established that As sorption on oxides is mainly pH dependent: arsenate is preferentially sorbed on hydrous oxides for pH values ranging from 4.0 to 7.0, whereas arsenite is preferentially sorbed for pH values ranging from 7.0 to 10.0 (Pierce and Moore 1980, 1982). However, desorption of arsenate from Fe-oxide surfaces

becomes favourable as pH values reach alkaline values (Fuller and Davis 1989; Dzombak and Morel 1990).

Environmental As exposure is a causal factor in human carcinogenesis and numerous non-cancer health disorders (Williams et al. 1998). The As contamination has been acknowledged as a “major public health issue” by the World Health Organisation (WHO 1999). Based on epidemiological data, As is classified as a Group A and Category 1 human carcinogen by the US Environmental Protection Agency (USEPA 1997b) and the International Association for research on Cancer (IARC 1987), respectively. Exposure to inorganic As has been associated with skin cancer (ingestion) and lung cancer (inhalation) (ATSDR 1993). Toxic effects of As have long been known and affect almost every major bodily function and metabolic pathway. As-contaminated environments are characterised by limited species abundance and diversity. Severe cases of As pollution and the consequent ill health of people from As poisoning have been widely reported in the literature (Borgono and Greiber 1971; Astolfi et al. 1981; Cebrian et al. 1983; Das et al. 1996; Nickson et al. 1998; Acharyya et al. 1999) and they drew attention all around the world to the problem of As pollution.

This paper aims to assess the As concentrations in soils and surface waters around the abandoned mine and metallurgical works of Santa Águeda Mine, in proximity to the Riaño water reservoir. To achieve this goal, the authors investigated the mineralogy of the mine wastes and the geochemistry of polluted soils affected by mine wastes and leachates. A specific objective of the present paper is to evaluate the influence of abandoned As spoil heaps on the quality of water in the reservoir.

Site description

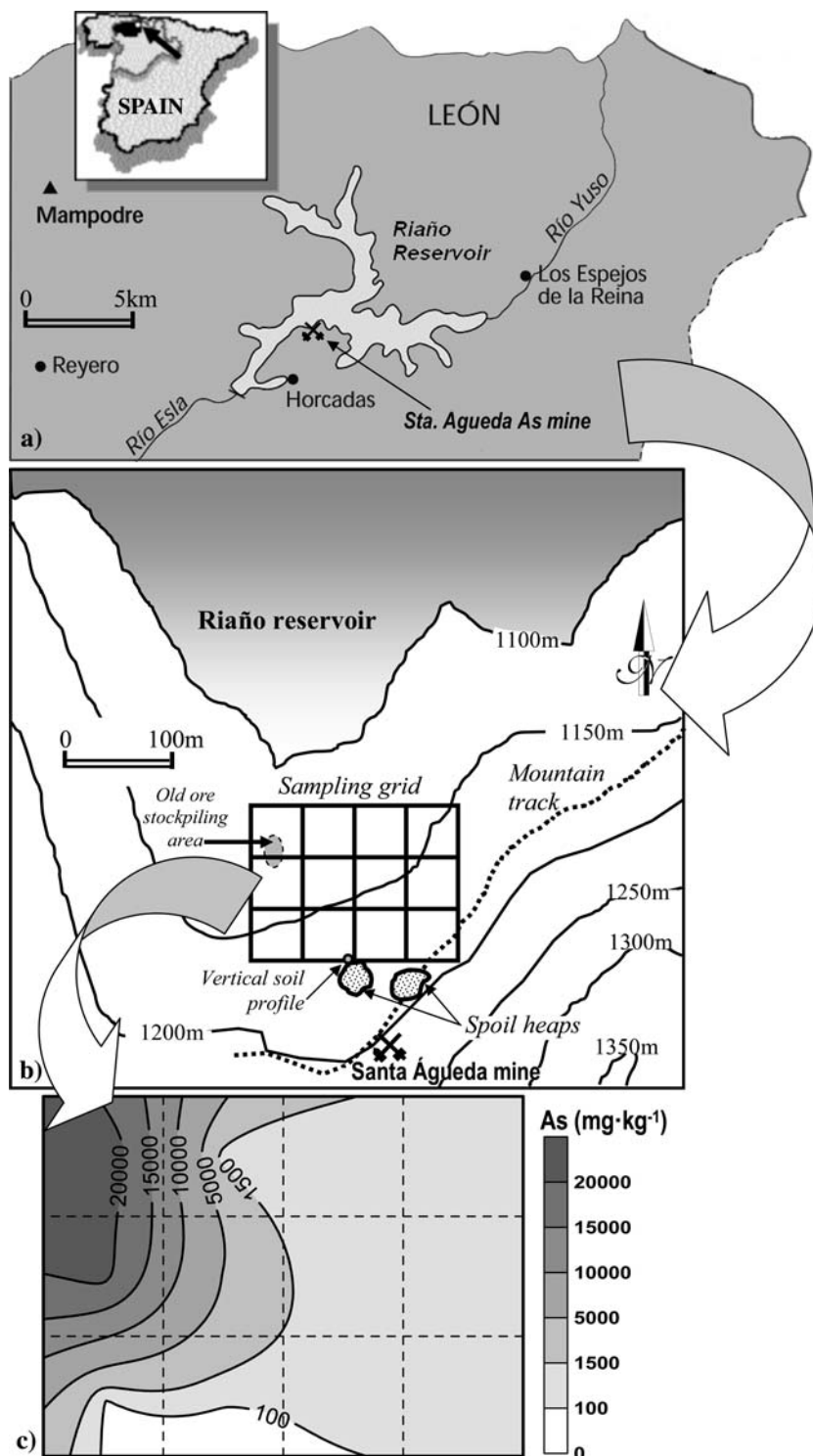
In the area of Riaño-Valdeburón (northern Spain), the occurrence mineralisations of As, Sb, Hg, Cu, and occasionally Au and Ag, are described in Soler (1883), Lacasa (1934), Luque (1985), Paniagua et al. (1988) and others. Only some of them have been an object of intermittent small-scale mining since the nineteenth century. This study focuses on Santa Águeda As mine, one of the aforementioned small exploitations in the area. These old mine works are located close to the Riaño reservoir, in the Northeast of León province, at a topographic level of 1,200 m (Fig. 1a, b).

Since mine abandonment, materials constituted by low-grade ore, enclosing rocks and smelting wastes remain lefted on land, in two spoil heaps at the mine site, inducing modifications of the landscape. These mine wastes contain sulphide minerals that are subject to weathering and oxidising processes. They may adversely impact the local soils and are potential generators of

acid rock drainage that can mobilise environmentally hazardous elements such as As downstream of the mine works. Average annual precipitation in the area is 560 mm per year (La Virgen del Camino meteorological station). An important aspect of this site is that Riaño

and other small villages in the valleys of the upper catchments of the local Esla, Yuso and Orza Rivers have been flooded to construct a water reservoir for electricity generation. Currently, sport fishing activities are carried out in this reservoir. The southern border of the dam is

Fig. 1 **a** Location of the former mine and the Riaño reservoir, **b** Location of spoil heaps and sampling grid in relation to the reservoir, **c** Contours of As concentrations in sampled soils



situated at about 300 m downstream from the mine works and spoil heaps (Figs. 1b, 2), and mine drainage and spoil heap leachates consequently flow from the mined area to the reservoir.

Geologically, “Santa Águeda” mine is included in the Riaño-Valdeburón area which is inserted in the western foothills of the Pisuerga-Carrion unit, in confluence with the Central Coal Basin and other important regions of the Cantabrian Zone (Julivert 1971). Stratigraphically, the area corresponds to Yuso Domain (Martínez-García et al. 1983), primarily a succession of detrital, pellicitic and carbonated materials of carboniferous age (from *Westphalian* to *Stephanian*). The area has a very complex structural geology, with numerous faults and overthrusts (Lobato 1977; Alonso Herrero 1981). The tectonic of the area is characterised by the presence of a great shear zone originated by the intersection of the Ventaniella fault, the León fault and some overthrusts of the Mantos de Ponga Region; all these structures give rise to an intense fracturing in the area and a brecciation of the limestones (competent rocks) with formation of a dense network of fissures filled by calcite. Dykes and sills of diorite, gabbro, granodiorite, quartzdiorite and quartzgabbro, with microporphidic characteristics are also dominant (Corretgé et al. 1985). The As–Sb–Au mineralisations are located in shear zones and fractures where dyke igneous rocks of basic nature are clearly connected to major structural lineaments (Paniagua et al. 1988). These mineralisations are superimposed to important hydrothermal alterations of the intrusive rocks.

The As-mineralisation exploited in Santa Águeda mine, in proximity to the Riaño reservoir, is associated with a fault breccia in Westphalian limestones (Bachende limestones) that forms part of the Lois-Ciguera Formation. It is an epithermal type minerali-

sation, where the ore body occurs as veins or stocks (originated by enlargement of the veins, which can reach a thickness up to 15 m) in silicified limestones. The ore is constituted by arsenopyrite, As-rich pyrite, marcasite, stibnite, bravoite, realgar, scorodite, Sb-ochres, and goethite, within a gangue of quartz and carbonate. The mineralisation appears as a fine-grained dissemination in a quartz-carbonated matrix constituted by jasperoid or millonitic to cataclastic fault breccias. Associated with the mineralisation, there is an important silicification of carbonates and argillisation with formation of kaolinite on fissure planes. The mineralisation has a clear structural control in an area strongly tectonised and with a high level of secondary permeability (Paniagua et al. 1988; Fernández 2002). The particular geological and hydrogeological characteristics of the site constitute major parameters affecting the potential pollution from abandoned mine works.

The first mining activities at the site was on a deep ditch to exploit the As-vein as an open pit. The underground works started from this ditch exploiting the vein by the chambers and pillars method. The most significant extraction period of the mine was between 1940 and 1960. A smelting furnace was constructed at the beginning of the fifties to treat the mineral on site. Wastes constituted by low-grade ore and rocks were stocked in two spoil heaps at the mining site. Currently, the legacy of these extractive activities remains as a network of old galleries and chambers through which water flows, two spoil heaps with widely ranging mineralogical composition and remainders of the smelting plant. The main galleries of the mine have collapsed and the mine, except for the upper gallery, is flooded. Unsatisfactory disposal practices of mine wastes and their abandonment inevitably produced As pollution. The environmental impact

Fig. 2 Mined area and Riaño reservoir at the background



associated with wastes disposal sites related to abandoned mines is a common problem for all old mining districts in the world (Smedley and Kinniburgh 2002).

Materials stored in spoil heaps have a variable composition and heterogeneous distribution. Macroscopically, arsenopyrite and pyrite are very abundant. Supergenic minerals (scorodite, Sb-ochre, goethite and pararealgar) are also frequent among the mine wastes. Typically, sulphide mineral oxidation is followed by dissolution of leachable and precipitation of secondary minerals, which are the first to be available to the environment and have the potential to produce acids with the onset of rainfall. Acidic leachates reach water courses and finally the water reservoir or they infiltrate the soil.

Materials and methods

In former mining areas, assessing environmental problems and selecting suitable strategies to reduce environmental risks, rely upon the availability of relevant analytical data. At the Santa Agueda mine site, environmental analytical data did not exist when this study was carried out. In consequence, a preliminary exploration campaign for environmental assessment was accomplished at the site.

To undertake environmental studies at former mine sites, the survey of bibliographic and historic information is a relevant and decisive step, especially when the current field investigations may find only ruins of mine workings and mine facilities, as in this case. The sampling design (density and location of sampling points around the mine works and spoil heaps) has been decided upon the accessible information of the site conditions, the relevant historical mining aspects, the area of influence of the mine works, the physico-chemical properties of potential pollutants and the supposed preferred migration pathways. At the former mine site, representative samples of mine wastes stocked on the spoil heaps have been collected for mineralogical and geochemical studies.

A soil survey has been performed in an area of 30,000 m² downstream from the mining/smelting works and around the spoil heaps (Fig. 1b). Surface soils have been sampled at a depth of 0–15 cm, according to a systematic methodology based on a regular grid with 12 square units of 50×50 m. Four sub-samples of 1 dm³, uniformly distributed on each square unit, were collected. These sampling increments, once blended together in the same proportion, constitute a composite sample representing the whole square unit. In order to assess the vertical As distribution in soils, a vertical profile with samples from 0–20 cm, 20–40 cm, and 40–80 cm depth, was carried out right downstream from

one of the spoil heaps. Local geochemical background concentrations have been determined in samples collected in areas not affected by the mine wastes and mine drainage (Fernández 2002).

The sampling was carried out by hand and stainless steel equipment was used. Soil samples were dried in an oven for 48 h at a temperature below 40°C to minimise volatility of elements (Alloway 1995). After drying, stones and other large particles were removed by hand, and the components of the samples were desegregated in an agate mortar. It is commonly accepted that the concentration of soil contaminants increases with decreasing particle size due to the large surface area of all the particles combined (Wilber and Hunter 1979). The usual emphasis is on the finer fraction such as silts and clays which have negative surface charges (Striegl 1987), since these are perceived to be more significant in terms of their contaminant-carrying capacity. Additionally, particles with a diameter < 100 µm can be resuspended and are easily transferred between soil and atmospheric aerosol, posing a higher risk for organisms. Then, samples were ground and sieved through a 149 µm (ASTM 100-mesh) aperture stainless-steel sieve. The retained fraction was quartered by means of an aluminium riffle (which was cleaned between samples using compressed air), to provide representative samples of 0.5 g. The measurement of pH in soils was made using the saturated paste method (US Salinity Laboratory Staff 1954; Robbins and Wiegand 1990).

Sulphides are typically unstable under surface conditions and, therefore, tend to be less resistant to weathering. Carbonate rocks in the rock piles act as buffer materials partly neutralising the acidity. Therefore, the mineralogical characteristics of the mine wastes influence the level of impact that the waste rock piles have on the environment. As the mineralogy of mine wastes has a major role to play in the development of pollution and influence on soils and waters, mineralogical characterisation of materials from representative spoil heap samples has been made by study of polished and thin sections of ore and enclosing rocks under the polarising optical microscope by transmitted and reflected light.

Chemical characterisation of soil samples were performed by multielemental analysis of the soluble fraction resulting from a strong acid attack of the sample. Samples of 0.5 g were digested with 3 ml of 3–1–2 HCl–HNO₃–H₂O at 95°C for 1 h and then diluted to 10 ml with distilled water. Concentrations of major and trace elements (Mo, Cu, Pb, Zn, Ag, Ni, Co, Mn, Fe, As, U, Au, Th, Sr, Cd, Sb, Bi, V, Ca, P, La, Cr, Mg, Ba, Ti, B, Al, Na, K, W, Tl, Hg) were determined in all samples, by means of Inductively Coupled Plasma-Mass Spectrometry (ICP-MS), at ACME Analytical Laboratories in Vancouver (Canada), accredited under ISO 9001:2000. It should be noted that an aqua regia digestion as used in

this study, although recommended by the European Soil Bureau for the establishment of background and reference values in soils (European Soil Bureau 2000), is not a total decomposition. Although not all minerals are decomposed during the digestion, the results obtained for arsenic and heavy metals in the aqua regia extraction are considered as total concentrations, due to the fact that hot aqua regia totally decomposes sulphides, which are the major sources of these elements. All analyses were performed using the same extraction and measuring methods. Quality control methods involving the collection of field duplicates, using control standards (STD SO-17, certified in-house against 38 Certified Reference Materials including CANMET SY-4 and USGS AGV-1, G-2, GSP-2 and W-2; Methods and Specifications for Analysis of ACME Analytical Laboratories Ltd, personal communication) and analytical duplicates have been observed. Approximately 5% of the samples were analysed as internal and external control samples. Variability was found to be <10% in all cases.

Surface water samples have been collected upstream and downstream the spoil heaps in intermittent streams flowing through the site. The water samples were filtered (using 0.22 μm sterile syringe driven MILLIPORE filters, which do not allow harmful bacteria to pass) and placed in plastic bottles and refrigerated until analysis. In order to keep metals in solution, special precautions were used including the previous acidification of samples with HNO_3 . In situ measurements of pH and electrical conductivity have been undertaken by calibrated HANNA portable field equipment. Multielemental chemical analyses have been performed by ICP-MS at ACME analytical laboratories.

Results and discussion

The mineralogical study of samples from the spoil heaps shows the abundant presence of arsenopyrite and pyrite in a low state of alteration. Idiomorphic crystals of arsenopyrite appear frequently within the carbonate matrix. In general, they appear associated to borders of calcite grains that show characteristic twins (Fig. 3). Idiomorphic pyrite crystals are sometimes included together with arsenopyrite crystals in the enclosing carbonate rocks (Fig. 4). Marcasite, bravoite, sphalerite, and cinnabar appear occasionally as relicts in pyrite and arsenopyrite crystals in some samples.

Instead, the alteration grade of the ore is low, the geochemical processes developed as a consequence of weathering of the sulphide minerals in the spoil heaps cause the oxidation of As-bearing sulphides. Weathering of As-rich sulphides may form a complex assemblage of secondary minerals. As a general rule, secondary As

minerals can be considered to be mainly composed of arsenates. The stability of these secondary As-bearing phases depends on parameters such as pH, cristallinity and molar Fe/As ratios (Krause and Ettl 1989), but also on microbial activity (Pongratz 1998). In these spoil heaps, the weathering and oxidation of pyrite and arsenopyrite in low-grade ore and enclosing rocks have resulted in the formation of secondary minerals such as scorodite and goethite, accompanied also by the release of As to runoff waters. It is known that scorodite has a limited solubility under most pH/Eh conditions, and its formation constrains the generation of As-rich leachates in many case-study sites (Williams 2001). The solubility of scorodite has been discussed by Dove and Rimstidt (1985), Robbins (1987), and Nordstrom and Parks (1987). According to Kavanagh et al. (1997), from studies accomplished on mine wastes of the Tamar valley (SW England) the percentage of As extracted by water in those wastes range from 0.02 to 1.2%. Arsenopyrite oxidises rapidly in the low-pH conditions that prevail in some spoil heap impoundments (Richardson and Vaughan 1989) and the As released can remain in solution (as it occurs in the surface As-rich water downstream the mine) or be trapped by on secondary phases and colloids or by coprecipitation reactions.

Local geochemical background concentrations in soils of the area are 150 mg kg^{-1} As, 0.6 mg kg^{-1} Hg, and 3% Fe. As background concentrations in soils of the world range from 1 to 40 mg kg^{-1} , with mean values often around 5 mg kg^{-1} (Bowen 1979; Beyer and Cromartie 1987). The local As geochemical background in soils of the "Santa Águeda" mine is higher than the reference values for unpolluted soils in the world, but this high local As background in soils may be associated with geological substrata such as sulphide ores. Arsenic concentrations may exceed 27,000 mg kg^{-1} for contaminated soils by mine or smelter wastes (USEPA 1982). In this case, a maximum value of 23,800 mg kg^{-1} has been found. An important factor controlling the mobility and the concentration of As in spoil heap materials and soils is the pH, because it affects all adsorption mechanisms and the complexing of metals in the soil solution. The sampled soils show a great variation of pH, ranging from acidic (4.1) to alkaline (8.0). These values are influenced by the dominant lithology (limestones), so the concentration of Ca in soils appears to be highly correlated to the pH. At the studied site, soils show a high correlation between As and Fe ($r=0.897$; significant at $P=0.01$) as a result of the adsorption of As by iron hydroxides.

A summary of the analytical results and univariate statistics of total As, Hg, Fe, Cu, Pb, Zn and Sb content in the surface soil horizon at the mining site are shown in Table 1. Other analysed elements are not present in significant concentrations to be considered here. Relative dispersion of As, Hg and Sb is higher than 1,

Fig. 3 Idiomorphic arsenopyrite (*Apy*) crystals associated to borders of carbonate grains (reflected light; parallel polars)

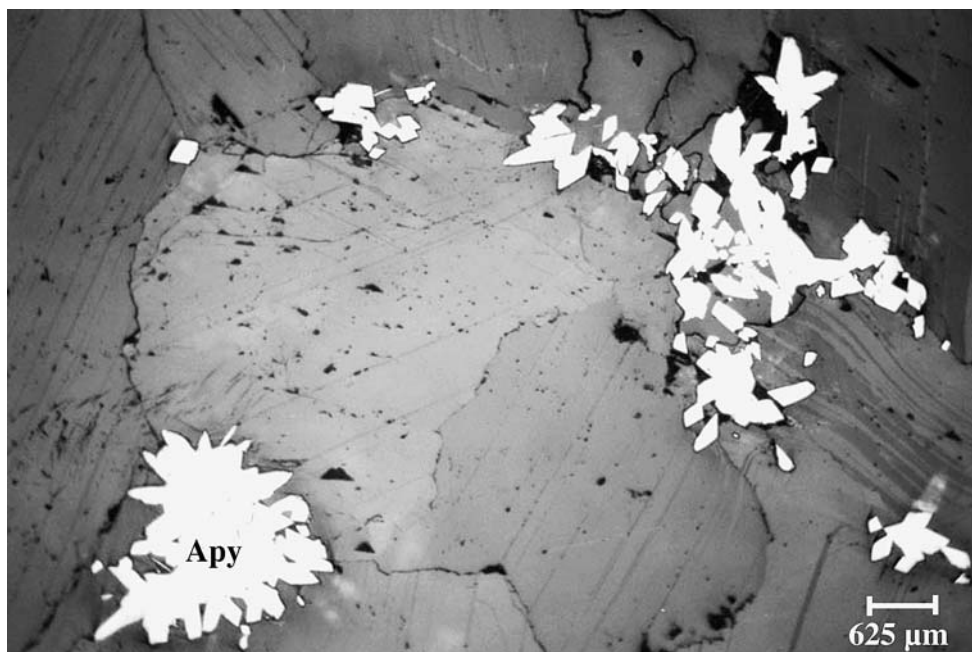
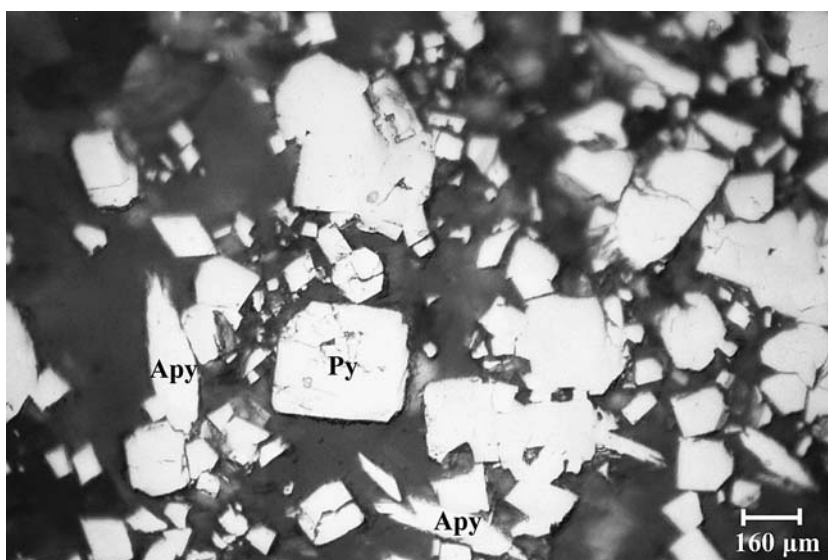


Fig. 4 Arsenopyrite (*Apy*) in association with idiomorphic crystals of pyrite (*Py*) (reflected light; parallel polars)



showing a non homogeneous distribution of these elements in soils. Furthermore, as the asymmetry coefficient is positive for all of them, the mean is higher than the median (Table 1) reflecting the presence of outliers values. Only the concentrations for As and, to a much lesser extent, Hg can be considered as anomalous. The As concentration in soil samples were used to plot contour lines (Fig. 1c). Geochemical anomalies are clearly related to the area where the ore was stocked prior to the concentration process (which constitutes a hot spot sampling point), reaching 4.6 mg kg^{-1} Hg, and $42,600 \text{ mg kg}^{-1}$ As. Concentrations of total As along the

vertical soil profile where samples were taken in different soil horizons, show an increase of concentration with depth, not only for As, whose content is about 2.8 times higher at a depth of 40–80 cm than in the more superficial soil layer (0–20 cm), but also for other elements such as Cu, Fe, Hg, Pb, Sb, Zn, etc. In particular, As content increases from $2,040 \text{ mg kg}^{-1}$ at the surface to $5,690 \text{ mg kg}^{-1}$ at 40–80 cm, which is believed to be related to its affinity to iron oxides, as Fe content increases from 3.6 to 4.1% in the same interval.

In order to quantify geochemical associations between elements, and to detect similarities between

Table 1 Univariate statistics of chemical analytical results for soils

Element	As	Hg	Fe (%)	Cu	Pb	Zn	Sb
Min.	150	0.6	2.02	15.2	15	22	1
Max.	23,800	35	6.02	122	91	114	69
Mean	4,650	6.8	3.49	37.6	35	55.4	9.8
Median	808.7	1.2	3.05	22.3	21.4	44.0	1.8
Std. Deviation	8,450	11.3	1.22	34.8	27	34.2	20
Rel. Dispersion	1.82	1.6	0.35	0.89	0.8	0.59	2.0
Asymmetry	1.99	2.1	1.09	2.0	1.8	0.75	2.8
Kurtosis	2.53	3.3	0.32	2.9	1.9	-0.9	8.2

12 composite samples; concentrations in mg kg^{-1} , except for Fe

variables, geochemical data were subjected to multivariate statistical analysis techniques (hierarchical cluster analysis and factorial analysis). The geochemical data shows a strong correlation of As with Cu, Hg, Pb, Sb, Fe and Ag, which form part of the ore paragenetic sequence. The hierarchical cluster analysis by variables shows two main groups of associated elements at an euclidean distance of 24 (Pb–As–Ag–S–Cu–Hg–Fe–Sb–Ca–Zn–Sr–Cd–Au and Ni–Sc–Co–La–V–Cr–Ba–Al–K–Mn–Mg). The first group, subdivided in two close subgroups, include the elements associated to the mineralisation and its enclosing rocks, whereas the second main cluster groups those geogenic elements related to the soil substrate, whose relative dispersion is lower in the studied area, as they are more homogeneously distributed in it (Fig. 5). The application of hierarchical cluster analysis by cases shows different groups of samples according to their As content, and in consequence, their grade of pollution. The use of factor analysis was tested as a way to reduce the large number of variables. A three-factor model was selected, where the first two factors explained most of the variability (85.4%) of the data set. The first factor shows high positive loading for the same elements that were included in the first group of the clustering analysis, which are related to the mineralisation. The second factor shows significant weights for practically the rest of elements, which can be associated to natural soil components influenced by the presence of igneous rocks. Finally, only elements such as Au and Mg, with weights in the third factor, have a mixed and not very clear origin. Both multivariate techniques show, therefore analogous results (Table 2). Mobility of As in the environment is strongly affected by adsorption phenomena and there is a large number of scientific papers addressing the mechanisms of As adsorption on mineral surfaces of Fe oxides and hydroxides (Gieré et al. 2003). The adsorption affinity is higher for arsenate under lower pH conditions and for arsenite under higher pH conditions (Stollenwerk 2003). As the arsenate is less mobile than the arsenite, special attention should be put in those alkaline soils in the site, which are closer to the Riaño reservoir water.

Arsenic is widely distributed in surface freshwaters, and concentrations in rivers and lakes in the world are generally below $10 \mu\text{g l}^{-1}$. However, individual samples may range up to 1 mg l^{-1} (Page 1981; Smith et al. 1987; Welch et al. 1988). Table 3 shows average values of pH, electrical conductivity and As, Ca, Cu, Fe, Hg, Mg, Na, Pb, S, Sb and Zn concentrations in surface waters at the abandoned mine site of Santa Águeda, both upstream and downstream from the mine works. In the latter case, water samples have been collected in two sporadic courses flowing through the spoil heaps to the dam. Currently, the Spanish legislation for mine/industrial effluents limits the total As content to 0.50 mg l^{-1} , and to 0.05 mg l^{-1} for surface waters for drinking water use (BOE 1985). Both limits are exceeded by leachates of spoil heaps in Santa Águeda mine site, whose average As concentration is 0.9 mg l^{-1} (Ordóñez et al. 2003). However, the input of this polluted flow to the Riaño reservoir is negligible, since the area of the catchment affected by the old mining works is only 43 ha, in contrast to the 60,400 ha of the reservoir catchment. The average surface flow from the mined area catchment to the dam is $241 \times 10^6 \text{ l}$ per year, which represents 0.07% of the total water flow to the Riaño reservoir.

Soils and water pollution might constitute a hazard if toxic substances reach receptors by diverse pathways.

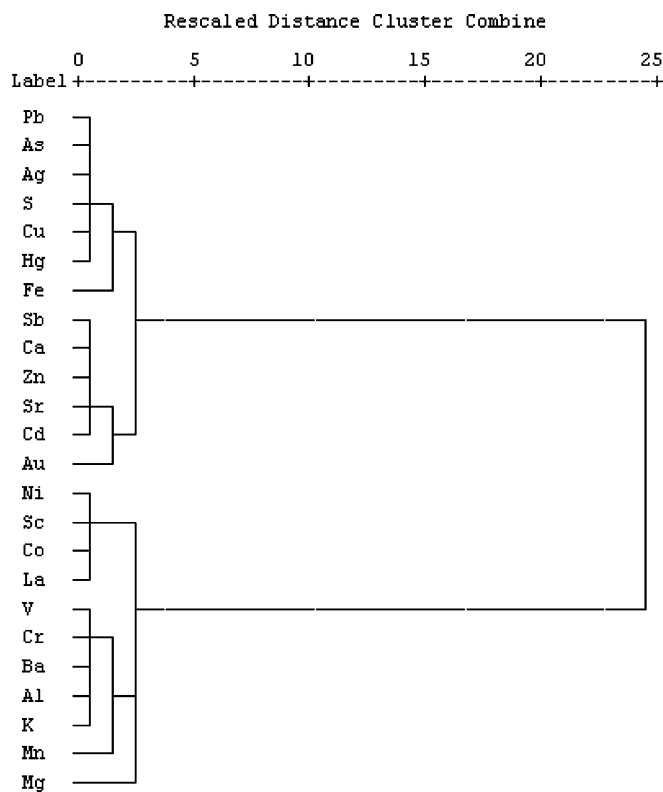


Fig. 5 Hierarchical cluster analysis: Dendrogram using Ward method

Table 2 Factor analysis of the results (mg kg⁻¹) for 19 variables

Variable	Factor 1	Factor 2	Factor 3	Communality
Cu	0.995			0.993
Ca	0.992			0.985
Hg	0.992			0.991
As	0.988			0.985
Pb	0.988			0.980
Ag	0.978			0.978
Sr	0.967			0.943
S	0.945			0.913
Fe	0.932			0.950
Sb	0.928			0.881
Zn	0.872			0.889
Mn		0.966		0.942
V		0.954		0.954
Sc		0.944		0.921
Ni		0.922		0.903
Co		0.911		0.882
Cr		0.902		0.938
Al		0.893		0.904
Ba		0.879		0.953
La		0.862		0.962
K		0.849		0.842
Cd	0.459	0.825		0.894
Au			-0.811	0.696
Mg	0.533	0.418	0.549	0.760
Variance (%)	46.4	39.0	6.4	91.8

Factor loadings < 0.4 have been omitted for clarity. Extraction method: principal components; Rotation: Varimax

The extent to which abandoned mining works become an environmental problem depends on the relation between the identified hazards and their proximity to water resources, publicly accessible land, etc. In this case the proximity of the mine works to the Riaño reservoir, makes the site vulnerable to environmental risks. The mine operations developed in the area did not have an important size but the characteristics of the pollutants and their proximity to a water reservoir give a particular interest to the site. According to the mineralogical and chemical characteristics of wastes, they can be considered as a potential source of pollution for local soils and watercourses. These abandoned mine works currently pose a potential threat to the environment in several ways: landscape modification, mechanical removal of waste material by wind and/or surface water runoff and drainage of toxic elements from the assorted mine wastes.

As this mine site exhibits an environmental degradation by the storage and weathering of mine wastes in spoil heaps, it is important to clearly identify the associated environmental risk. For the purposes of the risk assessment, the sources of contamination and the proximity of the Riaño dam to the spoil heaps has been considered. Then, in order to elaborate a site-specific assessment, the risks for potential receptors, which may include humans, the water environment, and the flora and fauna ecosystems, have been considered. Risk assessment of an abandoned mining site depends

fundamentally on the data available about the physico-chemical and social characteristics of the site, including contaminant sources, pathways and the potential receptors that may be at risk.

A risk assessment was conducted by means of the application of the RBCA Tool Kit for Chemical Releases software (Connor et al. 1998), including physico-chemical parameters of air, soil and water in the site, and different exposition pathways. As result of this analysis, it was concluded that the presence of As in quite elevated concentrations in soils constitutes an acceptable risk according to the EPA classification (USEPA 1997a) (Table 4). In particular, it was found that the target carcinogenic risk was exceeded for As at the mining site, in the soil exposure pathway, in terms of both dermal contact and ingestion, as well as in the groundwater exposure pathway (direct ingestion or soil leaching). There was also a non-cancer risk associated with the above exposure pathways. However, there was no estimated carcinogenic risk for off-site receptors at a distance of 300 m from the mining site. Table 4 shows the applicable risk-based exposure limits (RBELs), based on target risk limits, compared to the values found for the site. Nevertheless, given that the area is not inhabited and difficult to access to, the effective risk for human beings is negligible. The topographically elevated and rocky area, with a barren landscape and scarce vegetation represents a species poor habitat. Moreover, the influence of these old mining works on the reservoir water is not significant in relative terms. This was proven when the As content in the reservoir water was found to be below the detection limit of the analytical technique employed, and the quality of the water in the reservoir are called 'excellent'. The influence of other metals analysed are not considered here, as they were not found in high concentrations in the water and only two of the soil samples (located where the ore used to be stored, Fig. 1c) showed elevated Hg contents.

Table 3 Average elemental concentrations, electrical conductivity (EC) and pH values in surface water samples collected upstream and downstream from the spoil heaps

	Upstream (3 samples)	Downstream (6 samples)
pH	8.1	7.9
EC (mS cm ⁻¹)	0.25	0.30
As (µg l ⁻¹)	33	890
Ca (mg l ⁻¹)	60.3	77.5
Cu (µg l ⁻¹)	< 2	< 2
Fe (mg l ⁻¹)	0.08	0.11
Hg (µg l ⁻¹)	< 1	< 1
Mg (mg l ⁻¹)	2.4	2.7
Na (mg l ⁻¹)	0.8	0.9
Pb (µg l ⁻¹)	< 10	< 10
S (mg l ⁻¹)	4	18
Sb (µg l ⁻¹)	< 10	< 10
Zn (µg l ⁻¹)	< 5	< 5

Table 4 Applicable risk limits for risk-based exposure limits (RBELs) (USEPA 1997a) compared to the values found for soil and groundwater exposure pathways in Santa Águeda mine site

Health effect	Applicable risk limits for RBELs		Santa Águeda mine site	
	Individual COC (always meet)	Cumulative COCs (secondary check)	Groundwater exposure	Soil exposure
Cancer incidence	TR ≤ 1.0E-5	TR ≤ 1.0E-4	TR = 1.7E-3	TR = 1.2E-3
Non-carcinogenic effect	HQ ≤ 1.0	HI ≤ 10	HQ = 11 HI = 11	HQ = 7.6 HI = 7.6

COC Constituent of concern

TR Target risk

HQ Hazard quotient

HI Hazard index

Conclusions

In the area of abandoned mine works of Santa Águeda, surface runoff flows through the spoil heaps entering in contact with mine wastes under oxidising conditions. Then, the weathering and oxidation of leachable As-rich minerals in the spoil heap results in destabilisation of sulphides and transport of dissolved As into surface waters. Under these oxidising conditions Fe(III) oxide and hydroxides are stable and As is adsorbed. Total As concentrations found in soils (up to 23,800 mg kg⁻¹) and surface water (up to 890 µg l⁻¹) in the area affected by the mining and metallurgical activities, are critically above the local background levels and those stated by the literature in unpolluted areas. They constitute anthropogenic geochemical anomalies associated with mine activities in the area. The place where the ore was stocked after being extracted and previously to be sent to smelting plant constitutes the biggest anomaly reaching As contents of up to 42,600 mg kg⁻¹. As concentrations in soils increase with depth, at least on the first 80 cm which have been sampled and analysed. This is in agreement with a transport of As in solution and adsorption on clay components of the soil. Adsorbed As may be released in association to pH changes.

As a consequence, an important pollution migration in the main form of soluble As occurs from the mine site towards the Riaño reservoir, which is located at 300 m downstream of the mining works. Fishing practices are currently developed in the reservoir, increasing the

potential environmental risk associated to the incorporation of polluted leachates to the stored water. However, if surface water downstream of the mine works shows a significant pollution by oxidation of arsenopyrite, the absence of major deposits of this mineral or their oxidation products diminish the potential environmental risk. The application of a computing based risk assessment software (RBCA tool kit for chemical releases) to the site, concluded that As concentrations in soils and surface waters are sufficiently high to be considered, but in relation to water, the contribution of polluted water (spoil heap leachates) to the dam does not pose a significant environmental risk because of its dilution with clean runoff water from the catchment.

Furthermore, the input of the flow from the mining area, compared to the total water that the Riaño dam is receiving, is negligible. On a quantitative way the total contribution of runoff water to the reservoir in the catchment is 14,000 times higher than the contribution to the dam of the runoff water flowing through the site of the abandoned mine (mine catchment). This fact together with the moderate As concentrations, in general, of leachates and mine drainage does not involve a real significant contribution of the polluted water entering in the reservoir.

Finally, on the basis of the sampling accomplished and geochemical analytical data obtained, it can be concluded that the environmental risk associated to the presence of polluted water from the abandoned mine works in the dam can be considered negligible.

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