

Environmental impact of toxic metals and metalloids from the Muñón Cimero mercury-mining area (Asturias, Spain)

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Abstract

This paper presents the results of the sampling surveys carried out in order to evaluate the environmental problems associated to La Soterraña, an abandoned Hg mine in Asturias, north of Spain. In particular, this paper overviews the impact of mining and metallurgical activities on terrestrial and aquatic environments. The wastes generated during the mining activity (ore extraction and processing) and later accumulated on the ground, contain great amount of sulphides, becoming potentially acid-generating. Consequently, the mobility of heavy metals and other ecotoxic elements is enhanced. Wastes are generally located close to watercourses and on very steep hillsides, where they are exposed to oxidative weathering, posing a significant risk due to the release of ecotoxic elements to the environment. Background levels were determined at sites, which had not been directly affected by mercury mining. A multielemental geochemical study of mining wastes, soils, stream sediments, water and air samples collected in the area of influence of the old mining and metallurgical works was carried out. Total Hg and As concentrations in soils reach values up to 502 and 19,940 mg kg⁻¹, respectively, 500 and 2000 times higher than the local background levels. The effects of mining seem to be intense both in waters and stream sediments, as well as in the local atmosphere, whose Hg content is 10 times higher than the background level in the area. Therefore, the target carcinogenic risk was exceeded for As and Hg in La Soterraña site.

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1. Introduction

The Hg mines in the area of “Muñón Cimero” are part of a Hg district that consists of numerous deposits found in the Cantabrian Zone (geological unit of the Iberian Massif). These deposits were mined until the 1970s when Hg prices began to decline due to a falling demand, caused by emerging toxicological problems with Hg use and production and heightened public awareness with regard to environmental issues. Mercury mining was for years an important industry in Asturias (northern Spain). One of the most important Hg mining sites of the region was located close to the village of Muñón Cimero (Pola de Lena district), where vestiges of very old mine works attributed to Romans during his occupation of the Iberian Peninsula in centuries I and II, have been found [1]. Afterwards, the mine was

intermittently exploited by underground works, with rooms and pillars exploitation method, from the middle of the XIX century until 1972. From the smelter chimneys, Hg and As were emitted to the atmosphere as vapour and particles during the mining activity.

Other less important mining works in the area are practically unrecognizable, being the spoil heaps covered by dense grove and thickets or by pasture for cattle, blending in with the surrounding landscape. The mineral extracted in these small mines was subjected to an on-site raw concentration, but the obtained pre-concentrate was transported by lorries to be treated and purified at La Soterraña Mine site. There, the ore was crushed and roasted by means of retorts or tub furnace depending on grade of mineral to oxidise cinnabar to Hg vapour, which was condensed and then collected in flasks. Some Hg vapour and particles were emitted from two stacks during the process. The total volume of ore mined in La Soterraña was considerable, as this mine produced a great part of the Hg extracted in Asturias. Taking into account the evident losses during mining and inefficient smelt-

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ing, the release to the environment of Hg and accompanying elements, (among which As stands out), has been significant [2–7]. Pollution derived from the smelter's gaseous emissions, because of their high Hg and As content, is known as an existing problem.

The intense mining activity developed over decades in this area, was carried out without pollution control, in accordance with the absence of environmental legislation. Consequently, there was very little constraint over the waste disposal arrangements and their eventual abandonment. Since the closure of the mines, spoil heaps have not received any type of treatment to avoid the pollutants mobilisation, representing potential anthropogenic sources of contamination for soils and waters in the area. The site is located at 43° 11' latitude and –5° 50' longitude, between 650 and 341 m above sea level, within the scenic valley of a tributary of the Caudal river, which is one of the most important rivers in the region. Currently, the legacy of the historical mine works at La Soterraña remains in the form of old industrial installations and a big spoil heap with significant quantities of wastes from mine and metallurgical operations. These wastes, due to the weathering of solid inorganic materials under supergenic conditions, are being oxidised and a natural leaching of metals occurs. Formed mainly by the accumulation of processing residues, the spoil heap covers an area of about 17,000 m². The wastes were placed in the neighbourhood of the mine, in an area where the abrupt topography and drainage (in contrast to other Spanish regions, Asturias has a humid climate characterised by abundant precipitation during great part of the year), are important factors favouring the ore weathering and consequent water and airborne mobilisation of metals and metalloids to the environment, either in soluble or suspended forms.

Easily oxidisable metal-rich minerals present in the mine wastes, such as many sulphides, liberate their elemental constituents. Some of the mobilised metals are adsorbed or precipitated almost immediately, whereas others are sequestered by clay-sized phyllosilicates, organic matter or secondary oxides/hydroxides, or remain in solution [8]. The adsorption of heavy metals and/or As onto the soil constituents is also affected by parameters such as pH and ionic strength, as well as the concentrations of cations and complexing ligands in the solution. Metal processing facilities release metals and their compounds in aqueous effluents, as well as gases and aerosols or particulates from furnace stacks, ore stockpiles and tailings, being fixed eventually by sinks such as sediments, soils or biota. It is known that soils strongly bound Hg due to complexing with humic acids functional groups, and half-life of such complexes is estimated at 250 years [9]. Thus, Hg pollution of soils is of a stable durable character and may result in pollution of the atmosphere, waters, plant and animal biocenosis, affecting then the health of human beings.

In consequence, soils and superficial waters surrounding mining installations reflect the influence of both the natural mineralization and the anthropogenic contamination from waste products from mining and benefaction processes. Anthropogenic trace metals entered in the surrounding soils following different pathways: through aerial deposition, mine waters, waste disposal and waste utilisation. The soil metal enrichment depends

on many site-specific factors including the history and nature of emissions, distance from the point source, wind patterns, nature and composition of the parent substrate, and climate [8].

Hg is a heavy metal of environmental concern because high concentrations are toxic to organisms [10,11]. It has been identified as a persistent, bioaccumulative, and toxic chemical (PBT) by the U.S. Environmental Protection Agency, as well as some authors [12]. PBT chemicals are of great concern because they persist in the environment, posing a significant threat to humans and ecosystems. Additionally, many of these chemicals, included Hg, easily transfer from one media to another in the environment. Concern on Hg pollution arises from the extremely toxic forms in which this metal can occur [13,14]. All forms of Hg are toxic to some extent [15], but organic Hg compounds, especially methylmercury, are the most toxic forms [16]. Important ecological catastrophes due to Hg releases [17] drew attention all around the world to this element, and in consequence it began to receive a great deal of interest by the administrations which developed strict environmental regulations for Hg-rich wastes. Elemental Hg present in mine wastes volatilises at ambient temperatures, leading to air emissions. Research strategies are being developed to address the Hg problem through multimedia initiative [14]. Thus, the presence of Hg mines is potentially hazardous to humans and wildlife when any mine runoff and/or spoil heap leachates enter soils and streams.

2. Geology and hydrogeology

The ore deposit is located within the low levels of the Asturian Central Coal Basin (Carboniferous), in sandy pelitic sequences (known as “Lena Group”) where carbonated levels are interbedded. Significant structural characteristics of the area are the folding (N–S trend) and the intense fracturing, expressed in the form of faults and thrusts. Both folding and fracturing are structural guides for the studied hydrothermal mineralization, which is directly related to an anticline structure (fold axis area), which acquires a NW–SE trend in the mineralised area [18].

The mineralization itself is inserted in highly fractured limestones (wackestone to mudstone in the Dunham classification) with dispersion in the adjacent sandstones and lutites (common hangingwall and footwall of the mineralized areas). This mineralization appears either as irregular massive lenticular stocks in the limestones, or as irregularly distributed veinlets in fracture planes [19–21].

The mineralization exploited in La Soterraña mine is an epigenetic-type ore deposit, originated from low-temperature hydrothermal solutions [22]. The paragenesis of the ore deposit is constituted by cinnabar, orpiment, realgar, pyrite (usually with high concentrations of As), arsenopyrite, marcasite, and pararealgar, in a gangue of quartz and calcite. Native Hg has been observed and it is associated to organic matter rich limestones. From an environmental point of view, the presence of As minerals in the ore deposit paragenesis, is specially significant, as high As concentrations have been found in pyrites and iron oxides (Table 1, Section 4.2).

Table 1
Univariate statistics of microprobe analysis results

		Pyrite	As-rich pyrite	Arsenopyrite	Realgar	Iron oxides	Cinnabar
		No. of analyses					
		38	79	17	42	29	19
S content (%)	Mean	47.83	51.48	20.40	25.14	–	13.00
	Median	51.27	52.54	20.21	28.96	–	13.72
	Minimum	32.34	30.55	19.89	12.38	–	0.01
	Maximum	55.76	54.99	21.64	32.53	–	14.52
Fe content (%)	Mean	48.77	47.16	36.26	0.02	49.06	0.06
	Median	48.46	47.45	36.30	0.02	44.01	0.03
	Minimum	35.39	27.52	35.25	0.00	0.48	0.00
	Maximum	59.99	59.37	37.18	0.07	68.68	0.55
As content (%)	Mean	0.13	1.26	44.25	56.64	0.45	0.06
	Median	0.16	1.07	44.49	61.85	0.30	0.04
	Minimum	0.02	0.11	42.77	33.81	0.00	0.00
	Maximum	0.42	4.93	44.64	69.37	2.03	0.20
Hg content (%)	Mean	0.19	0.15	0.29	1.40	1.48	78.98
	Median	0.01	0.04	0.19	0.15	0.32	84.72
	Minimum	0.00	0.00	0.00	0.00	0.00	0.08
	Maximum	4.21	4.40	1.09	19.93	5.23	88.51

From a hydrogeological point of view, the substrate of the mineralised area is mainly composed of materials of the “Llanón-Tendeyón” unit, constituted by an alternation of limestones, sandstones and lutites (dominant), which can be considered impermeable excepting some limestones and sandstones bars which constitute small aquifers. The springs in the area are scarce and most of them associated to limestone bars. Springs associated to sandstones have a very poor flow. The mining site is drained by the Troncos stream, tributary of the Lena river, whose catchment has been estimated in 7.52 km² (Fig. 1A). The area occupied by mining/metallurgical works and the spoil heap (aprox. 80,000 m²) is 85% non-impervious, so the infiltration surface in this area can be estimated in 68,000 m². The average yearly rainfall in the area is 966 mm and the calculated Thorntwaite evapotranspiration is 691 mm/year, so an effective annual rainfall of 275 mm/year can be considered. Although the average infiltration coefficient (ratio of infiltration rate to rainfall) in the Asturian Central Coal Basin is estimated in 0.46 [23], in this case, an infiltration coefficient of 0.7 (no vegetal cover) can be used to calculate the rainwater infiltrated with chance to enter in contact with mining materials, which is about 13,090 m³/year.

3. Environmental prospecting methodology

Analysis of metal contents in the different milieu (soils, waters and atmosphere), as well as the quantification of the bio-available fractions of metals and metalloids and the assessment of intake and consequences for the target organisms (e.g. humans), are the means of quantifying contamination and potential environmental and human health risks. The sampling surveys described below were carried out under the framework of a project granted by the Government of Asturias.

3.1. Field procedures

An estimation of the local geochemical background in soils within areas not directly affected by former mining activity is a necessary step in order to establish a level of reference, expressing the natural concentration of a given element in a particular type of soil and at various soil horizons. As it is referred on the specialised literature [24], the depth of sampling in the soil profile is an important consideration when attempting to determine spatial variations in heavy metals distribution, and sampling depth will be dependent upon the characteristics of the particular site and determined through pre-screening methods. Then, as a preliminary stage for the sampling design, samples were taken at different depths in the same perforation, in some randomly selected points of the area, in order to determine the distribution of heavy metals in the soil profile, and then to define the most suitable sampling horizon for the particular case. It was found that Hg and As reach their maximum concentrations approximately at the 20–40 cm depth interval in the soil profile, which was selected for the later systematic sampling, following the same methodology both in the pilot and definitive sampling phases. A regular grid pattern centred on the site of the old mining and metallurgical works has been outlined (Fig. 1B), and soil samples were collected following this grid, both upstream and downstream the old mining works. The grid was limited to an area of 600 m × 600 m, with a distance of 50 m between the grid nodes, in which soil samples were taken. At each sampling point – or as close as possible – soil was sampled at its B horizon (20–40 cm). A total of 169 samples, weighing approximately 2 kg were collected in 1997, using manual drilling as cores of 50 cm length. With the aim of investigating the geochemical characteristics of the spoil heap in depth, as well as the vertical extension of the contamination, some trenches and drills were carried out at the lowest part of the spoil heap in 2001.

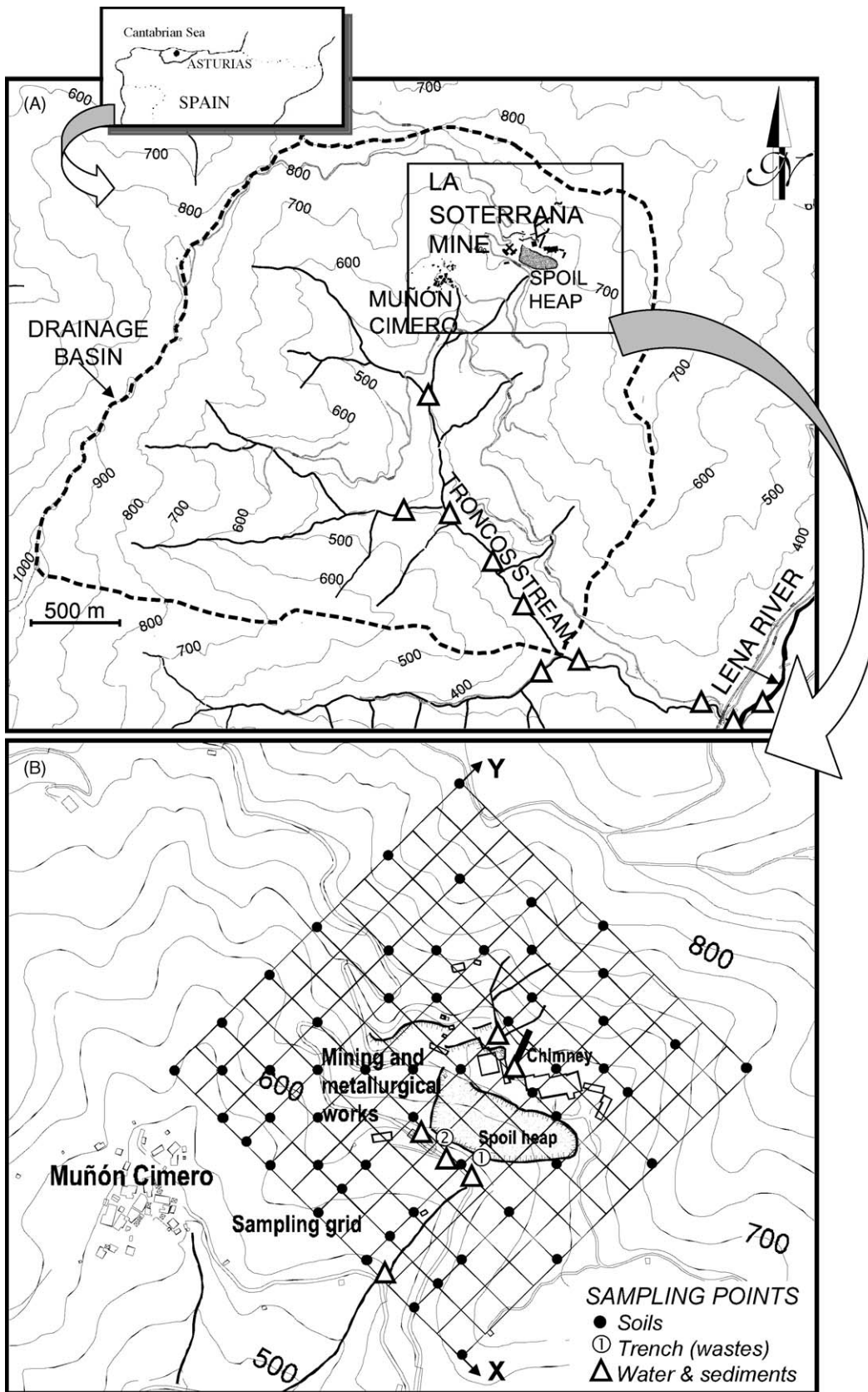


Fig. 1. (A) Location of the mine site within the drainage basin of Troncos Stream and (B) sampling grid, soil, water and sediments sampling points and spoil heap trenches.

Two kilograms point samples of waste materials and underlying clays were collected in this case.

Stream sediments were sampled from the upper 20 cm in the stream bed of the watercourse flowing through the mining works, both upstream and downstream of the spoil heap. The Troncos Stream was sampled at different distances from the mining site till its outlet into the Lena River, adding up a total of 16 sampling points that were selected preferably at the confluence of affluents (Fig. 1). One kilograms of sediments was collected in each site by means of a small shovel of inert material in 2002–2003.

In situ measurements of pH and electrical conductivity of surface water were undertaken using HANNA portable field equipment calibrated with standard buffers. Water samples were collected both upstream and downstream of the mining-metallurgical works and spoil heap, within the drainage basin. Surface water was sampled at the same sampling points used for sediments (Fig. 1) and in the same period, whereas, groundwater was sampled at springs and manmade drills. The water samples were placed in plastic bottles and refrigerated until analysis. In order to conserve their chemical characteristics and to keep metals in solution, special precautions, such as the previous acidification of the sample with HNO_3 , were used.

In order to assess the environmental significance of Hg emissions from abandoned Hg-rich waste, total Hg concentrations in $\mu\text{g Nm}^{-3}$ have been measured in the ambient air in 2003–2004. Twenty-five sampling points were selected as follows: six within the mining site (around spoil heap, mining ruins and chimney), four in the urban centre of Pola de Lena (both groups were monitored every 15 days) and the rest of points distributed within the drainage basin, preferentially located close to rural villages, such as Muñón Cimero and others (monitored every four months). Measurements were made with a portable analyser (Mercury Tracker-3000), which allows obtaining the Hg concentration in the atmosphere at real time by atomic absorption spectroscopy (AAS). The equipment is easy to transport and handle, and it has been programmed to measure Hg concentrations in $\mu\text{g Nm}^{-3}$ for an exposure time of 6 min. The detection limit of the Hg analyser is $0.1 \mu\text{g Nm}^{-3}$ (which is considered as background value in the area) and the range of measurements is $0.1\text{--}2000 \mu\text{g Nm}^{-3}$. Although the main wind direction was taken into account when sampling, the study focussed mainly on the determination of Hg concentrations in air due to volatilization effects from mine wastes in abandoned mine sites and their surroundings.

In order to assess the samples representativeness, as well as testing the natural heterogeneity of the soil, pairs of field duplicate samples were included as a routine component of the survey. To be able to discriminate the geochemical trends related to geological factors from those resulting from spurious sampling or analytical errors, a number of quality control measures should be implemented in both the field and laboratory (usually one randomly selected site in 20 is sampled as duplicate in accordance with established protocols).

3.2. Laboratory procedures

Characterisation of wastes was based on mineralogical and chemical analyses of samples collected in the spoil heap. Miner-

alogical analysis was made by application of optic and electronic microscopical techniques to representative samples from the spoil heap. Detailed investigations of As distribution in pyrite and goethite were carried out using an electronic microprobe (CAMEBAX-SX50). Analyses of $1\text{-}\mu\text{m}$ diameter spot have been made over selected areas of polished sections.

Samples of soils, stream sediments and waste materials from the spoil heap were oven-dried at temperature 39°C to prevent evaporation of Hg. After drying, samples were desegregated in their entirety using a ceramic mortar, and then homogenised. The resulting powder was screened with a $147 \mu\text{m}$ (100 mesh) sieve to remove any remaining aggregate material, and the fines retained for analysis. The quartering of the samples was carried out using an aluminium riffle.

Chemical characterisation was performed by analysis of the soluble fraction resulting from a strong acid attack of the sample. Extraction of elements was made by partial digestion in 3 ml of 3:2:1 $\text{HCl-HNO}_3\text{-H}_2\text{O}$ (Aqua Regia) at 95°C for one hour and dilution to 10 ml with deionised (DDI) 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 and Hg) were determined in all samples, by means of inductively coupled plasma-mass spectrometry (ICP-MS), excepting the soil samples, which were analysed by inductively coupled plasma-atomic emission spectrometry (ICP-AES) and Hg by flameless atomic absorption spectrometry (FAAS), at ACME Analytical Laboratories in Vancouver (Canada), accredited under ISO 9001:2000. 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., and analytical duplicates have been observed. Approximately 5% of the samples were analyzed as internal and external control samples. Variability was found to be $<10\%$ in all cases. Detection limits were between 0.1 and 1 mg kg^{-1} for solid samples, excepting V (2 mg kg^{-1}), Fe, Al, Ca, K, Mg (0.01%), and Ti, Na and P (0.001%) and between 0.01 and $30 \mu\text{g l}^{-1}$ for water samples.

Since not all minerals are decomposed during the digestion [25], for the purposes of the study, the results obtained for As 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.

As pH and organic matter content are very important factors controlling mobility and concentration of elements in soils, determinations of these parameters were made over representative duplicates of samples used for analysis. Measurements of pH were carried out in situ by means of portable HANNA pH-meter and in laboratory according to ISO/DIS 10390 [26], and organic matter content in soil samples was determined according to Nelson and Sommers methodology [27].

Filtered and acidified surface and groundwater samples were analysed for 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 and Tl with ICP-MS technique in the laboratories of ACME Analytical

Laboratories in Vancouver (Canada), following a quality control analogous to that explained for solid samples. Analysis of Hg organometallic species: methylmercury (HgMe^+), ethylmercury (HgEt^+) and phenylmercury (HgPh^+) have been accomplished by HPCE (High Resolution Capillary Electrophoresis) for filtered samples of pounded spoil heap leachates in the laboratories of the Chemistry Department of the Universitat Autònoma de Barcelona (Spain).

4. Results and discussion

4.1. Soils

Although soils in the area are naturally rich in Hg in local geologic materials, the mining operations severely enhanced the mobilisation of Hg through deposition and storage of wastes on land and smelting activities. Soils have pH values ranging from 4.74 to 7.59. An estimation of the organic matter content, obtained through determination of the weight loss at 60 °C, ranges from 4.9 to 12.3% [28].

Average data corresponding to the particle size analysis and content of total Hg and As for different size fractions in soil samples, suggest that Hg and As content in soils increases as the soil particle size decreases. In the whole of the soil samples studied, the average Hg content increases from 4.2 mg kg⁻¹ in the size fraction coarser than 1651 μm to 36 mg kg⁻¹ in the size fraction finer than 0.147 μm. Analogously, the As content increases from 394 to 570 mg kg⁻¹, in the same grain size fractions.

In order to put the results of this sampling survey in perspective, background levels of Hg and As in soils in this area (4.18 and 39 mg kg⁻¹, respectively) were obtained in a previous study of nine samples undertaken in a neighbouring zone not affected by the mining activity, but with the same geologic and pedological substrate, that were subjected to the same methodology of sampling, preparation and analysis that those described in this paper. According to bibliographic data, Hg average concentration for uncontaminated world soils is about 0.03–0.37 mg kg⁻¹, and for areas near mineral deposits is 0.1–54 mg kg⁻¹ [29]. Some authors state that the average As concentration in uncontaminated world soils is about 5–10 mg kg⁻¹ [30,31], whereas in areas near mineral deposits it may range from 400 to 900 mg kg⁻¹ [32]. The comparatively low background level found for As in the uncontaminated soils of the area, can be due to the relatively low As content of the ore exploited at La Soterraña and the scarcity of ore outcrops in the area, which is

a small-scale Hg mining district. Besides, the As is irregularly distributed within the ore and it is present in a relatively stable mineral form.

Only 58 soil samples distributed regularly in the area (Fig. 1B) were taken and analysed due to difficult access and economical restrictions. The results of this multielemental geochemical analysis showed a great variation in concentrations of Hg and As in the soils of the area, ranging from 1.96 mg kg⁻¹ to a maximum value of 502 mg kg⁻¹ for total Hg, and from 32 mg kg⁻¹ to 19,940 mg kg⁻¹ for total As, in the <147 μm soil size fraction. The calculated Hg enrichment factors versus Fe ($EF_{\text{Hg}} = ([\text{Hg}]/[\text{Fe}]_{\text{studied soil}})/([\text{Hg}]/[\text{Fe}]_{\text{crust}})$) and Al are 273 and 611, respectively, which means that the studied soils have a clear enrichment in Hg, of anthropogenic origin [33].

Univariate statistics of concentrations of some environmentally significant elements analysed in soil samples, contrasting with their local background geochemical levels, are summarised in Table 2. In general, the spread of values for all considered elements is very large due to the great difference between polluted areas and the local background levels. It may be observed that the standard deviation is much higher for Hg and As than for other elements, this feature can be related to an anthropogenic addition of these elements.

From the statistical analysis of multielemental geochemical data, a clear positive correlation ($r = 0.877$) between the total Hg and As concentrations in soils and mining wastes, was observed in the area affected by the old mining works. This is in agreement with a common origin for the accumulation of these elements in soils, and it can be related to the weathering of the ore. Fig. 2 shows very alike contour maps for Hg and As concentrations in soils over the sampled area. The highest values correspond to the location of waste piles and smelter chimneys. Values above 100 mg kg⁻¹ occurred in the valley and at the base of the slopes. Lower values occurred at higher elevations and in more distant areas. The movement of Hg from the old mining works (maximum Hg) is outlined down slope, as physical and chemical transport of metals from waste piles is helped by gravity. The contents of other heavy metals linked to the ore are not very high in the soils, as they do not exceed 225 mg kg⁻¹ for Cu, 215 mg kg⁻¹ for Zn, and 142 mg kg⁻¹ for Pb.

In order to better describe and interpret the analytical results, a number of multivariate analysis techniques have been applied, (i.e. Hierarchical Cluster Analysis and Factor Analysis) using SPSS software, to the database of the soil samples results. Although 32 elements were analysed, only 19 were considered

Table 2
Statistical parameters of elemental concentrations in soils (No. of samples: 58; particle size <147 μm)

	Geochemical background	Minimum	Maximum	Mean	Median	S.D.
Al (%)	1.57	0.45	3.64	1.26	2.05	0.55
As (mg kg ⁻¹)	39.0	32.0	19940	1293	9986	3392
Ba (mg kg ⁻¹)	71.2	26.0	356	93.2	191	52.9
Cu (mg kg ⁻¹)	24.4	17.0	225	68.7	121	49.6
Hg (mg kg ⁻¹)	4.18	1.96	502	62.1	252	120
Fe (%)	3.71	1.54	4.96	3.39	3.25	0.68
Pb (mg kg ⁻¹)	27.1	20.0	142	47.2	81.3	23.8
Zn (mg kg ⁻¹)	86.2	46.0	215	116	130	40.8

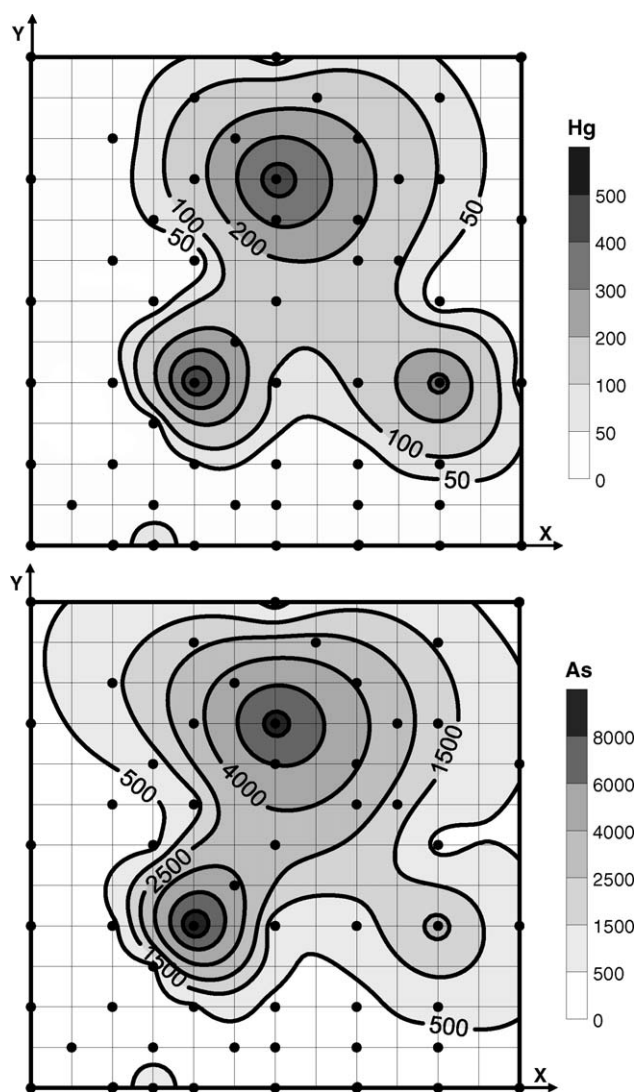


Fig. 2. Contour maps and distribution of total Hg and As concentrations (mg kg^{-1} , dry weight) in the sampled soils.

in the statistical analysis. The rest of variables were excluded for having more than 50% of observations below the method's detection limit and/or for not being considered relevant for this study. Most of the considered variables approximate normal distributions.

Factor analysis results are shown in Table 3. Four factors explain most of the variability (85.1%) of the data. Factor 1 displays a very strong association of Ca, Mg, Sr, K, Ba, Al, Pb, As and Hg, which is clearly related to the mineralization and its host rock and later anthropogenic dispersion. Factor 2 displays a strong association between Mn, Co, Cu, Ni and Zn, elements with a similar chemical structure, usually linked in nature, but not associated to the ore in this case. Factor 3 displays an association of Fe, Cr and V; these elements of analogous geochemical behaviour, and whose relative dispersion is the lowest in the set of variables, are considered geogenic elements with a homogeneous distribution within the studied area. Finally, the fourth factor appears to represent a natural matrix of the soil that remains fairly constant throughout the whole set of sam-

Table 3

Factor analysis of the results (mg kg^{-1}) for 19 variables (factor loadings <0.4 have been omitted for clarity)

Variable	Factor 1	Factor 2	Factor 3	Factor 4	Communality
Ca	0.903				0.881
Mg	0.881				0.921
Sr	0.781		0.484		0.901
K	0.776				0.810
Al	0.738		0.406		0.802
Ba	0.731	0.568			0.898
As	0.629		0.550		0.853
Pb	0.608		0.426	0.473	0.793
Hg	0.594		0.487	0.459	0.807
Co		0.896			0.821
Mn		0.865			0.750
Ni		0.812			0.875
Cu		0.764			0.608
Zn		0.628		0.592	0.842
V			0.863		0.877
Cr		0.411	0.746		0.883
Fe		0.522	0.603		0.713
Th				0.819	0.694
La				0.709	0.709
% Variance	50.5	15.0	11.4	8.3	85.1

Extraction method: maximum likelihood; rotation: varimax.

ples, unaffected by anthropogenic activity, and characterised by La and Th. The results obtained by means of the Cluster Analysis of the standardised data (linkage method: Ward) are analogous and complementary to those obtained by means of Factor Analysis, so they have not been discussed here in detail. Only the close association of Pb with Hg and As, due to the relative immobility of these three elements under the prevailing pH soil conditions, appears to be more patent in the dendrogram generated by this multivariate analysis.

4.2. Mine wastes

Iron sulphides (pyrite, marcasite and pyrrhotite) are quantitatively the most important metalliferous minerals which decompose in the spoil heap, and breakdown of these minerals dominate the geochemistry of the spoil heap leachates. They are stable under reducing conditions in the mine but they become unstable under oxidizing conditions. The rate of decomposition varies with grain size. These abundant sulphides are typically in an advanced state of oxidation, with amorphous iron oxyhydroxides coatings, being goethite the most abundant. Some relicts of cinnabar, arsenopyrite and sphalerite have been also found among the oxidised minerals on the studied samples. The presence of realgar is frequent too. Arsenic content of As-rich pyrites ranges from 0.11 to 4.93%. High As concentrations have been also found in iron oxides, such as goethite (up to 2%). This can be observed in Table 1, which shows the results of electron microprobe analysis. Hg distribution in mining/metallurgical wastes is a function of the type of mining activities in the area rather than any geochemical process. Different metallurgical techniques may result in different Hg concentration and dis-

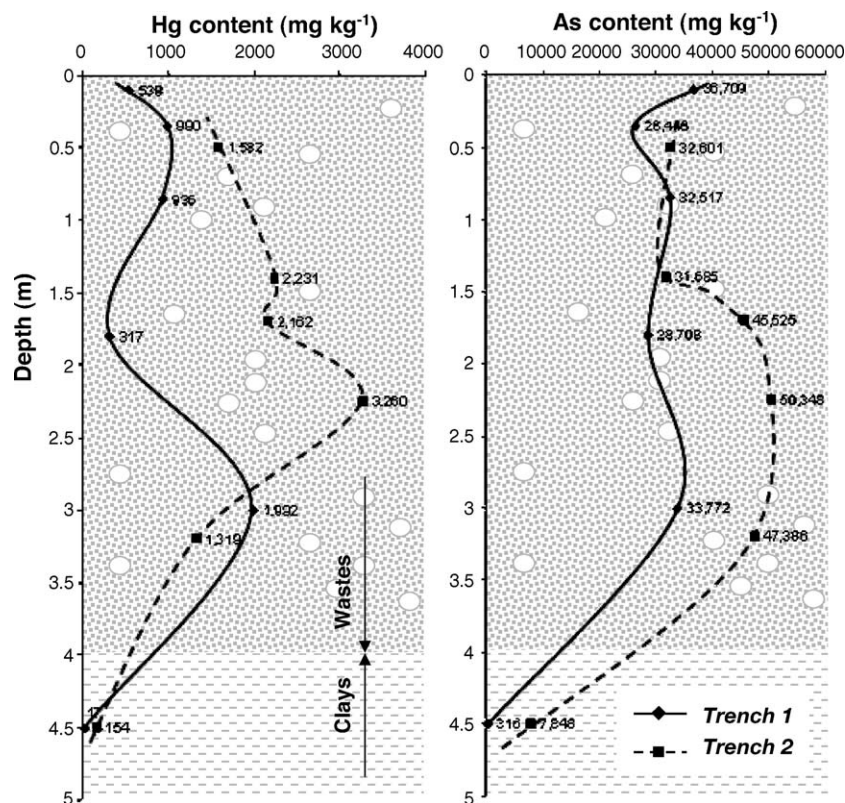


Fig. 3. Hg and As concentrations in two trenches within the spoil heap.

tribution in wastes. Typically, these concentrations range from 150 to 3200 mg kg⁻¹.

A major problem of such wastes is their high As concentration and long time span as a significant source of As to the environment. Tailings deposited over 40 or 30 years ago and containing up to 50,348 mg kg⁻¹ of total As are still present at the site without any preventive or corrective measure to impede the As mobilization to the environment. Fig. 3 shows the variability with depth of Hg and As concentrations in the wastes, within two trenches perforated at the southern part of the spoil heap (their location is shown in Fig. 1B); Hg and As concentrations are reduced in an average of 85 and 99%, respectively, in the clays underneath the spoil heap.

Moreover, some of these wastes have been used as aggregate for backfilling of local roads, leading to a hydromorphic dispersion of As.

4.3. Stream sediments

The geochemical background levels in sediments deduced from analysis of samples collected upstream of the mining works are <0.1 mg kg⁻¹ Hg, 14 mg kg⁻¹ As and 1% Fe. In contrast, Hg content found in samples of sediment collected downstream of the mining works and the spoil heap, increase notably (Table 4). It was found that Hg concentrations vary from 4371 mg kg⁻¹ right downstream of the mine site to 323 mg kg⁻¹ at 100 m downstream of the spoil heap. At a distance of 300 m downstream of the mining site, close to the village of Muñón Cimero, the concentration is 142 mg kg⁻¹ and from that point, Hg con-

centration decreases gradually downstream till reaching a value of 18 mg kg⁻¹ at the mouth of the Troncos Stream (Fig. 1A). Dispersion of Hg downstream of La Soterraña mine is highly localised suggesting a low mobility of this element.

Analogously, total As concentrations decrease from 28,060 mg kg⁻¹ in samples collected at the mining site to 3549 mg kg⁻¹ at a distance of 300 m downstream from it. At a distance of 1200 m downstream of the mine, the As concen-

Table 4
Range of concentrations of selected elements in sediments and waters

	Stream sediments (concentrations in mg kg ⁻¹ ; no. of samples: 12)						
	Sb	As	Cu	Pb	Hg	Fe (%)	Zn
Minimum	1.0	26.8	15.3	16.2	6.10	0.40	39
Maximum	208	28060	68.2	222	4371	6.55	614
Mean	31.4	4771	27.7	48.0	581	2.78	143
	Surface water (concentrations in µg l ⁻¹ ; no. of samples: 16)						
	Sb	As	Cu	Pb	Hg	Fe	Zn
Minimum	<10	<30	<2	<2	<0.5	<10	<5
Maximum	167	290593	13.0	<2	90.8	600	12.0
Mean	48.5	51530	4.80	<2	6.97	200	5.73
	Groundwater (concentrations in µg l ⁻¹ ; no. of samples: 4)						
	Sb	As	Cu	Pb	Hg	Fe	Zn
Minimum	40.3	15853	0.30	<2	1.00	<10	1.60
Maximum	57.7	474679	1.20	<2	13.5	<10	2.30
Mean	46.3	179069	0.83	<2	6.10	<10	1.90

tration in the sediments has been reduced to 645 mg kg^{-1} to end up in 300 mg kg^{-1} As before entering the Lena River. It can be noted that the reduction of concentration with the distance from the source is more significant for Hg than for As, which appears more dispersed within the Troncos Stream basin.

Iron concentration decrease from 6.55% in samples collected close to the mining site to 2% (Table 4) at a distance of 300 m downstream from it. The diminution of As content in sediment samples located far from the spoil heap can be related to its predominant dispersion in solution and sorption by iron hydroxides, whereas the predominant dispersion of Hg is in suspension as fine particles of ore. Rytuba et al. [34] found Hg in streams impacted by mining in the New Idria district to be dominantly particulate and not dissolved. Hg is not highly mobile under most environmental conditions, however, Hg is known to associate with suspended solids and colloidal matter in aquatic systems, and thus Hg adsorption and transport on fine particles is a likely candidate as a supportable hypothesis for Hg mobility [35,36].

4.4. Surface water and groundwater

Some results of analyses of surface and groundwater sampled within the Troncos Stream drainage basin are shown in Table 4. The measured pH values are circumneutral, ranging from 6.7 to 8.8 units. Total Hg concentrations found in the local stream vary from <0.5 to $90.8 \mu\text{g l}^{-1}$, whereas the content in the local springs range from 1.0 to $13.5 \mu\text{g l}^{-1}$. Average contents of Hg in surface and groundwater are 6.97 and $6.10 \mu\text{g l}^{-1}$, respectively, which are above the maximum contaminant level considered by the U.S. Environmental Protection Agency, which is $2.0 \mu\text{g l}^{-1}$ [37]. Expected Hg concentrations in natural waters from non-Hg-enriched waters ranges between 0.002 and $0.02 \mu\text{g l}^{-1}$ [38]. Then, results of analyses of local waters are higher than those expected for natural waters, indicating that water-rocks and/or water-wastes interaction has produced elevated Hg levels within the area of old mining works.

The literature studies [39–42] indicate the possibility of methylation of Hg in soil medium. It is assumed that the mechanism by which the conversion from inorganic Hg to methyl Hg takes place is the same as in aquatic environments. Hg in soil may be methylated both chemically and biologically. Some parameters affecting the formation of methyl Hg in soils are: pH, Eh, soil Hg content, soil organic content, organic heavy metal content, salt content and composition of soil, presence of sulphur and chlorides, temperature and microbial activity [43]. The concentration of Hg organometallic species (HgPh^+ , HgEt^+ and HgMe^+) in surface waters (mine drainage and spoil heap leachates) is below 2 mg/l for all analysed samples.

Although Hg leaching from wastes seems to be a slow process, through the years, the dispersion of fine fractions of wastes may be the most important Hg dispersal mechanism. In general, there is a strong tendency for Hg, in all of its elemental, ionic and organomercurial forms to sorb to nearly every available surface, including sediments and soil organic matter. Prokopovich [44] found a significant relationship between Hg content and the clay fraction in old California tailings.

Taking into account the aforementioned data concerning the distribution of Hg and As in soils, waste materials, stream sediments and waters, it can be proved that in this site, polluted by historical Hg mining and metallurgy, high concentrations of toxic elements persist in the environment from the closure of the mining/metallurgical operations in 1972. Then, mining operations in areas with cinnabar mineralizations can be major sources of Hg for many years, even after mining has been abandoned. Moreover, the sulphide form of Hg released during historic mining is the same form of Hg that dominates in these media today, as it was proved by means of microscopical and microprobe analysis. This is predictable and substantiated with Eh-pH diagrams, which reflect and describe the distribution and behaviour of Hg species at equilibrium for P-T-X conditions, in surficial environments [45–47]. The primary method of transport of Hg away from the anthropogenic sources constituted by abandoned mining works is by a stream flow, which can carry Hg in dissolved or particulate phases far away from the source. The deposition of Hg downstream of the source can result in the remobilization of Hg that is available for methylation. Hence, secondary sources of toxic forms of Hg can be produced at great distance from the original source.

4.5. Hg in the atmosphere

The atmosphere in areas of Hg deposits is always naturally enriched in this metal. Furthermore, the mining operations increase the secondary porosity of Hg-rich waste materials stored at the surface in spoil heaps as well as the underground mine voids, favouring the Hg degassing. Therefore, volatilisation is an important process by which Hg is mobilised to the atmosphere from mine wastes [40,48,49]. The volume of Hg liberated to the atmosphere depends of its concentration in the wastes and the volume of wastes stored on the surface. Other environmental parameters influencing the Hg degassing from mine wastes are temperature and humidity.

According to the literature, contaminated soils tend to show degassing rates linearly proportional to Hg concentrations in the first 15 cm of soil [50], similar to soils over geological anomalies [51]. Surface temperature also exhibits a very strong influence on Hg^0 degassing from contaminated soils [52]. In general, areas surrounding Hg-rich waste storages are naturally enriched in this metal, and the magnitude of the Hg release to the atmosphere is governed primarily by the Hg concentration in the waste. Environmental parameters such as temperature, incident sunlight, rainfall, wind direction, etc., also influence the magnitude of Hg emissions. Considering the average data compiled from the specialised bibliography [53,48,54–56], representative values of atmospheric Hg concentrations are in the order of $0.005 \mu\text{g Nm}^{-3}$ for non-industrialised areas, and higher than $10 \mu\text{g Nm}^{-3}$ in mine waste storage areas (spoil heaps). At the old mining and metallurgical works site, the total Hg concentrations in atmosphere reach up to $45.8 \mu\text{g Nm}^{-3}$ near to a Hg-rich mine waste storage, and $0.89 \mu\text{g Nm}^{-3}$ in a close urban nucleus (Muñón Cimero). The atmospheric Hg concentration varies seasonally, being higher in summer, when it triplicates the values of winter, due to an obvious temperature effect. The background

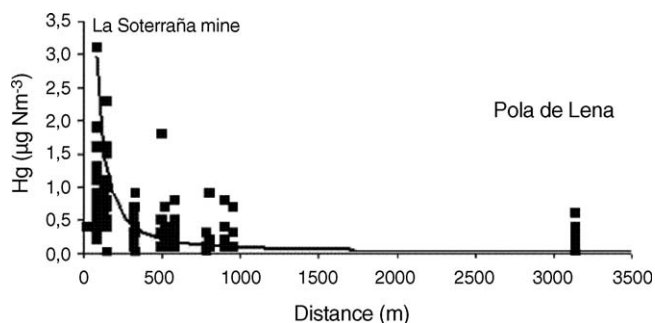


Fig. 4. Variation of atmospheric Hg content (measured at 20 cm above the ground) with distance downslide from La Soterraña mine.

value in this area is about $0.17 \mu\text{g Nm}^{-3}$, which is higher than the corresponding value found in the literature for urban and industrialised areas [57,58].

In Fig. 4, the variation of Hg content in the atmosphere during a year at different sampling points, from the mine site of La Soterraña to the main urban settlement (Pola de Lena), is represented (measurements made at 20 cm above the ground). Hg content in the spoil heap range from 0.6 to $1.9 \mu\text{g Nm}^{-3}$ depending on the period of the year when the sampling was carried out. In the area of the old chimneys of the smelting plant Hg content ranges from 0.5 to $2.0 \mu\text{g Nm}^{-3}$. Measurements made in the city of Pola de Lena, located 3 km far of the mine and spoil heap range from 0.2 to $0.6 \mu\text{g Nm}^{-3}$, but the highest values seem to be also affected by emissions from close power stations. Typically, the atmospheric Hg concentration in the abandoned mining site is about ten times above the local background.

4.6. Associated health risks

The extent to which abandoned mining works become an environmental problem depends on the relationship between the hazards, which have been identified and their proximity to water resources, publicly accessible land, etc. Based on the geochemical data and the characteristics of the La Soterraña mining site, a risk assessment was conducted to characterize potential health and environmental risks that may exist as a result of previous mining works and disposal activities. The RBCA Tool Kit for Chemical Releases software was applied to the geochemical analyses of soils and waters at the mining site and also physico-chemical parameters of air, soil and water, in the various

transport pathways, and considering limited time of exposure. As result of this analysis, it was concluded that the presence of As and Hg in quite elevated concentrations in soils constitutes an acceptable risk according to the U.S. EPA classification [59] (Table 5). In particular, it was found that the target carcinogenic risk was exceeded for As and Hg at the mining site, in the soil exposure pathway, in terms of both dermal contact and ingestion, as well as in the groundwater exposure pathways (direct ingestion or soil leaching). There was also a non-cancer risk associated with the outdoor air exposure pathway (inhalation of vapour and/or particulates). However, there was no estimated carcinogenic risk for off-site receptors at a distance of 3 km from the mining site. Table 5 shows the applicable risk-based exposure limits (RBELs), based on target risk limits, compared to the values found for the site. Alternative options to define acceptable levels of risk include comparison of site-specific data with background levels, with applicable and appropriate requirements, with generic criteria developed for categories of contaminated sites, etc. [60]. It can be noted that there is not agricultural activity in the vicinity of the old mine.

The above results justify the need of taking remedial actions at La Soterraña site. According to the Spanish legislation [61], the declaration of a polluted soil obliges to undertake the necessary actions for its environmental recuperation in the terms and deadlines imposed by the corresponding authority. The contaminated soils will loose this condition when they are subjected to decontamination actions, which guaranty that they do not pose an inadmissible risk for the human health or the ecosystems, according to the different uses to which they are meant. The remediation of a contaminated soil should be carried out applying the best available technologies considering the particular characteristics in each case. The remediation actions should perform permanent solutions, preferably involving in situ treatment techniques, focussed on the elimination of the pollution sources rather than the reduction of exposure. Specific remedial technologies for application at sites contaminated with Hg and As such as this include containment, solidification/stabilisation, extraction and pyrometallurgical technologies. In many cases, some particular remediation technologies are enhanced through the use of treatment trains, which use various remedial options applied sequentially to the contaminated soil, affecting the effectiveness of the technologies and their costs. Nevertheless, the required resources, not always available, impose severe constraints when trying to find adequate solutions to polluted sites.

Table 5
Applicable risk limits for risk-based exposure limits (RBELs) (U.S. EPA, 1997) compared to the values found for soil and outdoor air exposure pathways in La Soterraña site

Health effect	Applicable risk limits for RBELs		La Soterraña site	
	Individual coc ^a (always meet)	Cumulative cocs(secondary check)	Outdoor air exposure	Soil exposure
Cancer incidence	TR ^b $\leq 1.0\text{E}-5$	TR ^b $\leq 1.0\text{E}-4$	TR = $5.6 \text{E}-7$	TR = $7.3\text{E}-3$
Non-carcinogenic Effect	HQ ^c ≤ 1.0	HI ^d ≤ 10	HQ = 17 HI = 17	HQ = 65 HI = 69

^a COC: constituent of concern.

^b TR: target risk.

^c HQ: hazard quotient.

^d HI: hazard index.

5. Conclusions

At the Hg mine sites studied in Asturias, the presence of Hg-bearing and As-bearing ore and mine wastes are the primary environmental concerns. Although La Soterraña mine was closed more than 30 years ago, the mining district continues to deliver considerable quantities of Hg and As to the environment with elevated concentrations throughout the soil-subsoil system.

The mobilisation of heavy metals and As through the soil-subsoil systems is determined by a complex interaction of adsorption and complexation mechanisms (clays, hydroxides and organic matter contribute to the adsorption capacity of soil particles). The influence of past Hg mining activity in this area can be currently perceived by high concentrations of Hg and associated elements in the surface soils of the area, which are clearly predominated by abnormal values related to wastes weathering, aerial transport of fine particles and emissions from smelting facilities. The highest Hg concentration found in soils was 502 mg kg^{-1} (near the old metallurgical plant) and the average concentration was 62.1 mg kg^{-1} ; considering that the background level of Hg in soils found in this area is 4.18 mg kg^{-1} , an important environmental alteration may be deduced. The average As concentration in soils was 1293 mg kg^{-1} , with a maximum 15 times higher, which is also 511 times above the background level. This shows the elevated dispersion of these elements (as well as other associated metals, such as Cu, Zn or Pb) in the area, which pose an important environmental impact in the soils of the area. Geochemical anomalies are predominantly associated with the sites of wastes disposal and smelting chimneys.

The geochemical results and their representation to delineate anomaly maps prove that Hg and As are not uniformly disseminated in the area, but they are correlated and consequently show similar distribution patterns. The elemental dispersion seems to be clearly associated with the morphology of the area, according to the gravity-induced downslope migration of metals, both from natural and anthropogenic sources.

The old mining/metallurgical wastes represent a significant long-term environmental threat. However, it must be borne in mind that the impact of Hg and As stored in the spoil heap represent only a part of the whole amount of Hg and As released to the environment from the mining/metallurgical operations.

The soils surrounding the Hg mining site, close to Muñón-Cimero village, have been receivers of a dispersion of Hg, As and other metals, both from natural and especially anthropogenic origin (release of vapour and particles from the smelter chimney, aerial particulate transport from the spoil heap and leaching of wastes). The mining activities, the roasting of ore and the use of ore residues as aggregate for roads, as well as the naturally increased Hg content in the ground have heavily contaminated the area of the mine and its surroundings. The effects of mining seemed to be intense but localised in the vicinity of the mine. This can be also applied to the concentrations found both in waters and stream sediments.

The application of simple portable equipment led to delimitate anomalous areas in order to assess the potential risk that high Hg concentrations represent. In the studied area, the local

Hg background atmospheric level is 10 times higher than the general background level in the area.

The prospecting and risk assessment of abandoned mine sites plays a main role for the development of the area and an appropriate land reuse. In the particular case of La Soterraña Mine, the target carcinogenic risk was exceeded for As and Hg (elements with high variability within the site), both in the soil and the groundwater exposure pathways. Superficial contamination of the soils occurs primarily in the vicinity of the wastes disposal and along the chimney at the slope of the mountain, which indicates that some of the vaporised Hg was condensed and deposited. Moreover, As pollution from the abandoned tailing piles reveals as the most important environmental problem in relation with this old mining and metallurgical activity, due to its toxicity and that of their compounds. In particular, the observed levels of Hg and As in soils, partly consequence of a natural weathering spreading of the crushed mine wastes into soil and dust, suggest that remedial actions should be taken to reduce the risk of their toxicity, and a long term monitoring program in the area would be recommendable.

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