PAPER

Risk assessment of soils contaminated by mercury mining, Northern Spain

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Analytical results of soil samples taken in three different mercury mining sites in Northern Spain are studied to assess the potential adverse health effects of the exposure to trace elements associated with the mining process. Doses contacted through ingestion and inhalation and the dose absorbed through the skin were calculated using USEPA's exposure parameters and the US Department of Energy's toxicity values. The results of the risk assessment indicate that the highest risk is associated with ingestion of soil particles and that the trace element of major concern is arsenic, the exposure to which results in a high cancer risk value for all the sites ranging from 3.3×10^{-5} to 3.6×10^{-3}, well above the 1×10^{-5} probability level deemed unacceptable by most regulatory agencies. Regarding non-cancer effects, exposure to polluted soils yields an aggregate hazard index above the threshold value of 1 for all three sites, with As and Hg as the main contributors. Risk assessment has proven to be a very useful tool to identify the contaminants and exposure pathways of most concern in the soils from metal mining sites, as well as to categorize them in terms of action priority to ensure fitness for use.

Introduction

Due to the particular potential health risks that some metallic elements can pose to humans and ecosystems, considerable interest and concern have focused on the impact associated with mining and smelting activities upon soils. Pollution associated with base metal mining and smelting is widely reported in the literature.[1–6] The long-term off-site release of contaminants is particularly possible from mining and related processing or metallurgical wastes. Major factors influencing contaminant release from a specific mine site or waste repository include: the geology of the mined resource, climate and topography, and the specific mining and mineral processing activities.[7–9]

Mercury is of particular concern amongst global environmental pollutants, with contaminated sites abundant worldwide, many of which are associated with mining activities. Scientists and legislators have become more aware of Hg pollution in particular at the end of the 20th century[10–15] due to the significant risk it can pose to human and ecosystem health.[16] More than 4700 Mt of mining waste and 1200 Mt of tailings are stored all over the European Union[17] and the input of metals and metalloids to atmospheric, terrestrial and aquatic ecosystems as a result of mining have been estimated to be at several million kilograms per year.[9,18,19] The Hg as cinnabar remaining to be mined in Spain and Italy combined is 159 kt with an annual production for the year 2000 stated[20] as 237 t.

Based on the meetings of the Ad-hoc Open-Ended Working Group of the Mercury programme, UNEP agreed to prepare legislation specific to Hg since it is an element:"…that seriously affects human health and is becoming more serious, and will affect more and more people".[21]

The negotiations are due to conclude in 2013. However, mining has been important in the past in many countries in Europe, not least Spain wherein both the north and south large mines have

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Environmental impact

This article evaluates environmental exposure to contamination due to the historical legacy of mercury mining and includes an assessment of associated health risks. The risk assessment is used as a tool to identify contaminants and exposure pathways of most concern, as well as to categorize them in terms of remedial action priority. The methodology employed in three mining sites in Northern Spain—which integrates the characterization of mining processes, mineralogy of ore and waste, and site geology, climate and social habits to evaluate contaminant distribution and human exposure—is shown in detail, to enable its application to other sites with metal-polluted soils in the world, not only those derived from metal mining.

operated since antiquity, with evidence in some cases of activity on individual sites since the 1st and 2nd centuries AD.[22] As a result, mines have been abandoned long before the introduction of any environmental regulations to control metal release from associated spoil heaps and tailings ponds. In addition, with the recent closure of many of the world's largest Hg mining concerns, *e.g.* Almadén in Spain and Idrija in Slovenia,[23] the question of classification of risk and prioritisation of sites for a fitness for use assessment arises. Over the last few years, it has been found that Risk Assessment strategies extensively employed by regulatory authorities to define soil screening levels or soil guideline values can be successfully adopted in different environments such as soils polluted due to metal mining activities.[24–29]

The aim of this article is therefore to calculate the risk to human health from exposure to soils polluted with Hg and associated trace elements in the vicinity of three abandoned Hg mines in NW Spain (Lena, Asturias). The results of the risk assessment can then be used to determine the most relevant exposure pathways and the elements of most concern, and to categorise the three mining sites in terms of priority for required actions for human health protection.

Study location

Mining has been an important activity in Northern Spain, but owing to the lack of environmental regulation until recent times, old metal mine operations have led to many abandoned mine sites and, consequently, high metal concentrations in soils. Asturias, in particular, has abundant Hg deposits leading to it being an important Hg producer at the world scale. At its height, average annual Hg production was 15 000 flasks (1 flask = 34.47 kg).[16] Three abandoned Hg mine sites in Asturias (North Spain) are considered here: La Soterraña, Maramuñiz and Brañalamosa (Fig. 1).

La Soterraña mine is the second most important Hg mining site in Asturias, where vestiges of very old mine works attributed to the Romans during their occupation of the Iberian Peninsula in the 1st and 2nd centuries have been found.[22] Subsequently, the mine was intermittently exploited by underground works, using
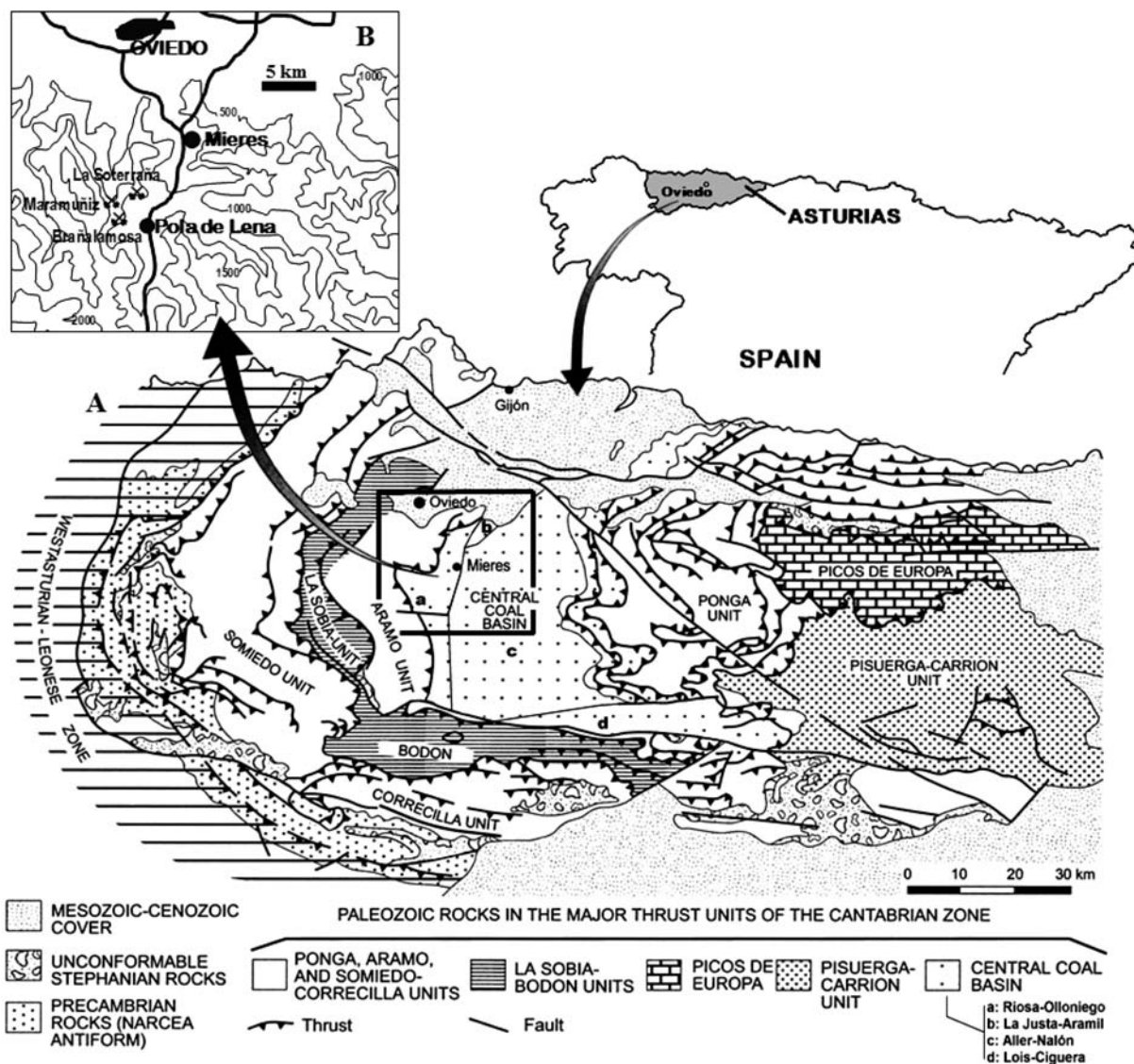
Fig. 1 Geological map of the Cantabrian Zone (A, modified from ref. 39), with the location of the studied area (B).

rooms and pillars, from the middle of the 19th century until 1972. There has not been any mining/metallurgical activity at this site since then, as a consequence of the drop in price due to the international Hg crisis caused mainly over health concerns and heightened public awareness of environmental issues.[30] The extracted ore was crushed and roasted here by means of retorts or tub furnaces, depending on the grade of mineral, in order to oxidise cinnabar to Hg vapour, which was then condensed and collected in flasks. The total volume of ore recovered at La Soterraña was considerable, as it produced a large part of the total Hg extracted in Asturias. Ore from other less important mines in Asturias, such as Brañalamosa and Maramuñiz (described below), was concentrated from the raw state on-site, followed by transportation *via* lorries for treatment and purification at La Soterraña mine site. Taking into account the losses during mining and inefficient smelting, the release of Hg and associated elements (such as As) into the environment has been significant.[31–34] The legacy of historical mining activities in the form of old industrial installations such as shafts, mine buildings, roasting furnaces and chimneys remains, as well as significant quantities of mining and metallurgical wastes whose stockpile covering 17000 m² have never received any type of treatment. Fig. 1 shows the mines' location, 4 km from Pola de Lena, a town of 9000 inhabitants located in a steep hillside.

The Brañalamosa mine exploited a mineral deposit from the 18th century until the closure of all mining activities in 1974, but the main works still remain, due to extraction activities carried out in the last decade of its life, using the room and pillar method.[35] Annual production of 100 flasks was reached in the 19th century.[22] From a mine shaft, 101.5 m deep, the galleries are distributed over four levels, but these mining works are now collapsed and inaccessible. The ore at Brañalamosa was crushed on-site and, as mentioned above, transported 7 km to the smelting plant at La Soterraña, where it was dried and roasted. There are remains of a metallurgical Bustamante-type furnace on the site, which was used at the end of the 19th century to roast the ore. In the old furnaces, Hg loss was about 20–40%,[10] but towards the end of its productive life, this had been reduced to 2–3%. Spoil heaps of waste from the mine (rock and low-grade ore), extending to an area of over 400 m², have not received any treatment to minimize their environmental impact. Most of them are now practically unrecognizable, since they are covered by dense stands of shrubs, or they are used as pasture for cattle grazing, and tend to blend in with the surrounding landscape. Mining wastes have also been used for the construction of rural paths in the area, causing widespread dispersion of potentially polluting material.[16] The site is located upslope of a stream valley, near the small village of Brañalamosa, 3 km NW from Pola de Lena (Fig. 1), an area generally sparsely populated.

Mining activity in the last site to be investigated, Maramuñiz, started at the end of the Spanish Civil War (1939), and continued intermittently until 1975, when it stopped due to the same reasons production halted at La Soterraña. The most productive decade at this site was during the 1960s, when the mine employed 20 people and a daily production of 675 kg of mercury was reached. Extracted mineral was driven by ox cart to the furnace, which employed a further 10 people where a simple smelting furnace reduced the cinnabar. Mercury was then transported to La Soterraña for a further purification process.[35,36] The mine has two shafts,

transversals and galleries up to four levels, ranging from +610 to +810 m a.s.l., there are two almost unrecognizable spoil heaps, which are covered in vegetation. This site is located 0.8 km from the small village of La Maramuñiz, 4 km NW from Pola de Lena (Fig. 1).

In terms of climate, unlike other regions of Spain, Asturias is humid with abundant precipitation during most of the year and mild temperatures. Annual average rainfall in the central area of the region, where the mines are located, is 1000 mm, average relative humidity is 80%, and the average monthly temperature ranges from 7 to 21 °C, with an annual average value of 12.5 °C. Thornthwaite evapotranspiration was estimated at 600 mm year⁻¹, so the average annual effective rainfall is around 400 mm. Thus, using an infiltration coefficient of 0.7 for an uncovered spoil heap, water infiltrating a total area of, for instance, 1000 m² and responsible for leaching and erosion is about 280 m³ year⁻¹.

The sites were chosen since their geographical, geological and climatological settings are similar. They are linked by the purification processes carried out at La Soterraña on the ore won at all 3 mines and their histories and impacts are also similar. The following section details these characteristics.

Geological setting and mineralization model

The three mines investigated in this study are located in an area of 3.25 km², within the so-called Cantabrian Zone,[37,38] which makes up the core of the Ibero-Armorican Arc and is the external expression of the Variscan Orogen in the NW Iberian Peninsula. On the basis of combined stratigraphic and structural features, Julivert[39] divided the Cantabrian Zone into several geologic units (Fig. 1): Somiedo-Correcilla, La Sobia-Bodón, Aramo, Central Coal Basin, Ponga, Picos de Europa and Pisuerga-Carrión.[40,41] Maramuñiz, Brañalamosa and La Soterraña mines are located in the Central Coal Basin, which has been further sub-divided according to mining and stratigraphic criterion, into four sub-units: Riosa-Olloniego, La Justa-Aramil, Aller-Nalón and Lois-Ciguera (Fig. 1). The specific area of study is therefore characterized by a thick (~2700 m) sedimentary sequence from Westphalian A to Westphalian D age in the Riosa-Olloniego sub-unit. Intensive coal mining activity in the area has differentiated a lower unit with limestone and scarce coal beds (Riosa non-productive Formations), distinguishable from the upper parts, which are made up of alluvial and deltaic sediments with abundant coal beds.

The origins of the three Hg mineralizations are considered to be later hydrothermal stages of magmatic filiation and are defined by the junction of structural (later Variscan normal faults) and lithological (organic-rich limestone horizons in the "Riosa non-productive Formations") factors. The ore has cinnabar [HgS] as its main mineral phase which is disseminated through the host rock or located in calcite veins, realgar [AsS] and, to a lesser extent, orpiment [As_2S_3]. Greater Hg concentrations are found in the highly fractured limestones as well as impregnating coal–organic limestone contacts. Sulfide phases mentioned above are often accompanied by pyrite [FeS_2], marcasite [FeS_2] and pararealgar [AsS]. However, in Maramuñiz mineralization, the host rock is locally impregnated with native mercury, filling inter-crystalline pores.[30] At Brañalamosa, chalcopyrite [$CuFeS_2$] and galena [PbS] have been observed[16,35] as well as the other sulfides already mentioned. Calcite (and/or) dolomite is the predominant gangue material, followed by quartz

Table 1 (A) Equations used to calculate dose received by receptor through four pathways. (B) Key to parameters in eqn (1)–(4)

(A) Equation   **Pathway**

(1)
$$D_{ingestion} = C \times \frac{IngR \times EF \times ED}{BW \times AT} \times 10^{-6}$$

(2)
$$D_{inhalation} = C \times \frac{InhR \times EF \times ED}{PEF \times BW \times AT}$$

(3)
$$D_{dermal} = C \times \frac{SA \times SL \times ABS \times EF \times ED}{BW \times AT} \times 10^{-6}$$

(4)
$$D_{vapour} = C \times \frac{InhR \times EF \times ED}{VF \times BW \times AT}$$

(B) where:

	Units	Parameter	Value
D	mg kg^{-1} day^{-1}	Dose	Dose contacted through ingestion ($D_{ingestion}$) and inhalation ($D_{inhalation}$) of substrate particles, through inhalation of vapours (D_{vapour}), and absorbed through dermal contact with substrate particles (D_{dermal})
C	mg kg^{-1}	Concentration	Concentration of trace element in soil (exposure point concentration)
IngR	mg day^{-1}	Ingestion rate	Adult (residential): 100 Child (residential): 200[43] Adult (shepherd/farmer): 330[45]
InhR	m^3 day^{-1}	Inhalation rate	Adult: 20[43] Child: 7.6[51]
EF	days year^{-1}	Exposure frequency	La Soterraña: 350 Brañalamosa and Maramuñiz: 23
ED	years	Exposure duration	Non-carcinogens: 6 (child) in La Soterraña, 30 (adult) in Brañalamosa and Maramuñiz Carcinogens: 6 as a child +24 as an adult in La Soterraña, 24 as an adult in Brañalamosa and Maramuñiz[43]
SA	cm^2	Exposed skin area	Adult (residential): 5700 Child (residential): 2800 Adult (shepherd/farmer): 3300[45]
SL	mg cm^{-2} day^{-1}	Skin adherence factor	Adult (residential): 0.07 Child (residential): 0.2 Adult (shepherd/farmer): 0.3[45]
ABS	Unitless	Dermal absorption factor	0.001 all elements except arsenic Arsenic: 0.03[48]
PEF	m^3 kg^{-1}	Particle emission factor	1.36 × 10^9[45]
VF	m^3 kg^{-1}	Volatilization factor	Elemental Hg: 32 376.4[45]
BW	kg	Average body weight	Adult: 70 Child: 15[43]
AT	days year^{-1}	Averaging time	Non-carcinogens: ED × 365 Carcinogens: 70 × 365 = 25550

and kaolinite and, eventually, fluorite and talc. As a result of these epigenetic mineralizations, some hydrothermal alterations, mainly argillitization, silicification and dolomitization, can be observed in the host rocks. 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.[34]

Materials and methods

Since all the research sites had been abandoned for more than 30 years, a survey of historic information was firstly undertaken. Field work was then performed in order to characterize the local geology of the site and to collect representative samples of soils in the potentially affected area.

Sampling, sample preparation and analysis

In all cases, soil samples were taken systematically downstream of the potential pollution sources (mainly spoil heaps and metallurgical installations), but the number of samples varied for each site: 56, 28 and 23 at La Soterraña, Brañalamosa and Maramuñiz mine sites, respectively. In all cases, a regular 50 m × 50 m sampling grid was used, and each square unit was represented by a two-kilogram composite sample made of four subsamples, which were collected from the upper 25 cm of the soil profile, with a manual auger, and transferred to a polyethylene bag for transport to the laboratory. The samples were oven dried at 40 °C to minimise the loss of volatile elements for 72 hours and then disaggregated in an agate mortar and sieved to below 63 μm to retrieve the size fraction which is more easily resuspended and able to adhere to the skin. Meticulous sample reduction resulted in a representative single sample of approximately 0.5 g for analysis. All samples were subjected to multielemental analysis by ICP-MS at ACME Analytical Laboratories, in Vancouver (Canada). In the case of the solid samples, partial digestion was achieved using 3 ml 3 : 2 : 1 $HCl : HNO_3 : H_2O$ at 95 °C for one hour and dilution to 10 ml with water. Since not all minerals are decomposed during the digestion, for the purposes of the study the results obtained under this extraction are considered as total concentrations, as sulfides, which are usually the major sources of trace elements in these soils, are totally decomposed. Quality controls involved routine analyses of standards and duplicates. Observations below the detection limit were assigned a value of half the detection limit.

Risk assessment model: description and assumptions

On-site exposure of receptors to trace elements from polluted soils can occur via four main pathways: (a) direct ingestion of soil particles, (b) inhalation of resuspended particles through the mouth and nose, (c) dermal absorption of trace elements in particles adhered to exposed skin, and, in the case of Hg, (d) inhalation of vapours. The dose received through each pathway considered has been calculated using eqn (1)–(4) (Table 1), adapted from the US Environmental Protection Agency.[42–44] Unless stated otherwise, the values assigned to the exposure factors used in these equations follow the USEPA guidelines for the derivation of soil screening levels.[45] For La Soterraña, a residential exposure scenario has been considered in which the most sensitive individual for non-cancer risk is a child and for

Table 2 Summary statistics of the analytical results for each site and exposure point concentration term, C (95% UCL), used for the risk assessment (all concentrations in mg kg^{-1}, except Al, in %)

		Al	As	Ba	Cd	Cr	Cu	Hg	Mn	Mo	Ni	Pb	Sb	Sr	V	Zn
La Soterraña mine	Min.	0.45	32	16	0.1	11	16	1.73	48	0.5	10	19	1	9	19	35
	Max.	3.64	9940	356	1.7	47	225	502	1482	2	61	142	82	736	73	215
	Mean	1.26	831	94.2	0.33	23.1	60.8	48.7	615	0.88	33	43.9	3.91	60	34.1	112
	Std. dev.	0.49	1930	50.4	0.28	7.23	45.7	107	322	0.32	11.2	21.8	11.4	105	12.1	39.4
	95% UCL	1.37	1249	105	0.4	24.7	70.8	72.7	687	0.96	35.5	48.8	6.38	82.8	36.8	121
Brañalamosa mine	Min.	0.49	19	19	0.1	8	8	0.5	132	0.5	12	19	1.5	9	19	54
	Max.	1.35	704	163	0.9	19	89	895	946	3	42	38	4	350	40	119
	Mean	0.83	110	77.5	0.38	12.8	21.9	79.6	590	0.89	24.5	27.2	1.64	54.6	25.4	87.1
	Std. dev.	0.25	167	33.9	0.19	2.86	15.5	213	196	0.72	6.79	5.81	0.54	84	4.68	14.7
	95% UCL	0.91	161	89.6	0.45	13.7	26.9	144	653	1.11	26.7	29.1	1.82	79.1	26.9	91.8
Maramuñiz mine	Min.	0.30	28.0	28.0	0.10	5.00	6.00	2.00	90.0	<1	5.00	17.0	<3	8.00	190	39.0
	Max.	1.18	1504	284	0.90	24.0	42.0	577	2153	3.00	56.0	57.0	<3	216	49.0	203
	Mean	0.81	365	73.3	0.43	13.2	18.8	83.0	849	0.92	25.8	29.9	<3	45.3	28.8	82.6
	Std. dev.	0.24	414	58.1	0.27	3.76	9.41	144	575	0.50	14.0	9.89	<3	50.4	6.23	34.1
	95% UCL	0.90	571	95.1	0.57	14.7	22.6	153	1080	ND	31.5	33.9	ND	66.4	31.4	92.3
Background		1.57	23–39	71.2	0.3–0.94	19	12.1–42	2.2–4.18	677	3	26–31	23–45	3	ND	ND	66–86.2

carcinogenic risk is an individual who spends 6 years there as a child and 24 years as an adult. The other two sites are sparsely populated and the individual considered for the risk assessment in both cases is an adult person who spends 2 hours per day, 7 days per week, and 36 weeks per year shepherding, and 8 hours per day, 1 week per year summer farming in the fields around the sites (for a total exposure frequency of 23 days year^{-1}). The exposure parameters for this individual are those suggested for a construction worker in the Supplemental Guidance for Developing Soil Screening Levels[45] to account for an increased contact with soil relative to a residential or commercial scenario.

The concentration term, C in eqn (1)–(4), in combination with the exposure parameters in Table 1, is considered to yield an estimate of the "reasonable maximum exposure", or maximum exposure that is reasonably expected to occur at a site[46] and is the upper limit of the 95% confidence interval for the mean (95% UCL). The estimate of the probability distribution function that best fits the concentration data and the calculation of the corresponding 95% UCL have been carried out with the ProUCL 4.0 software.[47] The results for each element are presented in Table 2.

The doses calculated using eqn (1)–(4) for each element and exposure pathway were subsequently divided by the corresponding reference dose to yield a hazard quotient, HQ (or non-cancer risk), whereas for carcinogens the dose was multiplied by the corresponding slope factor to produce a level of cancer risk. The toxicity values used in the analysis were taken from the US Department of Energy's RAIS (Risk Assessment Information System) compilation.[48] The only exception was Pb, whose reference doses have been derived from the World Health Organization's Guidelines for Drinking Water Quality.[49] Toxicity values for dermal absorption have been used as indicated in the Risk Assessment Guidance for Superfund:[46] oral reference doses are multiplied and slope factors divided by a gastrointestinal absorption factor to yield the corresponding dermal values.[44]

For the inhalation route, particles with diameters below 63 μm were selected because they are easily resuspended and can be inhaled through the nose or mouth. For those elements without inhalation reference concentrations or unit risks, the toxicity values considered for the inhalation route are the corresponding oral reference doses and slope factors, on the conservative assumption that, after inhalation, the absorption of the particle-bound toxicants will result in similar health effects as if the particles had been ingested,[50,51] especially for this extended particle size range.[44]

Results and discussion

Descriptive statistics of the analytical results for the soil sampling campaigns at all 3 sites are given in Table 2 where the elements shown are those used later in the risk assessment. Geochemical background levels obtained from previous studies are also shown in Table 2 for comparison purposes.[16,34,36]

Although the mine at La Soterraña was closed more than thirty years ago, the surrounding area still appears to be the source of considerable quantities of Hg and As (as well as other associated metals, such as Cu, Zn or Pb) to the environment with elevated concentrations throughout the soil system. The dissemination pathways of these contaminants include: weathering of wastes, aerial transport of fine particles and emissions from smelting

Table 3 Reference dose (RfD, mg kg^{-1} day^{-1}) and slope factor (Sf (mg kg^{-1} day^{-1})$^{-1}$) (from RAIS[48] as of Feb. 2010, except Pb, from WHO), and hazard quotient (HQ, unitless) and cancer risk (risk, unitless) for each element and exposure route in each site. HI = ΣHQ, RISK = ΣRisk. In bold: values of HI > 1 and risk > 1 × 10^{-5}

		Al	As	Ba	Cd	Cr	Cu	Hg	Mn	Mo	Ni	Pb	Sb	Sr	V	Zn		As	Cd	Ni
				Non-carcinogenic														**Carcinogenic**		
	RfD$_{Ing}$	1.0 × 10^0	3.0 × 10^{-4}	2.0 × 10^{-1}	1.0 × 10^{-3}	1.5 × 10^0	4.0 × 10^{-2}	1.6 × 10^{-4}	4.6 × 10^{-2}	5.0 × 10^{-3}	2.0 × 10^{-2}	3.5 × 10^{-3}	4.0 × 10^{-4}	6.0 × 10^{-1}	9.0 × 10^{-3}	3.0 × 10^{-1}	Sf$_{Ing}$	1.5 × 10^0	6.3 × 10^0	8.4 × 10^{-1}
	RfD$_{Inh}$	1.4 × 10^{-3}	4.3 × 10^{-3}	1.4 × 10^{-4}	1.0 × 10^{-3}	2.9 × 10^{-6}	1.2 × 10^{-2}	8.6 × 10^{-5}	1.4 × 10^{-5}	2.9 × 10^{-5}	2.9 × 10^{-5}	5.3 × 10^{-3}	8.0 × 10^{-5}	1.2 × 10^{-1}	2.0 × 10^{-5}	6.0 × 10^{-2}	Sf$_{Inh}$	1.5 × 10^1	6.3 × 10^1	
	RfD$_{der}$	1.0 × 10^{-1}	1.2 × 10^{-1}	1.4 × 10^{-6}	1.0 × 10^{-2}	7.5 × 10^{-4}	2.3 × 10^{-2}	1.1 × 10^{-5}	1.9 × 10^{-3}	1.9 × 10^{-1}	5.4 × 10^{-3}	1.8 × 10^{-4}	2.0 × 10^{-5}	1.8 × 10^{-1}	9.0 × 10^{-5}	5.2 × 10^{-3}	Sf$_{der}$	3.7 × 10^0	3.7 × 10^0	
La Soterraña mine	HQ$_{Ing}$	1.8 × 10^{-1}	5.3 × 10^1	6.7 × 10^{-3}	5.1 × 10^{-3}	2.1 × 10^{-4}	6.3 × 10^{-1}	5.8 × 10^0	1.7 × 10^{-1}	2.4 × 10^{-3}	2.3 × 10^{-3}	1.8 × 10^{-1}	5.7 × 10^{-6}	4.9 × 10^{-8}	5.2 × 10^{-2}	5.2 × 10^{-3}	Risk$_{Ing}$	2.9 × 10^{-3}	5.2 × 10^{-6}	6.3 × 10^{-9}
	HQ$_{Inh}$	3.4 × 10^{-3}	1.0 × 10^{-1}	2.6 × 10^{-4}	5.0 × 10^{-5}	5.9 × 10^{-5}	2.1 × 10^{-4}	3.0 × 10^{-4}	1.3 × 10^{-2}	6.8 × 10^{-8}	4.4 × 10^{-4}	5.0 × 10^{-4}	2.9 × 10^{-4}	2.5 × 10^{-5}	6.6 × 10^{-3}	1.4 × 10^{-4}	Risk$_{Inh}$	1.9 × 10^{-6}	5.2 × 10^{-10}	6.3 × 10^{-10}
	HQ$_{der}$	4.9 × 10^{-3}	1.1 × 10^1	2.7 × 10^{-4}	1.4 × 10^{-3}	1.2 × 10^{-4}	2.1 × 10^{-4}	2.3 × 10^{-4}	1.3 × 10^{-3}	1.8 × 10^{-2}	2.4 × 10^{-4}	3.3 × 10^{-4}	2.9 × 10^{-3}	2.5 × 10^{-5}	1.5 × 10^{-2}	7.2 × 10^{-5}	Risk$_{der}$	6.8 × 10^{-4}	7.5 × 10^{-5}	
	HQ$_{vap}$							1.3 × 10^0												
	HI	1.8 × 10^{-1}	6.4 × 10^1	7.3 × 10^{-3}	6.5 × 10^{-3}	3.3 × 10^{-4}	2.3 × 10^{-4}	1.9 × 10^0	2.2 × 10^{-1}	2.5 × 10^{-2}	2.3 × 10^{-3}	1.8 × 10^{-2}	2.3 × 10^{-1}	1.8 × 10^{-3}	7.4 × 10^{-2}	5.2 × 10^{-3}	RISK	3.6 × 10^{-3}	5.2 × 10^{-6}	6.3 × 10^{-9}
Brañalamosa mine	HQ$_{Ing}$	2.7 × 10^{-3}	1.6 × 10^{-1}	1.3 × 10^{-4}	1.3 × 10^{-4}	2.7 × 10^{-4}	2.0 × 10^{-4}	1.4 × 10^{-1}	4.2 × 10^{-1}	6.6 × 10^{-5}	4.0 × 10^{-3}	2.5 × 10^{-3}	1.3 × 10^{-3}	3.9 × 10^{-5}	8.9 × 10^{-4}	9.1 × 10^{-3}	Risk$_{Ing}$	2.5 × 10^{-5}	5.9 × 10^{-8}	4.7 × 10^{-10}
	HQ$_{Inh}$	8.5 × 10^{-5}	5.0 × 10^{-3}	8.3 × 10^{-6}	2.1 × 10^{-6}	1.2 × 10^{-6}	8.9 × 10^{-6}	2.2 × 10^{-6}	6.1 × 10^{-4}	6.1 × 10^{-7}	4.4 × 10^{-6}	1.1 × 10^{-5}	6.0 × 10^{-5}	1.7 × 10^{-7}	1.8 × 10^{-4}	4.1 × 10^{-4}	Risk$_{Inh}$	1.6 × 10^{-8}		4.7 × 10^{-9}
	HQ$_{der}$	8.1 × 10^{-5}	3.5 × 10^{-2}	5.7 × 10^{-6}	4.0 × 10^{-5}	1.6 × 10^{-5}	2.0 × 10^{-6}	6.1 × 10^{-6}	3.2 × 10^{-4}	5.2 × 10^{-4}	4.4 × 10^{-6}	4.9 × 10^{-6}	2.0 × 10^{-4}	5.9 × 10^{-7}	2.7 × 10^{-4}	1.4 × 10^{-6}	Risk$_{der}$	8.9 × 10^{-6}		
	HQ$_{vap}$							9.3 × 10^{-1}												
	HI	2.9 × 10^{-3}	1.9 × 10^{-1}	1.5 × 10^{-1}	1.7 × 10^{-4}	4.3 × 10^{-4}	2.0 × 10^{-4}	1.1 × 10^0	5.1 × 10^{-3}	6.7 × 10^{-5}	4.1 × 10^{-4}	2.5 × 10^{-4}	1.6 × 10^{-3}	4.0 × 10^{-5}	1.3 × 10^{-3}	9.2 × 10^{-5}	RISK	3.3 × 10^{-5}	5.9 × 10^{-10}	4.7 × 10^{-9}
Maramuñiz mine	HQ$_{Ing}$	2.7 × 10^{-3}	5.7 × 10^{-1}	1.4 × 10^{-1}	1.7 × 10^{-4}	2.9 × 10^{-4}	1.7 × 10^{-4}	1.5 × 10^{-1}	7.0 × 10^{-3}	—	4.3 × 10^{-4}	2.7 × 10^{-4}	—	3.0 × 10^{-5}	1.0 × 10^{-3}	7.9 × 10^{-5}	Risk$_{Ing}$	1.5 × 10^{-4}	7.5 × 10^{-8}	5.1 × 10^{-9}
	HQ$_{Inh}$	8.4 × 10^{-5}	1.8 × 10^{-2}	8.8 × 10^{-6}	2.6 × 10^{-6}	1.3 × 10^{-6}	7.5 × 10^{-6}	2.4 × 10^{-6}	1.0 × 10^{-3}	—	1.3 × 10^{-5}	1.2 × 10^{-5}	—	1.3 × 10^{-9}	2.1 × 10^{-4}	3.5 × 10^{-5}	Risk$_{Inh}$	5.6 × 10^{-8}		5.1 × 10^{-9}
	HQ$_{der}$	8.0 × 10^{-5}	1.2 × 10^{-1}	6.1 × 10^{-6}	5.1 × 10^{-6}	1.7 × 10^{-6}	1.7 × 10^{-6}	6.5 × 10^{-6}	5.2 × 10^{-4}	—	4.7 × 10^{-6}	5.4 × 10^{-6}	—	4.5 × 10^{-7}	3.1 × 10^{-4}	1.2 × 10^{-6}	Risk$_{der}$	3.2 × 10^{-5}		
	HQ$_{vap}$							9.9 × 10^{-1}												
	HI	2.8 × 10^{-3}	6.9 × 10^{-1}	1.6 × 10^{-1}	2.2 × 10^{-4}	4.6 × 10^{-4}	1.7 × 10^{-4}	1.1 × 10^0	8.5 × 10^{-3}	—	4.5 × 10^{-4}	2.7 × 10^{-4}	—	3.0 × 10^{-5}	1.6 × 10^{-3}	8.0 × 10^{-5}	RISK	1.8 × 10^{-4}	7.5 × 10^{-8}	5.1 × 10^{-9}

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facilities. In spite of the natural dispersal of this contaminated material, the maximum As concentration at this site is between 430 and 250 times higher than the background level, and that of Hg is between 228 and 120 times. The dispersion of these polluted particulates is probably associated with the morphology of the area wherein gravity promotes their downslope movement, both from natural and anthropogenic sources.[34]

The Brañalamosa Hg mine may not be as large as other old Hg mining sites in the region, but it provides an example of environmental damage caused by mining in a picturesque valley where the land is used for cattle grazing and where the rural paths, many of which have been constructed using ore residues as aggregate, are frequently used by walkers. Mining activities and

the roasting of ore, as well as the naturally increased Hg content in the ground have heavily contaminated the site and its surroundings. High Hg and As concentrations have been found in soils (400 and 30 times higher than the local background, respectively[16]) and other heavy metals occur in significant concentrations. Since the area is used for grazing, the transfer of these elements to cattle[52] could be a potential problem.

Soils sampled from Maramuñiz exhibit high Hg and As concentrations (between 260 and 138, and 65 to 38 times the local background for Hg and As, respectively), as well as significant Ni, Cu and Zn values. These elements in particular are found around the spoil heaps, their relative mobility dictating the distance they are found from their primary source. In common
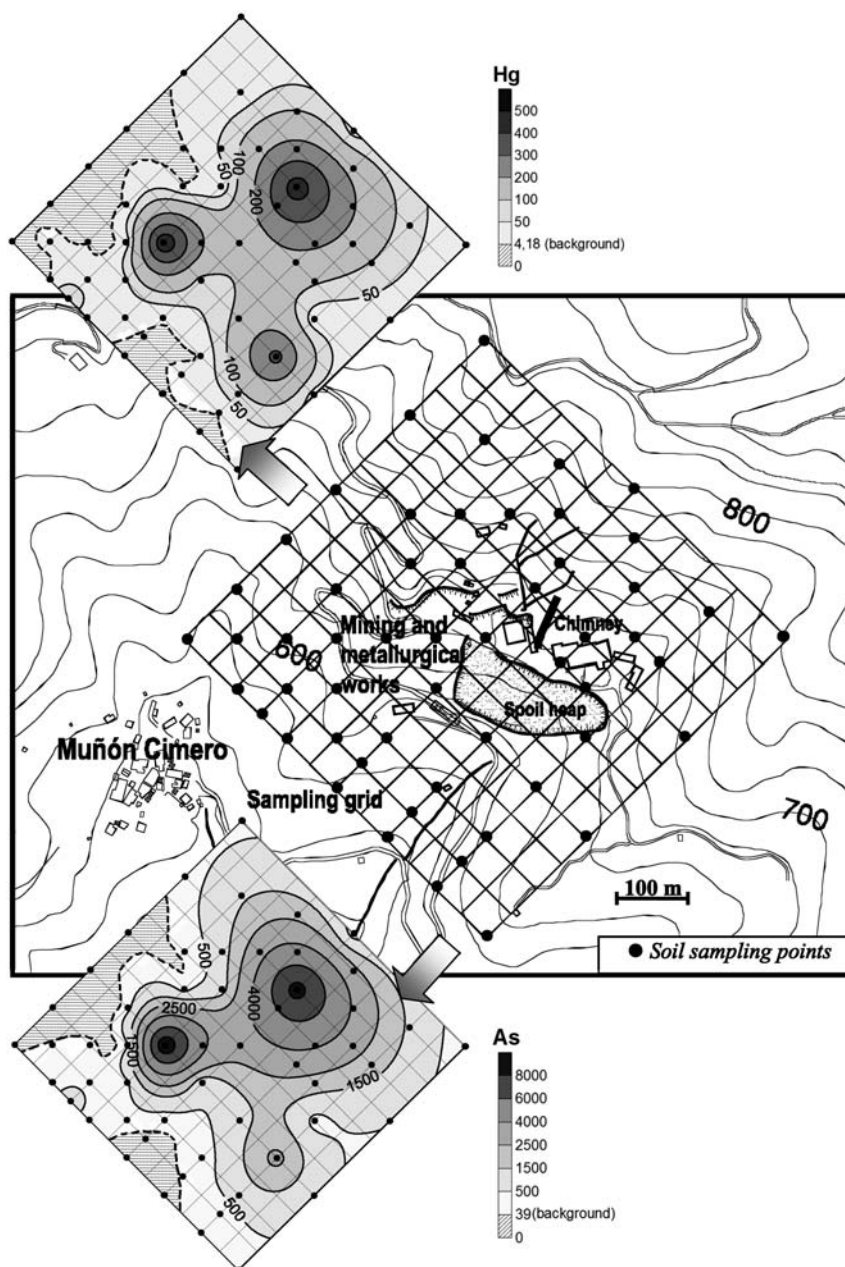

Fig. 2 Location of soil sampling points and Hg and As (mg kg^{-1}) spatial distribution at La Soterraña site.

with the other 2 sites, metal enrichment in the soils at Maramuñiz has been caused by the physical erosion of metal-bearing minerals from abandoned low-grade ore in spoil heaps followed by adsorption and coprecipitation of dissolved metals and metalloids in reactive minerals, in particular the clay components of the local soil.

The results of the risk assessment are presented in Table 3. Hg, and particularly As, appear to be the largest contributors to the overall risk. Intake of As (which may cause increased lung cancer mortality through inhalation, and skin and several internal organ cancers through ingestion[44]) results in a value of carcinogenic risk for all the sites above the critical 1×10^{-5} level deemed unacceptable by most regulatory agencies, by as much as two orders of magnitude at La Soterraña. For non-cancer risk, As and Hg exhibit a Hazard Index (HI) of more than one order of magnitude above the benchmark value of 1 for La Soterraña, and slightly higher than 1 at Brañalamosa and Maramuñiz in spite of the low exposure frequency considered for these latter two sites. La Soterraña exhibits the highest HI for As at 64, and also the highest As carcinogenic risk at 0.0036. This is because its soil has the highest As concentration of all, and the residential exposure scenario includes children's exposure factors and an exposure frequency that is 15 times higher than that of the other two sites. Brañalamosa and Maramuñiz present similar concentrations of Hg in soil and therefore, almost identical values of non-cancer risk from exposure to this element. Mn, Sb, Pb and Al also have a significant contribution to the overall hazard index, with values ranging from 0.18 to 0.23. All the elements of concern are associated with mining activities and have been subsequently released to the soils.

The exposure pathway that has the highest contribution to the overall figure of risk appears to be ingestion of soil particles followed by dermal absorption of trace elements associated with these particles. In the case of Hg, the only element for which inhalation of soil vapours is significant, this pathway accounts for the main exposure in all three mines. However, there is a high uncertainty associated with this exposure pathway, arising both from the simplistic model used to infer the concentration in air from the concentration in soil, and from the fact that the volatility of the Hg species actually present in the soil is probably not well represented by elemental mercury's Henry's law constant. Inhalation of suspended particles is almost negligible when compared to the other routes of exposure.

Fig. 2 shows the location of the sampling grid at La Soterraña site, as well as the spatial distribution of Hg and As concentrations. As shown in Table 2, there is a great variation in concentrations of Hg and As in the soils sampled at this site, ranging from 1.7 to 502 mg kg^{-1} Hg and from 32 to 9940 mg kg^{-1} As. Accepting there may be some errors derived from interpolating individual data by means of isolines, nonetheless the contour maps for Hg and As concentrations are quite similar, with the highest values corresponding to the location of waste piles and smelter chimneys, as well as the valley base, whereas lower values occur at higher elevations and further away. The movement of Hg from the old mining works occurs downslope, due to transport of metals from waste piles by gravity.[34] If land use and the associated estimates of exposure variables for this site do not change, the estimated risk is undoubtedly linked to the spatial distribution of trace elements concentrations. For this case in particular, concentrations of As above 4 mg kg^{-1} would

lead to an unacceptable level of cancer risk, whereas the threshold for non-cancer risk is reached at 20 and 4 mg kg^{-1} for As and Hg, respectively. These values, however, arise from a very conservative risk model, both in terms of exposure variables and toxicity data. In fact, the maximum target concentration for Hg of 4 mg kg^{-1} is essentially equal to its natural background, and as Table 2 shows, the target concentration for As, *i.e.* 4 mg kg^{-1}, is well below its background distribution of 39 mg kg^{-1}. Even with these considerations in mind, Fig. 2 shows that the rural residential district nearest La Soterraña lies in an area with higher-than-background values with risk-triggering concentrations of As and Hg in soil. Further refinement of the results, which would involve *in situ* determination of exposure variables, particularly for the shepherding and farming scenarios, was not undertaken in this study.

Despite the conservative assumption of 100% absorption efficiency (*i.e.* bioavailability) for all elements in the model, the uncertainty arising from estimates of exposure rates and the frequently updated toxicity data used in the assessment, the surprisingly high values of HI and carcinogenic risk in the risk analysis strongly indicate that exposure to the soil at all of the sites might result in adverse health effects. These results warrant intervention, if nothing else in terms of soil use and planning, and should be employed to prioritise individual sites in terms of suitable actions required to guarantee the safe future expansion of residential areas and suitability for use. La Soterraña should obviously be the top priority for these actions because it is the largest of the three sites, rural residential homes exist in it, and it is also the site where purification of the ore extracted from all three mines took place, resulting in concentrations of Hg and As in soil much higher than those found in the other minor mines.

Conclusions

This study has shown that as a consequence of historical mining and metallurgical operations, some of which dates back almost 2000 years, involving the stockpiling of large quantities of Hg and As-rich waste materials, there remains a significant environmental impact at the three sites studied. This is reflected in elevated concentrations of these elements in soils and levels of human-health risk from exposure to those concentrations that exceed commonly accepted permissible levels by up to two orders of magnitude at the most contaminated site.

In this particular study, and as a consequence of the mineralogy of the ore that was mined, the elements of most concern in terms of potential health effects are Hg and especially As. The latter is the main risk-driver due to its carcinogenic nature and the highly elevated concentrations, up to nearly 10000 mg kg^{-1}, that are found in the soils around the mining and metallurgical facilities. These concentrations and rural residential development in the proximity of the most contaminated site, La Soterraña, result in a level of carcinogenic risk of 3.5×10^{-3}, significantly higher than the regulatory acceptable threshold of 1×10^{-5}. The exposure pathway with the largest contribution to the overall risk is ingestion of soil for all elements except Hg for which the importance of inhalation is probably overestimated given that the physico-chemical properties and toxicity data used for this element in the risk assessment are those of elemental Hg. The spatial distribution of Hg and As concentrations shown in Fig. 2

indicates that both elements have spread downslope from their sources with time, resulting in contour lines of unacceptable risk that already overlap with residential areas around the mining sites. Should future plans for these areas include further landscaping, residential or industrial use, very careful consideration needs to be undertaken as to its fitness for purpose.

These results underscore the usefulness of risk assessment as a tool to identify contaminants and exposure pathways of most concern, and more importantly as an instrument for registering, classifying and prioritising contaminated sites, to confirm that they are fit for their current or intended uses, and to guide actions needed to ensure fitness for use.[53] In terms of planning for the future, an assessment of risk could provide information on possible safe distance from old mining activities to site a settlement, or to redevelop the site. However, a risk assessment then becomes a blunt instrument and would require considerable refinement to enable such an application. For instance, social data would be required to ascertain behaviours of those in the area such as the adult/child balance, whether the individual was working in the land, full time resident or just a visitor. This would enable the risk model to be modified to account for site specific characteristics and also human behaviour.

Although this study is concerned with abandoned Hg mining sites in Spain, risk assessment would be an equally useful planning and decision making tool in any other geographical setting and for any other mineralization.

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