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Screening risk assessment tools for assessing the environmental impact in an abandoned pyritic mine in Spain

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ABSTRACT

This paper describes a new methodology for assessing site-specific environmental impact of contaminants. The proposed method integrates traditional risk assessment approaches with real and variable environmental characteristics at a local scale. Environmental impact on selected receptors was classified for each environmental compartment into 5 categories derived from the whole (chronic and acute) risk assessment using 8 risk levels. Risk levels were established according to three hazard quotients (HQs) which represented the ratio of exposure to acute and chronic toxicity values. This tool allowed integrating in only one impact category all the elements involved in the standard risk assessment.

The methodology was applied to an abandoned metal mine in Spain, where high levels of As, Cd, Zn and Cu were detected. Risk affecting potential receptors such as aquatic and soil organisms and terrestrial vertebrates were assessed. Whole results showed that impact to the ecosystem is likely high and further investigation or remedial actions are necessary. Some proposals to refine the risk assessment for a more realistic diagnostic are included.

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1. Introduction

Contamination of the environment with trace elements has increased dramatically since the onset of the industrial revolution (Nriagu, 1979). The main anthropogenic sources of the contamination by metal(loid)s are fossil fuel burning, mining and smelting of metalliferous ores, municipal waste, landfill leachates, fertilisers, pesticides and sewage (Forstner, 1995). Concerning mining activities, presently mines are specifically designed with mitigation methods to manage potential environmental impacts; however, in former mines the extracted mineral deposits may remain after mines have been abandoned and usually become a large and uncontrolled source of metal and metalloid contamination. There are many areas impacted by pyritic mine spreading all around Spain (Álvarez et al., 2003; Clemente et al., 2006; Rufo et al., 2007), which after becoming derelict

sites now require environmental rectifications. In the pyrite deposits, natural weathering interaction may release elements such as As, Zn, Pb, Cu, Mn, Cd, Mo, Cr, and Ni which may contaminate water, soil and plant ecosystems at unacceptable levels (Quevauviller et al., 1989; Santos Oliveira et al., 2002). Releases may cause direct adverse effects on terrestrial and aquatic organisms. Moreover some trace elements can be incorporated in plants and/or animals leading under certain circumstances to secondary poisoning in vertebrates due to the consumption of contaminated food (Anawar et al., 2006; Chen and Liu, 2006; McLaughlin et al., 2000). Therefore, the management of abandoned derelict mines is a major concern. Risk assessment methodology has been recognised as a powerful tool for the decision-making process in contaminated sites management, especially when contamination of soil or water is involved (Suter et al., 2000; US-EPA, 1998). The use of risk assessment techniques in mining activities has mainly focused on human health issues (Kim et al., 2005; Lee et al., 2006). Ecological risk tends to be considered a second priority however to propose remediation techniques or new occupation plans of these contaminated sites is very difficult if the potential risks to biological communities are not considered.

Through this paper, we propose a screening methodology for quantitative impact assessment based on Environmental Risk Assessment (ERA) tools. The proposed screening methodology established

Abbreviations: BcF, Bioaccessibility Factor; W, Body Weight; DD, Daily Dose; DS, Distant Sites; FIR, Food Ingestion Rate; HQ, Hazard Quotient; IDS, Intermediate Distance Sites; Iml, Impact Index; NB, Nearby sites; RI, Risk Index.

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eight risk levels according to the values of three complementary hazard quotients (HQs). Later, the expected impact is classified according to the short term and chronic potential risks.

This evaluation model has been applied to an abandoned pyrite mine in Bustarviejo (Madrid, Spain). This site is included in an environmental reserve proposed for the Natura 2000 Network under [Council Directive 92/43/CEE \(1992\)](#). Furthermore, the mine site itself is the object of a national rehabilitation project creating the first Geological and Mining Interpretation Centre in Madrid as well as cultural and scientific facilities. The potential environmental risk on this site comes mainly from the tailings with high concentrations of arsenic and metals such as copper, cadmium and zinc leading to significant contamination of soil, plants and waters at the streams ([Moreno-Jiménez et al., 2009, 2010](#)) which may represent an environmental concern.

The main objectives of this work are: i) to develop a new screening procedure for assessing environmental impacts in contaminated sites using risk assessment tools, ii) to establish a ranking of expected environmental impacts based on hazard quotients and iii) to apply the method in the environmental evaluation of an abandoned pyritic mining site in Spain as a case study.

2. Materials and methods

2.1. Description of the environmental impact method

The methodology developed in this work applies generic principles for chemical risk assessment, such as those described in EU Technical Guidance Document (TGD) ([EC, 2003](#)), for setting a semi-quantitative impact value. The expected environmental impact of contaminants was determined for each environmental compartment in two stages.

The first stage consisted in the risk quantification model which allowed estimating the risk indexes (RI). The second stage consisted in establishing a ranking of potential impacts divided in five categories of increasing concern based on the RI.

2.1.1. Derivation of the risk indexes

Potential risk of the site was classified on eight risk levels or categories established according to the hazard quotients (HQs) values ([Table 1](#)). The HQ was expressed as the ratio of the exposure concentration (environmental concentrations or total daily intake) and a set of toxicity values to target organisms (reference doses or the acute toxic dose). A scoring system of eight risk indexes (RIs) ([Table 1](#)) was defined. RIs from 0 to 4 were based on chronic exposure and RIs from 5 to 7 were based on acute exposure.

PNEC (Predicted non-effect concentration) and NOEC (Non-observed effect concentration) were the two reference doses employed to cover long term effects and L(E)C50 (50% lethal (effect) concentration) was

Table 1
Risk index derivation based on the hazard quotients and on the potential level of disturbance in the environmental compartments.

	Hazard quotient (HQ)	Risk index (RI)	Level of disturbance
<i>Chronic risk</i>			
HQ _{PNEC}	<1	0 ^a	Negligible effects
HQ _{PNEC}	1–10	1 ^b	Sensitive species
HQ _{NOEC}	1–10	2 ^b	Standard species
	10–100	3	Community
	>100	4	Ecological structure
<i>Acute risk</i>			
HQ _(LC50)	1–10	5	Standard species
	10–100	6	Community
	>100	7	Ecological structure

^a Prevails over all other impact values.
^b Only use the highest value in the series.

used to cover acute effects. PNEC, which is a modeled value, was used as an expression of precautionary concern because it covers species more sensitive than those on which toxicity has been measured. NOEC or NOAEL (Non-observed or adverse effect concentration) of the most sensitive taxa were used because they represent the actual long term concern. Finally, L(E)C50 of the most sensitive taxa was chosen and it represents the actual short-term concern.

2.1.2. Classification and ranking of the impact indexes

The second part of the conceptual model evaluates the overall potential impacts of the site based on the named Impact Indexes (ImIs). These indexes were obtained as the sum of the chronic and acute RIs ([Section 2.1.1](#)). Finally, the ImI obtained was assigned to five different categories from “negligible” to “very high” impact according to the following criteria:

$$\begin{aligned} \text{RI (HQ}_{\text{chronic}}) + \text{RI (HQ}_{\text{acute}}) = \text{ImI} \leq 1 & \text{ “negligible impact”} \\ \text{ImI} \leq 2 & \text{ “low impact”} \\ \text{ImI} \leq 7 & \text{ “moderate impact”} \\ \text{ImI} \leq 9 & \text{ “high impact”} \\ \text{ImI} > 9 & \text{ “very high impact”} \end{aligned}$$

2.2. Application of the environmental impact method

2.2.1. Site description

The site extends across 200,000 m² within La Mina stream valley, between the following UTM coordinates: 30 T – X=0438606, Y=4524302; X=0437797, Y=4523518, where a shrub land (higher sites) and a woodland (lower sites) are developed. Further description is detailed in [Moreno-Jiménez et al. \(2009, 2010\)](#). Two water streams (with water depth between 10 and 15 cm) were present at the studied site: La Mina and La Barranca.

2.2.2. Soil, water and plant sampling

Surface soils (0–30 cm) for chemical analyses were sampled in the surroundings of the Mónica mine in May and June 2006. Samples were distributed into three groups according to their mine distance: nearby sites (NB: 3–312 m), intermediate distance sites (IDS: 459–657 m) and distant sites (DS: 771–1229 m). Five soils from each group were collected, dried at 50 °C for 7 days, sieved to 2 mm and analyzed to be used in the exposure assessment ([Fig. 1](#)).

Soil samples (nearby tailing soil and control soil) for the earthworms bioconcentration assay were taken from the top soil layer (0–20 cm), air-dried and sieved (2 mm mesh). A representative contaminated soil was taken from a nearby tailing site. Main physicochemical characteristics of this soil were: pH 5.93 and organic matter (OM) 0.85%; and element levels were: As 5698 ± 98, Cd 27 ± 1, Zn 10,185 ± 807 and Cu 1997 ± 107 mg/kg d.w. (dried weight). Control soil was collected from a field located near Madrid (Spain). This soil was also used to prepare dilutions series of contaminated soil. Main physicochemical characteristics of this soil were: pH 7.27, OM 1.9%, and element concentrations of As 4.4 ± 0.3, Cd 0.144 ± 0.005, Zn 87 ± 7 and Cu 8.4 ± 0.3 mg/kg d.w.

Surface waters from the La Mina and La Barranca streams were sampled twice, in early summer and in late winter, to evaluate the effects of discharge variations. Sampling points are detailed in [Fig. 1](#). Samples M1 and M2 were taken in a stream that goes through the mine and leaves without being diluted with adjacent streams, M1 within and M2 outside mine. M3 was taken upstream of the mine in order to obtain background levels for waters in the site. M4 and M5 samples were taken in streams which cross mine surroundings. M9 sample was taken in the stream, in flowed from adjacent streams, at the most distant site. Surface waters (100 mL) were sampled in plastic flasks and HNO₃ was added at a ratio of 1 mL of HNO₃ per 40 mL of

Orthophoto of adjacent soils to the Monica mine

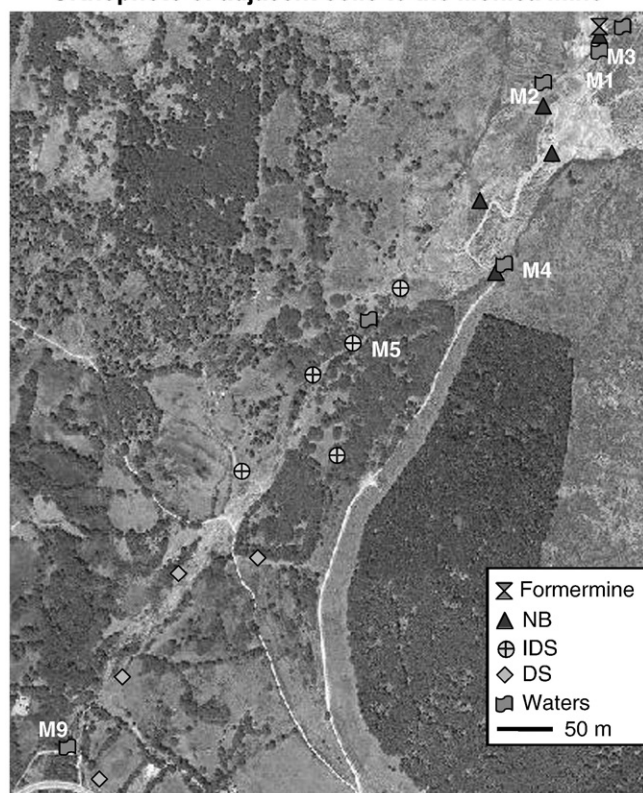


Fig. 1. Orthophoto of adjacent soils to the Monica mine. Soil and water sampling points are shown in the figure. Former mine is located on the right top of the photo. NB = nearby sites, IDS = intermediate distance sites, and DS = distant sites. Water samples were identified as M1, M2, M3, M4, M5 and M9.

water. Non filtered samples were stored at 4 °C for 20 days to be further analyzed.

Plants (shoots) were sampled in the surroundings of the Mónica mine in May and June 2006. They were natural species from the mining site and previously identified (Moreno-Jiménez et al., 2009). They were selected on the basis of their abundance in each vegetation unit of each plant group (ferns, herbaceous plants, shrubs and trees). Shoots were collected, as well as representative soil samples adjacent to the sampled plants. Plant material was milled to a fine powder with a grinder and then stored in plastic bags until the sample mineralization following Lozano-Rodríguez et al. (1995).

2.2.3. Plant bioconcentration assay

Three plant bioconcentration factors (BCF_{plants}) were calculated according to the distance from the mine and corresponding to NB, IDS and DS sampling sites, using data from soil and plants in each zone. The BCF for plants were determined for each chemical as the ratio between the measured element concentrations in the aerial part of the plant and in the adjacent soil, from the same site (or sampling point), both related to dried weight. The BCF corresponding to each zone was an average considering seven plant species: *Cytisus scoparius*, *Genista cinerascens*, *Pteridium aquilinum*, *Silene vulgaris*, *Digitalis thapsi*, *Centaurea nigra* and *Salix atrocinerea*.

2.2.4. Earthworm bioconcentration assay

The earthworm bioconcentration factor (BCF_{worms}) was obtained from a laboratory study set as follows: Earthworms (*Eisenia fetida*) from our own culture were exposed for 21 days to different dilutions of sample soil with control soil (12.5, 25, 50 and 100%, w/w) prepared

on a dry-weight basis and produced by manual mixing. These percentages of soil dilution were established having into account the previously determined mean As and metal levels in each area and to mimic the site conditions as much as possible. Control and test soils were placed in 15 cm height × 15 cm diameter methacrylate columns (2.0 kg soil d.w. per column). Three replicates of each treatment were examined. Earthworms between 300 and 600 mg of wet weight were washed with distilled water and kept for 24 h on moist filter paper to depurate the gut content. Next, 20 adult earthworms were added per column on each soil surface. Columns were incubated in a climate room (20 ± 2 °C) and illuminated under fluorescent bulbs (800–1000 lx) with photoperiod (16/8) day/night light. Water was added to bring the soil to its water holding capacity. Columns were watered 5 days a week with 50 mL of dechlorinated water, and then allowing the soils to drain to field capacity. After the exposure period surviving earthworms were counted, washed with distilled water and kept for 24 h on moist filter paper. Then, they were frozen at –20 °C for 24 h, lyophilized (Telstar Cryodos) and analyzed for total As and metals as described in Chemical analyses section. The value of BCF_{worms} was calculated as the ratio between the measured concentrations of chemical in the body and in soil, both related to dried weight. Finally, BCF obtained for the 50, 25 and 12.5% laboratory soil dilutions were assigned to NB, IDS and DS, respectively.

2.2.5. Oral bioaccessibility assay

Three samples of soil from the three areas (NB, IDS and DS sampling sites) were selected to evaluate oral bioaccessibility (BacF) of As and metals after soil ingestion. The fraction of As and metals in the soil that may be absorbed in the gastrointestinal tract was determined using the Simple Bioavailability Extraction Test (SBET) following Lee et al. (2006). Briefly: 0.5 g of soil were suspended in a 30 g/L glycine solution, shaken for 1 h at 37 °C in a water bath, filtered with a num. 42 filter paper (Whatman) and As and metals were measured in the filtrate.

Samples were stored at 4 °C under darkness and measured as soon as possible. The BacF value was calculated as the ratio of the measured concentration from glycine soil extracts to the measured chemical in soil (C_{soil}).

2.2.6. Chemical analyses

After drying, sieving and homogenizing the soils, dichromate-oxidable organic matter (OM) and the pH of a 1:2.5 (soil:water) suspension were measured following the protocols of the Spanish Ministry of Agriculture (MAPA, 1994). Pseudo-total concentrations of elements were assayed after HNO₃:H₂O₂ digestion in an autoclave (Wenzel et al., 2001). Extracts were filtered (num. 42 filter paper, Whatman) and diluted with milli-Q water.

Plant material was washed thoroughly in tap water and later distilled water and dried at 50 °C for 7 days. Lyophilized earthworms were ground to a fine powder in an agate pestle and mortar. All earthworms belonging to the same column were treated and analyzed together. For acid mineralization of organism tissues, 10 mL of milli-Q water, 3 mL of HNO₃ and 2 mL of H₂O₂ were added to 0.5 g (d.w.) of tissue, digestion was performed at 1500 Pa and 125 °C in an autoclave (Lozano-Rodríguez et al., 1995). The extract was filtered and diluted with water to 25 mL.

As and metal concentration in samples of water, soil, plants and earthworms extracts, were analyzed by atomic absorption spectrometry (Perkin Elmer Analyst 800, Cd, Cu and Zn) or atomic fluorescence (PSAnalytical, As). Three analytical replicates were measured per sample.

2.2.7. Calculation of the hazard quotients

HQs were calculated as the ratio between environmental exposure and toxicity values (see Section 2.1.1).

2.2.7.1. Exposure assessment. In order to select the ecological receptors and exposure routes, three protection goals were considered: soil organisms, aquatic organisms and terrestrial vertebrates. For soil organisms, plants, earthworms and microorganisms were selected as examples of organisms living in direct contact with the contaminated soil and directly exposed. The exposure concentration in soil (Csoil) is represented by the mean of measurements in soil for As and metals (Cd, Cu, and Zn) performed at the sampling points belonging to the same area (NB, IDS or DS). Csoil values were also taken into account when assessing the exposure of terrestrial vertebrates.

For the aquatic compartment, species belonging to one single aquatic food chain were used, i.e.: algae, invertebrates and fish. The exposure was represented by the measured concentration of As and metals in the water samples (Cwater) of the La Mina and La Barranca streams. Again three areas were chosen for the exposure assessment to aquatic organisms and terrestrial vertebrates through drinking water: M2 was selected to represent aquatic exposure in NB, the mean value of M4 and M5 represents IDS and M9 the DS.

For the terrestrial compartment birds and mammals were considered as representative organisms. Five organisms were selected as indicator species for the exposure assessment based on their feeding habits (EC, 2002a): medium herbivorous bird (pigeon), insectivorous/vermivorous bird (wren), small herbivorous mammal (vole) and insectivorous mammal (shrew). An additional typical domestic herbivorous mammal (sheep) was included to cover risk for the site-livestock.

Three main exposure routes were considered for terrestrial vertebrates: oral food ingestion, soil accidental ingestion and drinking water. Unlike to soil and aquatic organisms, exposure levels for terrestrial vertebrates were estimated using exposure models, admitted by different regulations (EC, 2002a,b, 2003). Daily dose (DD) of As and metals through oral food ingestion is calculated by the Eq. (1):

$$DD(\text{food}) = \frac{FIR}{W} \times C_{\text{food}} \times \frac{(100 - MC)}{100} \quad \text{mg/kg b.w./day} \quad (1)$$

where FIR is the food intake rate of indicator species (Kg food fresh material per day), W is the body weight (b.w.) of indicator species (kg), Cfood is the concentration of As or metal in food related to fresh material (mg/Kg food) and MC is the moisture content of food source (%). FIR and W values for birds and wild mammals were obtained from the European regulation guidance document (EC, 2002a). For sheep, the FIR/W value described by Crocker et al. (2002) for fallow deer (0.086 Kg/d/kg_{bw}) was applied. This is based on the assumption that both animals have a similar weight (45 kg approximately) and similar feeding habits. The MC values were 76.4% for grasses and cereal shoots and 79.4% for worms (Crocker et al., 2002).

The element concentration in the food item (earthworm or plants) is regulated by the soil–plant and the soil–earthworm bioconcentration factor. This concentration is determined as:

$$C_{\text{food}} = BCF(\text{plant or earthworm}) \times C_{\text{soil}} \quad \text{mg/Kg food} \quad (2)$$

where BCF is the bioconcentration factor in plant or earthworm, and Csoil is the concentration of As or metal in dry soil (mg/Kg soil d.w.).

Exposure level through soil accidental ingestion with the food is estimated according to Eq. (3):

$$DD(\text{soil ingestion}) = \frac{FIR}{W} \times (C_{\text{soil}} \times F_{\text{soil}}) \times B_{\text{acF}} \quad \text{mg/kg b.w./day} \quad (3)$$

where FIR and W are detailed above (Eq. (1)), Fsoil is the soil fraction uptake with food related to total food amount (unitless) and BacF is the oral bioaccessibility factor (unitless). Fsoil values were obtained for wild birds and mammals from Beyer et al. (1994) and for sheep from Abrahams and Steigmajer (2003).

Exposure levels through contaminated drinking water are expressed by Eq. (4):

$$DD(\text{drinking water}) = C_{\text{water}} \times \frac{\text{ingestion rate}}{W} \quad \text{mg/Kg b.w./day} \quad (4)$$

where Cwater is the concentration of corresponding element in water (mg/L). The water ingestion rate was calculated allometrically according to Calder and Braun (1983) from the body weight of indicator species (W) in kilograms:

$$\text{Ingestion rate} = 0.059 W^{0.67} \quad (\text{L/day}) \quad (\text{in the case of birds}), \quad (5)$$

$$\text{Ingestion rate} = 0.099 W^{0.90} \quad (\text{L/day}) \quad (\text{in the case of mammals}) \quad (6)$$

Total DD for terrestrial vertebrates was the sum of values obtained from each exposure pathway (food, soil and drinking water). For the risk assessment, the highest total DD within each group (mammals and avian) was selected.

2.2.7.2. Selection of toxicity values. Toxicity data were obtained from the literature for the indicator organisms. Our study was carried out with metals and arsenic present initially in tailings (or mining sites) under oxidant slightly acid conditions. Although toxicity depends on chemical speciation of the element, we assumed that elements were present in their oxidized inorganic forms. Toxicity data were collected accordingly. The dataset of soil organisms considered three taxonomic groups: plants, soil invertebrates and microorganisms. For aquatic organisms, toxicity data to algae, aquatic invertebrates and fish were gathered. Values of terrestrial vertebrates were from mammalian and avian toxicity studies.

Data selected were acute L(E)C50s and chronic NOEC(NOEL) values for ecologically relevant endpoints (mortality, growth and reproduction or development in the case of mammals). The assessment endpoints for microorganisms were related to community function (i.e. carbon mineralization, nitrogen transformation). PNEC values for each particular compartment were determined following a conservative deterministic approach from the lowest NOEC/NOEL values (EC, 2003). For Cd, and Zn it exists an European Risk Assessment document (EU, 2007, 2008a,b, 2010) from where the endpoints of toxicity to all involved taxonomic groups were extracted. The toxicity values for As and Cu were obtained from the literature considering only those tests performed applying international standard protocols (e.g. ISO, OECD, ASTM). Data on the most sensitive species in each compartment were selected for the risk assessment.

2.2.8. Statistical analysis

All statistical analyses were performed using the STATGRAPHICS software (Version 5.0). Multifactor analysis of variance (ANOVA) was used. A probability level of $P < 0.05$ was chosen to establish statistical significance.

3. Results

The environmental impacts for As and metals in the ecosystem surrounding the pyrite mine were calculated applying the methodology described above.

3.1. Exposure assessment

The exposure levels for the different receptors through all the selected routes of exposure were determined. Data on As and metal content in the soils sampled at different distance points from Mónica

Table 2

Data of pH, dichromate-oxidable organic matter (OM) and trace element concentrations in soils (Csoil) surrounding the Mónica mine.

	Distance (m)	OM (%)	pH _w	Csoil (mg/kg)			
				As	Cd	Cu	Zn
<i>Nearby sites</i>							
	3	0.67	4.02	3 002.5	23.4	590.3	845.0
	126	0.69	3.89	1774.8	7.9	213.8	512.5
	171	0.85	4.34	1549.8	13.7	371.5	636.0
	257	1.11	4.86	1787.1	8.9	301.6	1475.9
	312	8.61	5.08	2137.1	34.9	606.0	2243.0
Mean	173 ± 54	2.4 ± 1.6	4.4 ± 0.2	2 050 ± 256	17 ± 5	417 ± 78	1142 ± 172
<i>Intermediate distance sites</i>							
	459	6.22	5.64	689.2	13.6	387.0	685.7
	526	5.34	5.07	745.3	13.6	186.7	1141.4
	543	9.97	4.81	33.0	3.0	13.4	84.7
	572	7.10	5.02	13.7	2.7	5.8	38.4
	657	7.48	5.12	41.6	5.3	18.2	161.9
Mean	551 ± 32	7.2 ± 0.8	5.1 ± 0.1	304 ± 169	8 ± 2	122 ± 74	422 ± 214
<i>Distant sites</i>							
	771	7.42	4.18	14.9	2.62	10.2	69.0
	811	4.87	4.95	15.1	5.60	9.9	103.9
	972	2.21	5.19	11.2	1.39	6.2	33.9
	1229	7.74	4.30	5.3	3.15	17.3	113.2
	1311	3.46	5.28	209.1	2.45	34.9	155.4
Mean	1019 ± 109	5 ± 1	4.8 ± 0.2	51 ± 40	3.0 ± 0.7	16 ± 5	95 ± 21

mine surroundings are collected in Table 2 together with some soil physicochemical characteristics.

Levels of As, Cu, and Zn in NB were very high, reaching up to 3003, 606, and 2243 mg kg⁻¹ respectively. Cd levels were around 2 orders of magnitude lower than the rest of elements (up to 35 mg kg⁻¹), but this difference did not give rise to the lowest level of impact for this metal, as it is shown below.

The relation of pseudo-total concentrations between NB and DS samples were evaluated by [Csoil]_{NB}/[Csoil]_{DS} ratio. This method informed on how easy is a contaminant dispersed from the source to the receptor site. The [Csoil]_{NB}/[Csoil]_{DS} ratio indicated a lower migration of As (40) and Cu (20) compared to Zn (12) and Cd (6), which were easily dispersed. This aspect had implications in the risk estimated in the three study areas.

As and metal exposure levels for aquatic organisms were directly measured in the water columns (Table 3). Samples M1 and M2 reached the highest concentration of As and metals and the lowest pH due to they were sampled at the closest points from the mine. Water metal concentration increased in the order Cd < Cu < Zn, which was according to the soil concentration. M3 was taken in order to obtain background levels for waters in the site; however, values higher than expected were obtained for Zn. The concentrations of As, Cu and Zn in all the sampling points exceeded the Spanish indicative values for surface waters (Ministerio de Medio Ambiente, 2000). Values for Cd are not legislated yet. Although As extractability is low in soils under

oxidant conditions, the surface waters showed large concentrations all over the studied area. At the farthest sites As levels were still higher than the World Health Organisation (WHO) recommendation of 10 µg/L for drinking water related to human health protection (Steinmaus et al., 2006).

Exposure concentration for terrestrial vertebrates was estimated through three exposure pathways. Metal concentration in food depends on the transference of contaminant from soil to foodstuff which is regulated by the bioconcentration factor.

BCFplants obtained from As and metals concentration in plants from each study area are shown in Table 4. There was not a lineal relation between BCFplants and metal soil concentration because the BCFplants values in each zone depended on soil concentration and naturally occurring plant species (see Section 2.2.3). BCFplants was less than 1 for all elements except for Cd, which was consistent with the described high bioavailability of Cd to plants (Moreno-Jiménez et al., 2009). The lowest BCFplants value was for As, approximately two orders of magnitude less than for the other elements, indicating very low transfer of As from soil to plants. This agrees with literature where soil–plant transfer coefficients <0.01 are described for this element (Adriano, 2001; Warren et al., 2003). Transference of trace metals from soils to plants decreases with soil concentration increase (McLaughlin, 2001), even showing a plateau when soil concentration exceeds a certain limit (Hamon et al., 1999). Plants have many physiological mechanisms to control the influx and translocation of elements in order to avoid their toxicity (Clemens et al., 2002; Hamon et al., 1999). Despite that, values obtained for each area studied in the present work were not very different in general.

Table 3

Metal content in water samples (Cwater) in the streams surrounding the Mónica mine. Values shown are the medium concentrations of samples taken in two different seasons (early summer and late winter).

	pH	Cwater (mg/L)			
		As	Cd	Cu	Zn
M1	4.16	0.175 ± 0.003	0.122 ± 0.005	1.310 ± 0.023	5.812 ± 0.048
M2	4.34	0.313 ± 0.003	0.109 ± 0.007	1.343 ± 0.008	5.644 ± 0.054
M3	7.00	0.038 ± 0.010	0.004 ± 0.002	0.040 ± 0.028	0.218 ± 0.039
M4	6.95	0.119 ± 0.066	0.024 ± 0.003	0.079 ± 0.061	0.288 ± 0.130
M5	7.05	0.190 ± 0.076	0.029 ± 0.007	0.109 ± 0.030	0.178 ± 0.084
M9	7.29	0.059 ± 0.006	0.005 ± 0.002	0.056 ± 0.075	0.088 ± 0.015

Table 4

Bioconcentration factor for plants (BCFplants) and oral bioaccessibility factor (BacF) from ingested soil at different distance sites.

	BCFplant (Moreno-Jiménez et al., 2009, 2010)				BacF			
	As	Cd	Zn	Cu	As	Cd	Zn	Cu
Nearby	23 E ⁻⁴	0.89	0.25	0.32	0.021	0.003	0.014	0.267
Intermediate	33 E ⁻⁴	1.53	0.45	0.62	0.021	0.002	0.013	0.324
Distant	75 E ⁻⁴	1.35	0.66	0.66	0.017	3 E ⁻⁵	0.048	0.078

Table 5Bioconcentration factor for earthworms (BCF_{worm}) obtained at different contaminated soil concentrations.

Sampling site	Soil dilution (%)	Csoil (mg/kg _{d,w})				BCF _{worm}			
		As	Cd	Zn	Cu	As	Cd	Zn	Cu
NB*	100	5658 ± 98 ^d	27 ± 1 ^e	10,185 ± 807 ^d	1997 ± 107 ^d	0.12 ^a	0.20 ^a	0.13 ^a	0.12 ^a
IDS**	50	3245 ± 610 ^c	11.9 ± 0.5 ^d	4391 ± 94 ^c	862 ± 28 ^c	0.17 ^a	0.40 ^{ab}	0.22 ^a	0.20 ^a
DS***	25	1552 ± 138 ^b	6.4 ± 0.2 ^c	2585 ± 131 ^b	489 ± 26 ^b	0.20 ^a	0.48 ^b	0.17 ^a	0.15 ^a
	12.5	700 ± 130 ^a	3.2 ± 0.1 ^b	1151 ± 22 ^{ab}	220 ± 8 ^a	0.38 ^b	1.18 ^c	0.21 ^a	0.15 ^a
						Mean		0.18 ± 0.08	0.15 ± 0.07

a–e: different letters indicate significantly different values using one-way ANOVA (LSD; $P < 0.05$).

* Nearby sites (NB) are related with Csoil from columns filled with 50% diluted soil.

** Intermediate distance sites (IDS) are related with Csoil from columns filled with 25% diluted soil.

*** Distant sites (DS) are related with Csoil from columns filled with 12.5% diluted soil.

The BCF_{worms} values for studied elements are included in Table 5. In this study, values for As and especially Cd showed an increase of the BCF factor with soil decreasing levels. Consequently, for the As and Cd exposure assessment different values of BCF_{worms} at 50, 25 and 12.5% soil concentration were assigned to NB, IDS and DS respectively. Conversely, at the tested concentrations, BCF for Zn and Cu were independent of soil concentration. In this case the mean BCF values of 0.18 and 0.15 were derived based on the lack of statistical significance (ANOVA). BCF_{worms} values for all elements were less than 1 except for Cd at the lowest concentrations, indicating that cadmium was concentrated from the soil into the earthworm body. BCF_{worms} for As were higher than in plants and they were in the same magnitude order than Zn and Cu. BCF_{worms} values were, in general, lower than values in the literature from non contaminated or moderately contaminated sites (Van Vliet et al., 2006). Moreover, the expected decrease of BCF_{worms} concentrations with the increase of soil concentration (Nahmani et al., 2007; Spurgeon and Hopkin, 1999) was not observed in this work. These results are consistent with the capacity of earthworms to partially regulate concentrations of contaminants in their body, especially in the case of essential metals such as Zn and Cu (Langdon et al., 2003; Lee and Kim, 2008; Peijnenburg et al., 1999).

An additional transference parameter, the oral bioaccessibility factor (BacF), was determined in order to correct the amount of As or metal which can be absorbed through the soil portion accidentally ingested by vertebrates. Bioaccessibility is defined as the fraction of a substance in soil that is available for absorption in the gastrointestinal tract (Ruby et al., 1999). Data on BacF obtained in this study are shown in Table 4. Except for Cu, values obtained were very low ($3 \cdot 10^{-5}$ to 0.048) indicating that the pool of As and metals that terrestrial vertebrates may incorporate from soil ingestion is only a small fraction of total soil metal content. Copper showed the highest values of BacF (0.078–0.267), which did not correlate with the highest BCF values in plants and earthworms.

The daily ingestion for the generic terrestrial vertebrates considering the three exposure pathways are shown in Table 6. Values for FIR/W and Fsoil are also included.

Comparing the three exposure pathways for terrestrial vertebrates, food is the main exposure route except for sheep exposed to As. Thus, at NB, the main exposure pathway of As for livestock is accidental soil ingestion. It was due to its high soil concentration and its low BCF_{plants} values, which increase the soil ingestion versus diet for metal exposure (Fairbrother et al., 2007). The relative importance of drinking water compared to soil ingestion contribution depended

Table 6

Food ingestion rates based on fresh food material (FIR), soil fraction uptake (Fsoil) and arsenic and metal daily dose (DD) for birds and mammals through food, accidental soil and drinking water in nearby, intermediate and distant sites from the mine.

	FIR/W Kg _f /d/kg _{bw}	Fsoil	As			Cd			Zn			Cu		
			DD (mg/kg _{b,w} /d)			DD (mg/kg _{b,w} /d)			DD (mg/kg _{b,w} /d)			DD (mg/kg _{b,w} /d)		
			Food	Soil	Water	Food	Soil	Water	Food	Soil	Water	Food	Soil	Water
Nearby sites														
Pigeon	0.76	0.139 ^a	0.85	1.07	0.03	2.84	0.001	0.01	51.41	0.40	0.49	24.00	2.78	0.12
Wren	1.04	0.10 ^b	73.19	0.90	0.08	1.49	0.001	0.03	43.1	0.33	1.52	13.12	2.34	0.36
Vole	1.39	0.024 ^b	1.51	0.33	0.04	5.06	0.000	0.02	91.39	0.12	0.81	42.66	0.85	0.19
Shrew	0.63	0.04 ^b	45.31	0.22	0.05	0.92	0.000	0.02	26.73	0.08	0.88	8.12	0.58	0.21
Sheep	0.086	0.176 ^c	0.09	0.15	0.02	0.32	0.000	0.01	5.71	0.05	0.44	2.67	0.39	0.10
Intermediate distance sites														
Pigeon			0.18	0.16	0.01	2.11	4 E-4	0.002	34.22	0.14	0.03	12.64	0.99	0.01
Wren			12.79	0.13	0.02	0.77	3 E-4	0.007	15.97	0.11	0.08	3.85	0.83	0.02
Vole			0.32	0.05	0.02	3.75	1 E-4	0.004	60.83	0.04	0.04	24.25	0.30	0.01
Shrew			7.92	0.03	0.02	0.48	8 E-5	0.004	9.88	0.03	0.05	2.38	0.20	0.01
Sheep			0.02	0.02	0.01	0.23	1 E-4	0.002	3.80	0.02	0.02	1.51	0.14	0.01
Distant sites														
Pigeon			0.29	0.09	0.005	3.12	3 E-6	4 E-4	47.70	0.48	8.7 E-3	7.87	0.13	3 E-4
Wren			20.20	0.09	0.015	3.73	3 E-6	13 E-4	17.80	0.47	0.027	2.45	0.13	8 E-4
Vole			0.53	0.03	0.008	5.70	1 E-6	7 E-4	87.24	0.15	0.014	14.40	0.04	4 E-4
Shrew			12.24	0.02	0.009	2.26	1 E-6	8 E-4	10.78	0.11	0.016	1.48	0.03	5 E-4
Sheep			0.11	0.04	0.004	1.15	1 E-6	4 E-4	17.57	0.22	7.8 E-3	2.90		

^a From Cal/ECOTOX Database, 2010.^b From Beyer et al 1994.^c From Abrahams and Steigmajer, 2003.

on the trace element. In general, exposure through drinking water was lower than accidental soil ingestion, except for zinc at NB and IDS and mainly for cadmium where 1 or 2 order of magnitude lower was observed for soil ingestion.

3.2. Toxicity assessment

The toxicity values are shown in Table 7. The source of each data is indicated under the value and the most sensitive species is indicated by footnotes to the table. Toxicity varied substantially depending on element and species. For the aquatic organisms, the most toxic elements were Cd and Cu. Differences between acute and chronic toxicities were low, except for Cd. Thus, EC50 and NOEC values for As, Cu and Zn were in the same order of magnitude whereas for Cd the difference was of 2 orders of magnitude, with a change in the most sensitive species. In the case of soil organisms, Cd was the most toxic element with a narrow difference between acute and chronic effect concentrations. The toxicity increases as follows: Cd>Zn>As>Cu. Acute effects were 10 fold chronic effect concentrations for As, Zn, and Cu, and 2 fold for Cd. In the case of mammals and birds, the toxicity decreased in the order Cd>Zn>As>Cu. In general, acute and chronic toxicity were similar or higher to mammals than to birds except for As NOEC that was one order of magnitude lower for mammals.

PNEC values were calculated from NOEC or NOAEL (in the case of mammals) data; consequently, they follow the same tendency as chronic values, except for the As PNEC value for soil organisms and Zn PNEC value to mammals. This different tendency is due to the large assessment factors (AF = 100 against AF = 2–10) needed to deal with the uncertainty derived from the few chronic toxicity data (EC, 2003), which led to more conservative PNEC values.

3.3. Risk quantification

The HQs values related to each of the three study areas are shown in Fig. 2. HQ_{PNEC} values were higher than 1 indicating potential risk to sensitive species in all the compartments and areas considered except for livestock in IDS and DS (Fig. 2A). For soil organisms the risk associated with the As exposure was the highest at all distances considered. This is due not only to the high As soil concentration found in the mine surroundings but also to the conservative value of PNEC obtained for this element. The assessment factor influenced HQ_{PNEC} value since HQ_{NOEC} and HQ_{L(E)C50} for As and the metals were more homogeneous (Fig. 2B and C, respectively). For aquatic species, the risk associated (HQ_{PNEC}) with cadmium is the highest due to the high chronic toxicity of this element and hence the low PNEC value derived. Unlike soil species, for aquatic organisms As HQ_{PNEC} is of lower concern than metals as result of its low toxicity and the low concentration of this element measured in water samples.

HQ_{PNEC} values for terrestrial vertebrates were highly influenced by the source of food: plants or worms (Table 6). Thus, As showed the highest differences between mammals and livestock due to the higher DD_{food} to organisms feeding on earthworms than plants for this element. As result, exposures via food for livestock (plants) were lower than for other vermivorous mammals. The risk to vertebrates decreases with the distance from the mine faster for As and Cu than for Cd and Zn, due to the higher migration found for these elements. Consequently, the exposure to As and Cu is more dependent on the distance from the mine than the exposure to Cd and Zn.

In Fig. 2B are represented the values of HQ_{NOEC} data related to the target organisms at the three studied areas. In the NB and IDS all values were higher than 1, except for livestock, which only showed potential chronic risk for Cd. At DS, risk of chronic effects for soil and

Table 7

Acute (L(E)C50) and chronic (NOEC) toxicity values and PNEC for the most sensitive aquatic and soil organisms and terrestrial vertebrates to arsenic and metals.

	As	Cd	Zn	Cu
<i>Aquatic organisms</i>				
L(E)C ₅₀ (μg/L)	159 ^a (Chen et al., 1994)	35.2 ^a (EU, 2007)	40 ^a (EU, 2008b)	9 ^a (De Schamphelaere and Janssen, 2006)
NOEC (μg/L)	100 ^a (Pawlik-Skowronska et al., 2004)	0.16 ^b (EU, 2007)	17 ^a (EU, 2008b)	3.12 ^b (EFSA, 2008)
PNEC (μg/L)	10	0.016	8.5	0.62
<i>Soil organisms</i>				
L(E)C ₅₀ (mg/Kg _{dw})	207 ^c (New Zealand Ecotoxicity Test Results, 2007)	2.8 ^d (EU, 2007)	80 ^d (EU, 2008b)	302 ^c
NOEC (mg/Kg _{dw})	10 ^c (Vaughan and Greenslade, 1998)	1.8 ^d (EU, 2007)	17 ^c (EU, 2008b)	30.3 ^c (EU, 2008a,b)
PNEC (mg/Kg _{dw})	0.1	0.18	8.5	3.0
<i>Mammals</i>				
LC ₅₀ (mg/Kg _{bw} /d)	70.6 ^f (Schafer and Bowles, 1985)	1.5 ⁱ (EU, 2007)	60 ⁿ (Worthing, 1991)	163 ^g
NOAEL (mg/Kg _{bw} /d)	0.75 ^h (Nemec et al., 1998)	0.15 ⁱ (EU, 2007)	19.9 ⁱ (EU, 2008a)	16.3 ^g (SCHER, 2008)
PNEC (mg/Kg _{bw} /d)	0.075	0.015	0.2	1.6
<i>Birds</i>				
LC ₅₀ (mg/Kg _{bw} /d)	19 ^j (Nemec et al., 1998)	1.6	7.5 ^m (Johnson and Fagerstone, 1992)	173 ^l
NOEC (mg/Kg _{bw} /d)	9.3 ^k (Stanley et al., 1994)	0.16 ^k (EU, 2007)	2.0 ^k (Gwaltney-Brant, 2004)	5.1 ^l
PNEC (mg/Kg _{bw} /d)	0.93	0.016	0.2	0.51

^a Algae.

^b Aquatic invertebrate.

^c Terrestrial invertebrate.

^d Terrestrial plant.

^e Microbial activity.

^f Mouse.

^g Rat.

^h Rabbit.

ⁱ Monkey.

^j Hamster.

^k Duck.

^l Quail.

^m Goose.

ⁿ Sheep.

HQs to target organisms related to the distance to the mine based on toxicity values of the elements

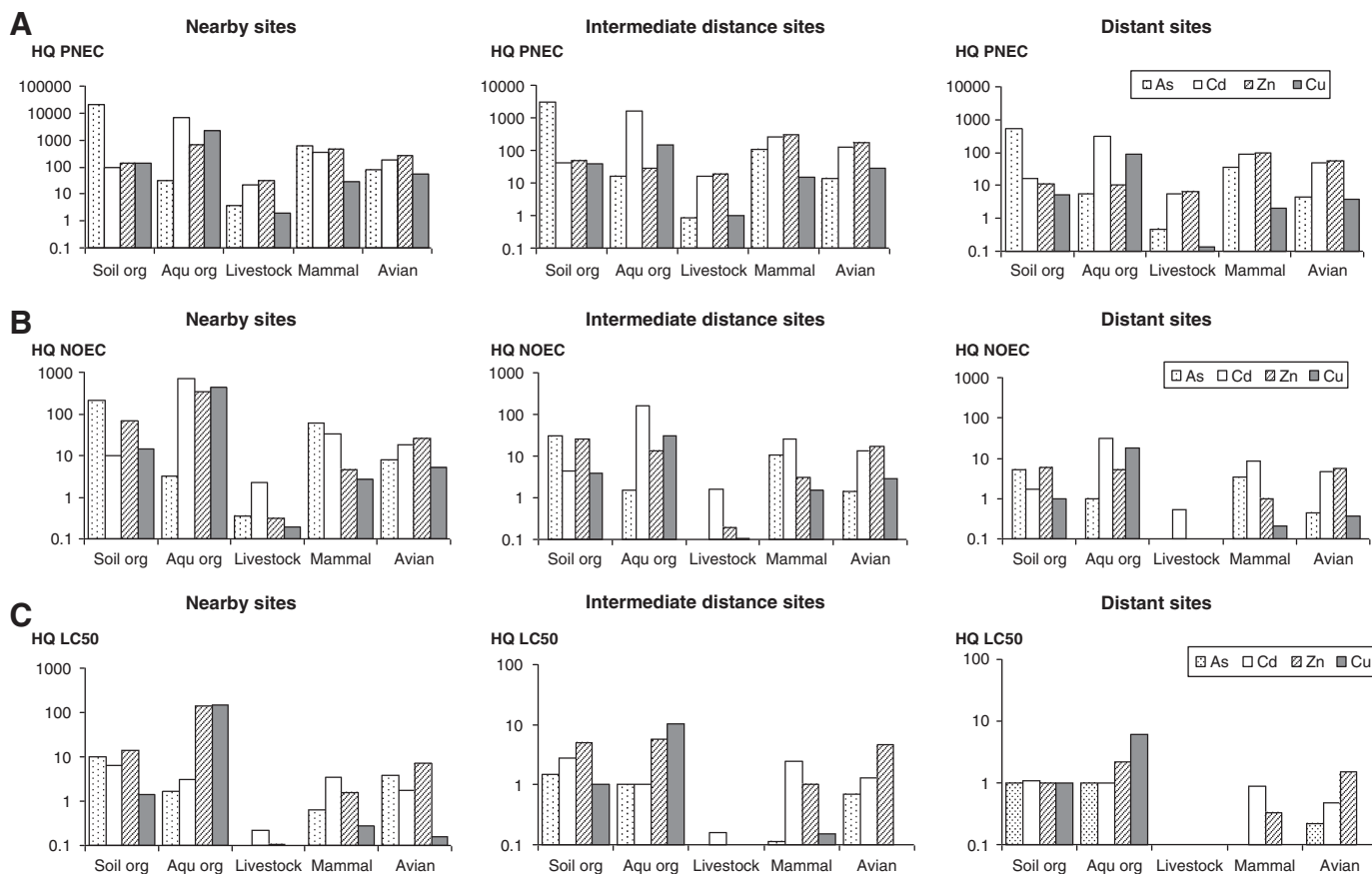


Fig. 2. Hazard quotients (HQs) to soil and aquatic organisms and terrestrial vertebrates related to the distance to the mine. Three HQs are presented according with the ratio of exposure to (A)PNEC, (B) NOEC and (C) LC50 toxicity values.

aquatic organisms persisted except for Cu and As, respectively; for terrestrial vertebrates, chronic risk was only detected to mammals for As and Cd, and to birds for Cd and Zn.

The analysis of HQ_{LC50} indicates the risk for acute effects (Fig. 2C). The profile showed by HQ_{NOEC} and HQ_{LC50} figures is similar. However, remarkable chronic-to-acute differences were found for Cd in aquatic organisms and As in mammals. In NB, the highest risk is to aquatic organisms with HQ_{LC50} values > 100 for Cu and Zn. In DS, unacceptable risk of acute effects was only detected to aquatic organisms due to Zn and Cu and to avian due to Zn.

3.4. Classification and ranking of impacts

Finally the screening model evaluated the overall potential impact of As and metals according to the sum of chronic and acute indexes of risk (RIs) associated to every trace element and every target in sites located at the three different distances. According to this model, risk is quantified by the Imls (Fig. 3).

The application of this conceptual model to the scenario studied here showed, in most situations, a concern about the old mining activity on ecological receptors even in the distant sites (Fig. 3). According to the ranking of impacts proposed in Table 1, very high impact, reaching above 9 in the NB, was expected for aquatic organisms due mainly to Zn and Cu. Even at long distances from the mine high impact ($Iml \geq 7$) was obtained for these metals. Also high impact to soil organisms was foreseen in both NB and IDS. However, at DS a low impact index was found for soil organisms because of the lack of acute unacceptable risk. Low impacts were expected for livestock ($Iml < 2$) even at NB distances. Other terrestrial vertebrates

(birds and mammals) were expected to be seriously affected by Cd and Zn concentrations based on the Iml of 7 and 8, (moderate and high impact) in NB and IDS sites. By contrast, at DS Cd and Zn showed low impact values except for birds exposed to Zn due to the contribution of unacceptable acute risk of this metal ($RI = 5$) as a result of its high acute toxicity to birds.

4. Discussion

4.1. Environmental impact method

The screening impact model has been developed as a tool for ranking the environmental potential risks associated to contaminated sites. This model can be applied to any environmental compartment and considers simultaneously chronic and acute exposures to contaminants.

4.1.1. Derivation of the risk indexes

The assignation of RIs to the HQ values is proposed to quantify the potential risks associated to the contaminated sites. The RI consists of two contributions based on the exposure period (Table 1). The first part corresponds to chronic hazards (RI from 0 to 4) and it is derived from HQ_{PNEC} and HQ_{NOEC} . The second part takes into account acute hazards (RI from 5 to 7) and it is based on HQ_{LC50} . The value of each RI scores the weight of the potential risk, the higher index value the higher potential risk. This is different from other approaches where a common score system is used for both chronic and acute risk quantification and an additional parameter is included to consider the time-scale hazard (Finizio et al., 2001). Other approaches have

Expected environmental impacts in the surroundings of the Monica mine

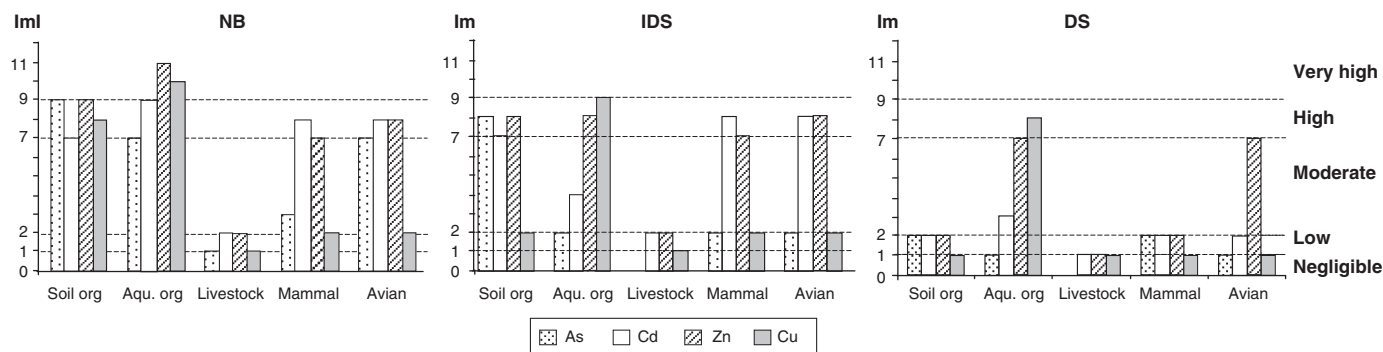


Fig. 3. Expected environmental impacts of As, Cd, Zn and Cu on target organisms in the surroundings of the Monica mine. Classification of environmental impacts is based on the Impact Indexes (ImIs) obtained for the trace elements at three different distance sites.

into account exclusively the value of NOEC (Lu et al., 2003) or LC50 (Sala and Vighi, 2008).

The HQ_{PNEC} covers the potential risk of non-tested sensitive species. The standard inter-species application factor is 10 (EC, 2003), as a consequence, HQ_{PNEC} values lower than 1 means that not enough contaminant concentrations are present for producing any damage, the risk is acceptable and then the RI assigned is 0. A HQ_{PNEC} ranging between 1 and 10, (meaning an exposure level within one order of magnitude above the PNEC) should be identified as a potential risk for sensitive species, RI is 1. HQ_{PNEC} above 10 are expected to be covered by the other reference dose (NOEC, with RI value higher than 1).

Three levels of RI (from 2 to 4) were defined for the reference dose NOEC based on increased 10-fold values according to EC (2003) safety factors. Every step represents a different level of ecosystem protection. HQ_{NOEC} represents a potential long term risk to the most sensitive standard species tested. As a result, the HQ_{NOEC} ranging between 1 and 10 (meaning an exposure level and NOEC are of the same order of magnitude) is associated with a RI of 2. If HQ_{NOEC} is between 10 and 100, according to the inter-species application factor of 10, a potential long term risk is expected for additional species others than the most sensitive. At this point, an alteration of populations resulting in a community impact could occur; in this case the RI assigned is 3. HQ_{NOEC} higher than 100 suggests an extremely serious effects on communities which could affect the ecological structure of the site, and RI equal to 4 is applied.

The potential consequences of short term exposures are categorized by the values of the $HQ_{L(E)C50}$ based on acute toxic effects. The $HQ_{L(E)C50}$ are associated to a real hazard so the highest risk indexes, from 5 to 7 were assigned. Similar to NOEC, the RI values were based on increased 10-fold of $HQ_{L(E)C50}$, according to EC, 2003 safety factors. The $HQ_{L(E)C50}$ data is a sign of the potential for recolonization/recovery of species in the site.

4.1.2. Classification of the impact indexes

The RIs derived from chronic and acute HQs are joined in the impact assessment for the derivation of the ImIs into five categories (see Section 2.1.2). In this sense, ImIs consider both the affectation of species living currently in the site and the potential for colonization of others which could have disappeared (HQ_{NOEC} and $HQ_{L(E)C50}$ contributions, respectively).

ImI of 1 or lower is obtained when the environmental concentration is equal or lower than the PNEC value. In this case, the impact is likely “negligible”.

ImI lower or equal to 2 is obtained only in terms of chronic potential risk for the most sensitive tested species. In this state other species belonging or not to the same taxonomic group but with similar functions in the ecosystem, can replace it. In addition, no acute

effect is detected allowing the recolonization of the zone by species coming from adjacent zones; consequently “low impact” is expected.

Total ImI lower or equal to 7 can be reasonably obtained when the most sensitive tested species is subject to chronic and acute exposure ($RI_{chronic} + RI_{acute} = 5$). In this situation, chronic and acute affectation of the most sensitive species is identified, and accordingly “moderate impact” is expected.

ImI lower or equal than 9 are obtained with the suspicion of undesirable community effects under both time scales chronic and acute ($3 + 6$) or in terms of serious potential chronic harm of the ecosystem structure and also acute effects of sensitive tested species ($4 + 5$). In both situations the risk associated to the long term exposures is high and the potential for colonization is doubtful. As result, based on the probable ecosystem damage the impact category assigned is “high impact”. The mathematical combination of RI ($2 + 7$) was not considered because $L(E)C50$ value 5 orders of magnitude greater than NOEC for the same contaminant is very unlikely.

Impact index values higher than 9 implicate possible chronic effects affecting both the ecological structure of the site and the recovery of a range of species. Under this situation the impact provoked by the contamination is so high that the recovery of the zone without a previous cleaning of the site would be compromised. Hence, the impact category is stated as “very high”.

4.2. Application of the environmental impact method

4.2.1. Exposure assessment

As expected, exposure levels for birds and mammals through food (DDfood) was highly dependent on the source of food (plants or worms) and the relative importance of the bioconcentration factor of plants and earthworms. BCF varies depending on soil type and soil concentrations up to 50-fold or higher within the same metal (Ma, 1982; Wright and Stringer, 1980; Fairbrother et al., 2007). Consequently, values of BCFplants were determined site-specific in order to reduce the uncertainty of risk of metals associated with the food transfer. BCFplants also depends on plant species, thus, plants naturally living in the site were used. The high mobility in the field demonstrated by earthworms complicates relating element soil concentration to worm body concentration to obtain bioconcentration factors. Hence, BCFworms for As and metals was obtained from a laboratory assay performed in columns at different soil concentrations under controlled conditions.

In the case of As, BCFplants (0.0023–0.0075) and BCFworms (0.17–0.38) differed strongly which meant, accordingly, much higher exposure levels for vermivores (wren and shrew) than for herbivores (pigeon and vole) (Table 6). For metals, BCFplants values are similar or slightly higher than BCFworms, hence DDfood was determined by the corresponding FIR/W values. Thus, the exposure to metals for

animals feeding on plants was higher than those feeding on worms according to the higher FIR/W for herbivores with the exception of sheep.

The estimation of exposure through accidental soil ingestion was improved using the BacF. This factor allows correcting metal absorption in gut from soils (Ollson and Koch, 2009). Its importance depends on the manner in which an element occurs in soils. In mine sites, As and metals are present in poor soluble forms and consequently, their bioaccessibility is expected to be low (Ruby et al., 1999). In general, values of bioaccessibility were very low except for Cu, indicating low release from soil under gastric conditions (Table 4). Consequently the incorporation of this factor allowed reducing uncertainty and obtaining more realistic risk estimations (Ollson and Koch, 2009).

4.2.2. Risk assessment

In NB and IDS (Fig. 2), soil organisms are expected to suffer acute effects both to species and to the community due to the presence of As and Cd, and Zn, respectively. In this zone the natural recovery could be threatened since survival of species is endangered and essential soil functions cannot be guaranteed. In DS, risk of long term effects for standard species of soil was detected caused by As, Cd and Zn. For As and Zn, values of NOEC (10 and 17 mg/kg d.w., respectively) were lower than naturally occurring levels (51 and 85 mg/kg d.w., respectively) described by De Miguel et al. (2002). Consequently, chronic effects to standard species were detected which may lead to an overestimation of risk. One method of obtaining more realistic risk estimation is to quantify the fraction of metals in soils that is really bioavailable. However, at present a method which allows correlating toxicity to soil organisms and bioavailable fraction in soil is not generally admitted (Berthelot et al., 2008; McLaughlin et al., 2000). Moreover, the sensitivity of metal bioavailability to temporal changes in soil conditions complicates the use of models based on the free ion activity or extractant solutions. Therefore, risk assessment based on total concentration seemed more appropriate in this first stage. Consequently, to exceed such levels does not mean that a high risk exists but that a site-specific risk assessment may be needed (Fairbrother et al., 2007).

For the aquatic compartment the total As and metal concentrations in the water column was used assuming the worst case situation. The risk assessment showed a potential risk due to acute effects even in distant zones, as a result, mainly, of Zn and Cu exposure. In NB, $HQ_{L(E)C50}$ values higher than 100 were estimated. Consequently, unacceptable risk of acute exposure affecting to aquatic ecosystem could be expected. Similar to soil organisms, refinement for the aquatic organisms should be based on bioavailability since stream characteristics such as pH, hardness, organic content and suspended solids levels can significantly affect element exposure to affected organisms.

For the terrestrial vertebrates Cd and Zn were the most concern. Cadmium can be bioaccumulated and biomagnified through food chains (Chen and Liu, 2006). In this work, high HQs were estimated as a consequence of its high toxicity to mammals and birds and its bioconcentration in plants and worms ($BCF > 1$) in spite of the fact that Cd soil concentration was the least. It is remarkable, the high HQ values to mammals and birds obtained for Zn, in spite of Zn together with Cu are essential elements and auto-regulated in plants, invertebrates and vertebrates. BCFs for zinc were lower than 1 for plants and earthworms, however, due to the high Zn soil concentrations, high Zn levels were detected inside plants growing in the zone with values in the range of 30–708 mg/kg shoot d.w. (Moreno-Jiménez et al., 2009) and in worms (246–1330 mg/kg d.w.), as measured in this work. Consequently, high Zn DDfood (Table 6) and hence high HQs were detected for terrestrial vertebrates. Potential risk to livestock was lower than to mammals and birds due to the lower exposure through food.

Data for terrestrial vertebrates were based on worst case estimations which assume that wildlife consumes 100% of their diet from the contaminated sites. This is not an actual case because birds and mammals use a large territory to develop their activity. Risk related to a more realistic situation; feeding habitats, composition of diet and time spent on each of the different zones (NB, IDS and DS) should be considered in order to obtain a closer and more accurate definition of concerns.

4.2.3. Impacts categories

The site study showed that As and metals may cause from low to high impacts in the whole area studied affecting at all potential receptors (Fig. 3). The only exception was As and Cu to livestock at all distance sites, where Iml of 1 or lower were obtained.

According to the proposed classification, the ecosystem in the NB sites was affected by very high impact to the aquatic compartment due to Zn and Cu, and high impact to soil organisms (all elements) and to avian and mammals due to Cd and Zn. For livestock the impact was low for all elements.

At IDS high impact was expected to all organisms except for livestock. One special case was identified for Cd in aquatic organisms (Iml of 4). According to the proposed method, a structural damage in the ecosystem was expected as a result of exclusively long term exposures. This situation could be of high concern depending on the affected species, the endpoint and the type of effect. The extent of the damage would need additional assessment to classify the impact as moderate or high having also taken into account that no acute consequences were identified and the replacement of affected organisms by others from adjacent areas is possible.

At DS low impact was detected to all organisms with the exception of aquatic organisms as result of Cd and Zn (moderate impact) and Cu (high impact) and avian in the case of Zn (moderate impact).

These results could be over protective due to all values were calculated under the worst case assumption. In other words, the most sensitive endpoints of the most sensitive species within a group, only one type of contaminated food rather than a distribution of items in the diet and the continued stay of species in the site were selected to determine the possible impacts (risk). In addition, the assessment was based on the total soil and water concentrations. The bioavailable fraction and trace element speciation could be considered key factors for a more realistic approach. The accurate application of the method requires extensive toxicity data. The limited database addressing toxicity for soil organisms was a source of uncertainty for As (soil organisms). Therefore, following the usual risk assessment methodology, a refinement of HQs based on more realistic exposure and/or toxicity assessment is advisable prior to further intervention.

The criteria to define different levels of risk and impact indexes have been arbitrary. This limitation is common to any classification based on scores values. They are based in our knowledge of environmental risk assessment and it is proposed as a tool to be sustained in the future by scientific validation.

Despite of the importance of the associated uncertainties to the above issues, we consider that this approach is a good method to classify risk to sites because it includes relevant exposure routes and toxicity data. The method could be very useful for comparative purposes and it is of universal application.

5. Conclusions

The proposed method is an attempt to integrate traditional risk assessment approaches with real variable environmental characteristics at local scale. The strength of the method is that integrates in an only value (impact index): element concentrations in the environmental compartments, element toxicity and other factors affecting exposure levels. Another advantage is that it could be applied to any isolated environmental compartment or to a whole area; in addition,

no specific requirements other than those needed for traditional risk assessment are necessary. The model is intended to represent the first stage and proposes a scientific and systematic tool to identify and prioritize main expected impacts in order to take action measures. However it still requires further refinement and experimental validation for a realistic assess of damage to the ecosystems.

The application of this impact quantification tool to the mining area indicated that the current presence of As and metals in the site may cause impacts that affect at all potentially receptors in the whole area studied with the exception of livestock. The high impact indexes suggest an ecosystem where most of biological species and in some cases even the whole ecosystem would be seriously affected. Moreover, the recovery of the zone could be seriously compromised. To reduce uncertainties generic and specific information data are required. Further refinements would include, at least, bioavailability assays together with feeding habits and behaviour of species. The knowledge of chemical speciation should be included when the cutting-edge analytical methodologies are more accessible.

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