



Potential release and bioaccessibility of metal/loids from mine wastes deposited in historical abandoned sulfide mines[☆]

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ABSTRACT

This study deals with the potential release of metal/loids from sulfide mine wastes upon weathering and the health risks associated with their accidental ingestion. To address this, a complete chemical and mineralogical characterization of a variety of sulfide mine wastes was performed alongside a determination of metal/loid bioaccessibility through leaching tests simulating human digestive and lung fluids. The mine wastes consisted predominantly of Fe (35–55% of Fe₂O₃) and exhibited high concentrations of trace metalloids such as As (382–4310 mg/kg), Pb (205–15,974 mg/kg), Cu (78–1083 mg/kg), Zn (274–1863 mg/kg), or Sb (520–1816 mg/kg). Most wastes with high concentrations of soluble compounds are considered hazardous according to the European regulations due to the exceedance of threshold values for As, Pb, Cr, Cu, Sb, sulfates, and Zn determined by standardized tests. In general terms, the absorption of waste-hosted metals through both digestive and respiratory routes was low compared to the total metal contents of the wastes, with values below 8% of the total concentration in wastes for most metal/loids including Cu, Zn, As, Cd, Tl, or U. However, some metals exhibited a significantly higher absorption potential, especially through the respiratory route, reaching values of up to 17% for Cr and 75% for Pb, highlighting the strong bioaccessibility of Pb in certain sulfide wastes. Despite the high metal/loid concentrations observed in the studied wastes, a health risk assessment indicated that some non-carcinogenic effects could be observed in children only following the accidental digestion of Pb.

1. Introduction

Mining activity has played a pivotal role in obtaining raw materials to maintain the economic growth of territories worldwide. However, over the years, mining activities have had a serious impact on the environment, especially in the past, with the generation and accumulation of huge amounts of wastes, in most cases dumped close to the mine areas without the implementation of any restoration measures. These wastes are exposed to weathering, being leached during rainfall events or transported by winds leading to their resuspension and deposition as fine particles even at large distances, thereby turning them into potential sources of pollution. Therefore, a complete

characterization of reactive minerals and their dissolution during their interaction with weathering agents is needed to estimate their pollutant capacity (Jamieson et al., 2015). Metals released into the environment from these wastes may also cause adverse health effects to humans through different exposure pathways such as ingestion or inhalation. In this sense, the dispersion of mine waste particles through air is a significant contributor of contaminants to the environment (Plumlee and Morman, 2011). Resuspended metal-rich particles can be deposited in the upper respiratory system and pass through the digestive system where metals may be absorbed depending on their bioavailability. In this sense, the term bioaccessibility has traditionally been defined as the portion of the total intake of pollutants available for absorption into the

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human body by different routes (Nathanail et al., 2005). Children in particular have been identified as susceptible targets of metal uptake through hand-to-mouth action (e.g., Hwang et al., 1997; Morman et al., 2009).

Therefore, the human exposure to metals from dumped wastes should be studied, especially in historical abandoned mines. In recent years, numerous studies (e.g., Ettler et al., 2019, 2020; Yin et al., 2021; Wang et al., 2022) have evaluated the mobility and bioaccessibility of metal/loids from mining wastes, highlighting the risks associated with their exposure. These risks are aggravated if metal-rich wastes such as those generated through sulfide mining are considered. Van Veen et al. (2016) studied the implementation of a new test for assessing plant bioaccessibility in sulfide wastes and soils based on their oxidation by H_2O_2 and subsequent metal/loid complexation with ammonium acetate. Ehlert et al. (2018) studied the As bioaccessibility from Fe–As precipitates formed through sulfide oxidation processes. However, information regarding sulfide mine wastes is generally scarce. Thomas et al. (2018) and Loredo-Portales et al. (2020) studied the metalloid bioaccessibility of particulate matter from sulfide mine tailings. Recently, Helsler et al. (2022) and Helsler and Cappuyns (2022) reported on the environmental and health risks associated with sulfide mine wastes through static and kinetic tests. Thus, bioaccessibility studies should be performed on wastes deposited in abandoned sulfide mines worldwide, paying particular attention to the mineralogy of these wastes. Indeed, Molina et al. (2013) highlighted the importance of mineralogy on the release of metal/loids and bioaccessibility. A representative example of this can be found within the Iberian Pyrite Belt (IPB), located to the SW of the Iberian Peninsula, one of the most important polymetallic

sulfide-mining regions in the world; the intense mining in the region throughout history has led to the accumulation of huge amounts of metal mine wastes, with around 4800 ha of the surface being occupied by these wastes only in the Spanish sector of the IPB (Grande et al., 2014) and a total of 20 tailings impoundments containing 109 Mm³ of wastes (Rodríguez-Pacheco and Gómez de las Heras, 2006). These deposits, mainly consisting of pyrite, have been exploited since the third millennium BC, although the more intense mining period only started during the second half of the last century, with the settlement of English mining consortia in the area (Leblanc et al., 2000). These wastes have been intensively weathered, leading to the total deterioration of around 37% of water bodies in the Odiel river basin (Sarmiento et al., 2009) and the complete pollution of the entire course of the Tinto River, which is around 100 km length (Cánovas et al., 2007). Consequently, the main goals of this study are to investigate the response to weathering of a variety of sulfide mining wastes as well as determining the potential bioaccessibility to humans by oral and pulmonary routes of the metal/loids hosted within these wastes. The novelty of this work is that the studied wastes represent common type of wastes generated during the mineral extraction, processing, and metallurgy of sulfides, unlike previous studies that focus on singular cases of wastes. To address it, standardized leaching tests and in vitro bioaccessibility methods were applied to a variety of metal mining wastes.

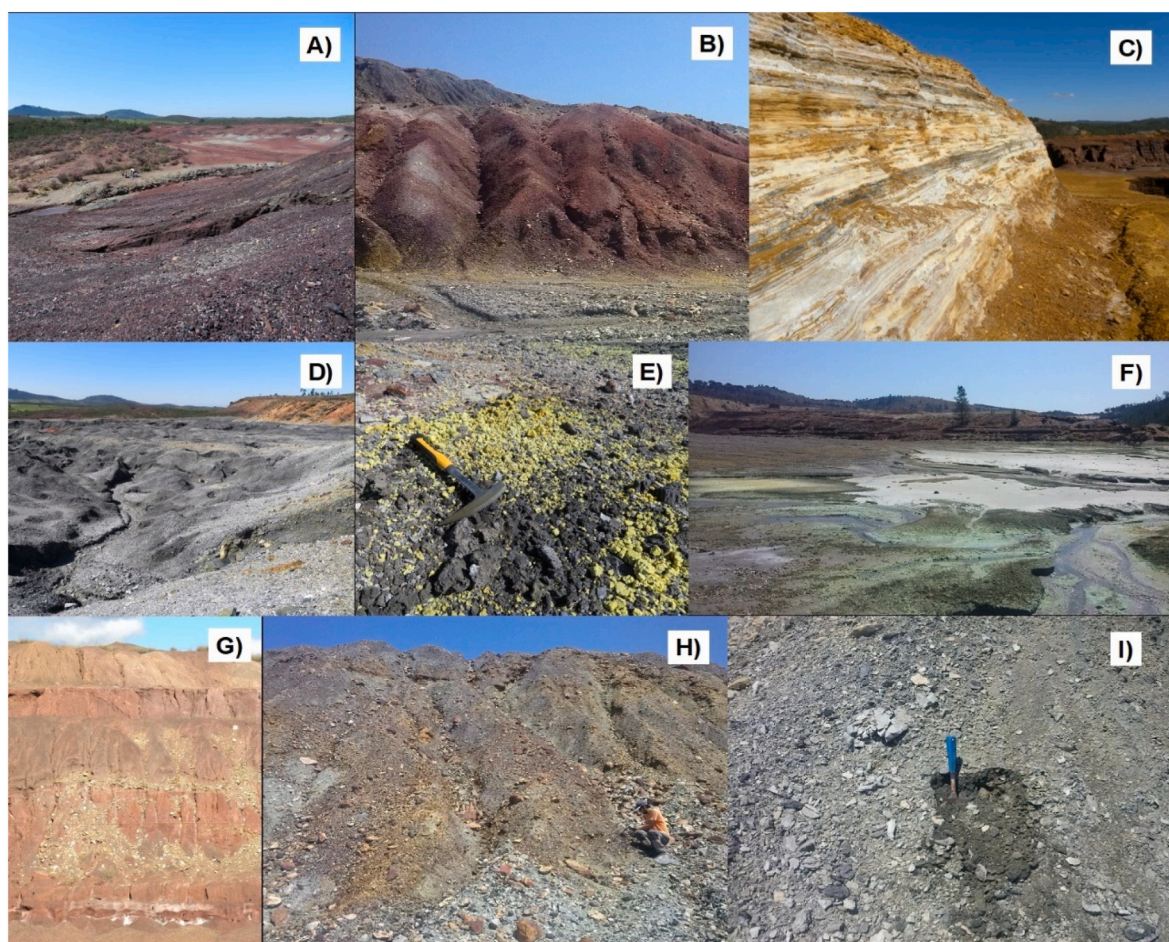


Fig. 1. Images of the mine wastes selected in this study; roasted pyrite wastes (A and B), flotation wastes with different material layers (C), metallurgical wastes (D) with an abundance of elemental sulfur (E), tailings (F), heap leaching wastes (G), and spoil heaps (H and I).

2. Methodology

2.1. Sampling

Different types of sulfide mine wastes were collected from different abandoned mines within the IPB (Fig. 1); these consisted of heap leaching wastes, roasted pyrite, metallurgical wastes, flotation wastes, spoil heaps, and tailings. The geochemical and mineralogical properties of these wastes varied noticeably and mainly depended on the original ore properties, the extraction processes, and the mineral processing methods they had been subjected to. The studied heap leaching wastes resulted from the processing of sulfide minerals to extract Au and Ag following leaching with cyanide solutions. Due to the presence of sulfides, the ore minerals are first commonly leached with high pH solutions ($\text{pH} > 10$) and even roasted to remove S if the sulfide content is too high (Lottermoser, 2010). Roasted pyrite wastes were the final product of the abovementioned roasting process. Thus, large piles of sulfides were grounded and burned in order to remove S, and then, the piles were leached with waters to dissolve the accumulated Cu-rich salts, which were subsequently directed to cementation channels where Cu was extracted by Fe scrap addition. The tailings consisted of solids and liquids resulting from physical (i.e., crushing and grinding) and chemical procedures (i.e., flotation, coagulation/flocculation, etc.) to separate the ore from the gangue minerals. The recovery of valuable minerals is hardly complete, and tailings always contain small amounts of the valuable minerals (Lottermoser, 2010). The studied spoil heaps were sulfide-rich wastes which were extracted but not exploited due to the low concentrations of economically valuable metals in these sulfides. The metallurgical wastes considered in this study were produced after obtaining elemental S and Cu concentrates following the ORKLA process (Salkield, 1987). Thus, the Cu-rich pyrites were smelted in an enclosed blast furnace, designed to prevent the ingress of air, and to recover both mattes (molten sulfides) and elemental S. The pyrites, fluxes, and coke were added, and after smelting, the labile S was distilled off, retained by electrostatic precipitators, and cooled to condense the S. Thus, the studied metallurgical wastes resulted from the cleaning of the furnace and the precipitators. Finally, the flotation wastes considered in this study comprised the residues from two different processes; i) the extraction of Au from Au-rich pyrites by cyanide leaching and ii) the extraction of Cu through the flotation of Cu-rich sulfide minerals. These different treatments led to the pronounced heterogeneity of the accumulated wastes. Composite samples of approximately 2 kg were collected at each site using a polypropylene shovel which had previously been cleaned with distilled water and alcohol. The first few cm of material were removed during sampling to collect fresh materials only. The samples were then stored in sterile polypropylene bags, taken to the laboratory, and dried at room temperature to avoid mineralogical changes. The samples were subsequently powdered in a ring mill and stored prior to chemical and mineralogical analyses.

2.2. Analytical determinations of wastes

The bulk major and trace element compositions of the samples were determined at MS Analytical (Langley, Canada) following a multi acid digestion procedure using a mixture of HCl, HNO₃, HClO₄, and HF. Then, the acid solutions were analyzed by inductively coupled plasma optical emission spectroscopy (ICP-AES) for major elements and inductively coupled plasma mass spectrometry (ICP-MS) for trace elements. The analytical accuracy was verified with the analysis of reference materials (OREAS 904), with recoveries ranging from 96 to 104%, while the analytical precision was assessed by duplicate analysis, showing differences below 5% for all elements.

2.3. Weathering simulation

The response of the different wastes to rainfall weathering was

investigated following the EN 12457-2 leaching protocol (CEN, 2002), based on the contact of distilled water with wastes (ratio 1:10) through continuous agitation for 24 h. Although other approaches seek to accelerate oxidation processes in sulfide wastes by adding strong oxidants (e.g., Silva et al., 2011), the contact with water may simulate weathering after rainfall more reliably. This test has traditionally been performed to evaluate whether wastes, including different types of mine wastes, were suitable for disposal in European landfill sites (e.g., Vemic et al., 2015; Macías et al., 2017; Cánovas et al., 2019). The solutions were subsequently filtered at 0.45 μm using cellulose nitrate Millipore filters, acidified to a pH of <2 , and analyzed at the R + D Services of the University of Huelva using ICP-AES (Jobin Yvon Ultima 2) for major elements and ICP-MS (Agilent 7700) for trace elements. The detection limits were 0.2 mg/L for S; 0.1 mg/L for Na; 0.05 mg/L for Fe, K, Mg, and Si; 0.02 mg/L for Al and Ca; and 2 $\mu\text{g/L}$ for the trace elements. The analytical precision was checked by triplicate analyses of the selected samples with values below 5% in all cases. Blanks were also analyzed in each analysis sequence, with all elements below the detection limit. The analytical accuracy was evaluated by the analysis of reference materials (NIST-1640) and home-made solutions, with differences below 6% between these and the referenced concentrations.

2.4. Bioaccessibility studies

In vivo methods to evaluate oral bioaccessibility are time-consuming and expensive. In this sense, in vitro methods have previously been performed and successfully validated against in vivo bioassays (Monneron-Gyurits et al., 2020). These protocols aim to mimic the processes of metal absorption in human bodies by assessing the fraction of metals released from ingested substances. The estimation of metal bioavailability from the deposited mine wastes was performed by applying the Physiologically Based Extraction Test (PBET) developed and validated by Ruby et al. (1993), simulating the absorption of metals/metalloids during the accidental ingestion of wastes. Thus, a solution mimicking human bile acids was prepared, consisting of 0.15 M NaCl, 0.5 g citrate, 0.5 g malate, 0.42 mL lactic acid, 0.5 mL acetic acid, and 1.25 g pepsin, which was adjusted to a pH of 1.5 with 12 M HCl. Then, 0.3 g of waste was put into contact with 30 mL of the prepared gastric solution (waste/solution ratio of 1:100) in duplicate in 50 mL polypropylene centrifuge tubes. The samples were shaken at 150 rpm and incubated at 37 °C for 1 h, simulating the digestion of matter by gastric acids in the human stomach. One aliquot was subsequently centrifuged and the supernatant was separated, filtered, and preserved until analysis. Then, NaHCO₃ was added to the second aliquot until a pH of 7 was reached, and bile salts (1.75 g/L) and pancreatin (0.5 g/L) were added to the samples thereafter. Finally, the samples were shaken at 150 rpm and incubated at 37 °C for 4 h, simulating the intestinal phase of human digestion.

The exposure of humans to inhalable mine waste particles was also investigated using an Artificial Lysosomal Fluid (ALF) and Gamble's solution (Colombo et al., 2008). Once released into air, particles may be inhaled by humans and stay in two different lung compartments: the extracellular environment characterized by lung fluids with a neutral pH and the more acidic intracellular environment within macrophages. Thus, the ALF would mimic the fluid in contact with inhaled particles after phagocytosis by alveolar and interstitial macrophages in the lung while the Gamble's solution would represent the interstitial fluid deep within the lung (Colombo et al., 2008). These fluids have previously been used to investigate the bioaccessibility of Co compounds (Stopford et al., 2003), Cu release from powder particles (Midander et al., 2007), and the metal release from stainless steel (Herting et al., 2007). The compositions of both lung solutions are listed in Table SM1. Although the $<10 \mu\text{m}$ particle fraction would commonly be the most desirable for inhalation bioaccessibility tests, the $<20 \mu\text{m}$ fraction was used here, following previous bioaccessibility studies (e.g., Guney et al., 2017; van der Kallen et al., 2020). Then, the samples were analyzed with an

Agilent 8800 triple quadrupole inductively coupled plasma mass spectrometer (ICP-QQQ-MS) following a specific protocol for organic matrices. In brief, the samples were diluted ten-fold with ultrapure water obtained from a water Purification System (Milli-Q Gradient system, Millipore, Watford, UK), and filtered using PVDF filters of 0.45 μm . For the quantification of elements, a 2A multi-element calibration standard solution (10 mg/L, Agilent Technologies) was used to prepare the calibration curves. In addition, 0.1 mg/L of Rh was used as internal standard. A Trace Element Control (Trace Element, Urine, Level II, RECIPE) was treated and analyzed using the same conditions as the samples to check the variability and reproducibility of the analysis. The percentage of the Bioaccessible Fraction (% BAF) represents the amounts of metals/metalloids released during the passage of materials through the digestive and respiratory routes, and can be calculated as follows:

$$\% \text{ BAF} = B_c / T_C \times 100$$

where B_c is the bioaccessible concentration (mg kg^{-1}) in the digestive or respiratory phase of the ingested phase from the mine waste and T_C is its total concentration (mg kg^{-1}).

2.5. Human health risk assessment

The human health risk posed by metal intake can be assessed through different methods. Among them, the daily intake calculation helps quantify the accidental metal ingestion of soil particles for children (2–6 years) considering their known sensitivity to metal uptake. This approach is based on calculating the daily metal intake (DI, $\mu\text{g metal kg}^{-1}$ of body weight [BW] d^{-1}) from the incidental ingestion of topsoil, expressed based on both the total and bioaccessible concentrations ingested through the oral and respiratory routes:

$$DI_{\text{oral}} = MC \cdot \frac{IR_o \cdot EF \cdot ED}{BW \cdot At}$$

$$DI_{\text{res}} = MC \cdot \frac{IR_r \cdot EF \cdot ED}{BW \cdot At \cdot PEF}$$

where MC is the metal/loid concentration (mg/kg); IR_o and IR_r are the ingestion rates via oral and respiratory routes, established as 200 mg d^{-1} and $5 \text{ m}^3 \text{ d}^{-1}$, respectively, for a 2–6 year old child (Adimalla, 2019; U.S. Environmental Protection Agency, 2011); EF is the exposure frequency (180 days yr^{-1} ; Hu et al., 2011); ED is the exposure duration (6 years); BW is the body weight, defined as 17.8 kg for a 2–6 year old child (U.S. Environmental Protection Agency, 2011); At is the averaging time (i.e., $6 \text{ yr} \cdot 365 \text{ days}$); and PEF is the particle emission factor ($1.36\text{E}+09 \text{ m}^3/\text{kg}$; U.S. Environmental Protection Agency, 2011).

2.6. Mineralogical characterization of wastes

The mineralogical composition of the mine wastes was determined by X-ray diffraction (XRD). The patterns of XRD in powder samples were acquired at the R + D Services of the University of Huelva using a Bruker D5005 X-ray diffractometer employing Cu K α radiation. The selected settings were 40 kV, 30 mA, a scan range of 3–65° 2 Θ , 0.02° 2 Θ step size, and 2.4 s counting time per step. Semi-quantitative chemical analyses and sample imaging were also conducted using a scanning electron microscopy coupled with energy dispersive spectroscopy (SEM-EDS; FEI-Quanta 200 equipped with an EDAX Genesis 2000 microanalyzer).

3. Results and discussion

3.1. Chemical and mineralogical composition of mine wastes

The chemical and mineralogical properties of wastes collected in this study are presented in Table SM2. The mine wastes predominantly

consisted of Fe, with Fe_2O_3 contents ranging from 35 to 55%, except in the case of the metallurgical wastes which exhibited very low Fe_2O_3 values (less than 1%; Table SM2). The SO_3 contents of the wastes were also considerable, especially in the tailings, spoil heaps, and metallurgical wastes, with values exceeding 25% of SO_3 ; minor SO_3 values were obtained for the roasted pyrite, heap leaching, and flotation wastes (values from 2.9 to 7.0%). These lower values may be related to the different mineral processing techniques. For example, the roasted pyrite, heap leaching, and flotation wastes were thermally treated to remove the S and enhance the extraction of target metals. The Al, Ca, Mg, Na, or K contents in these wastes were generally much lower than the Fe and S concentrations (e.g., 0.17–4.36% of Al_2O_3 , 0.01–1.1% of CaO and MgO, 0.03–0.59% of Na_2O , and 0.04–0.88% of K_2O). The studied wastes also exhibited high concentrations of trace metal/loids (Table SM2), such as As (from 382 to 4310 mg/kg), Pb (from 205 to 15,974 mg/kg), Cu (from 78 to 1083 mg/kg), Zn (from 274 to 1863 mg/kg), Sb (from 520 to 1816 mg/kg), and Sn (from 28 to 420 mg/kg). These chemical compositions reflect the mineralogical compositions of the wastes, as evidenced by the XRD patterns obtained. The heap leaching wastes mainly consisted of Fe minerals such as goethite, hematite, and jarosite, accompanied by quartz and gypsum. The XRD patterns of the tailings and spoil heaps revealed the occurrence of pyrite and quartz. On the other hand, the flotation wastes presented a wide variety of Fe minerals, including oxides/hydroxides (i.e., goethite, hematite), hydroxysulfates (i.e., jarosite), and evaporitic sulfates (i.e., szomolnokite and parabutlerite), together with barite and quartz. Finally, the mineralogical assemblage of metallurgical wastes included predominant elemental sulfur and anglesite, as well as quartz (Table SM2). However, XRD only provides information on minerals displaying crystal ordering, and therefore, amorphous secondary minerals could not be identified.

3.2. Response to rainfall and hazards classification

Mine wastes in abandoned mines, especially in historical mining districts, are commonly dumped without any restoration measures and therefore, they are exposed to atmospheric conditions. Under these circumstances, rainfall events are important drivers of metal/loid pollution in surrounding water bodies. Table SM3 and Fig. 2 and SM1 show the results of the EN 12457-2 leaching test performed on the samples. Our results reveal that the wastes showed different levels of reactivity during the leaching test, characterized by a significant release of dissolved solids (expressed in EC values) from spoil heaps ($8060 \mu\text{S/cm}$) and tailings ($7140 \mu\text{S/cm}$); a smaller amount of dissolved solids were released from roasted pyrite ($3215 \mu\text{S/cm}$), flotation wastes ($2598 \mu\text{S/cm}$), heap leaching ($1869 \mu\text{S/cm}$), and metallurgical wastes ($1587 \mu\text{S/cm}$; Fig. SM1). This reactivity is also evidenced by the release of high concentrations of sulfate (from 6053 to 119,221 mg/kg) and metal/loids such as Fe (up to 24,029 mg/kg), Al (up to 2903 mg/kg), Zn (up to 632 mg/kg), Cu (up to 569 mg/kg), Cr (up to 176 mg/kg), As (up to 133 mg/kg), Pb (78 mg/kg), or Mn (up to 63 mg/kg).

Regardless of their typology, most wastes released significant concentrations of Fe, sulfate, Al, Zn, Cu, or As (Table SM3). However, in the case of the heap leaching wastes, the release was only noticeable for sulfate (9898 mg/kg), exhibiting the lowest values of release for most metal/loids (e.g., 28 mg/kg of Zn, 11 mg/kg of Mn, 1.93 mg/kg of Al, 1.05 mg/kg of Cu, or 0.52 mg/kg of Fe; Table SM3). This may be related to the mineral processing these wastes underwent. In this case, the addition of sodium cyanide and lime produced an alkaline environment in which the mobility of metals was low, unlike for the rest of the studied wastes which were associated with sulfide oxidation promoting an acidic environment and thus enhancing the mobility of metals. As shown in Fig. SM1, the pH of the leachates was strongly acidic for most wastes (values from 2.19 for spoil heaps to 3.73 for flotation wastes) while exhibiting near neutral values (pH of 6.79) for the heap leaching wastes. This fact is also evidenced by the high release of Na (up to 50% of total Na; Fig. SM1) from the heap leaching wastes due to the dissolution of

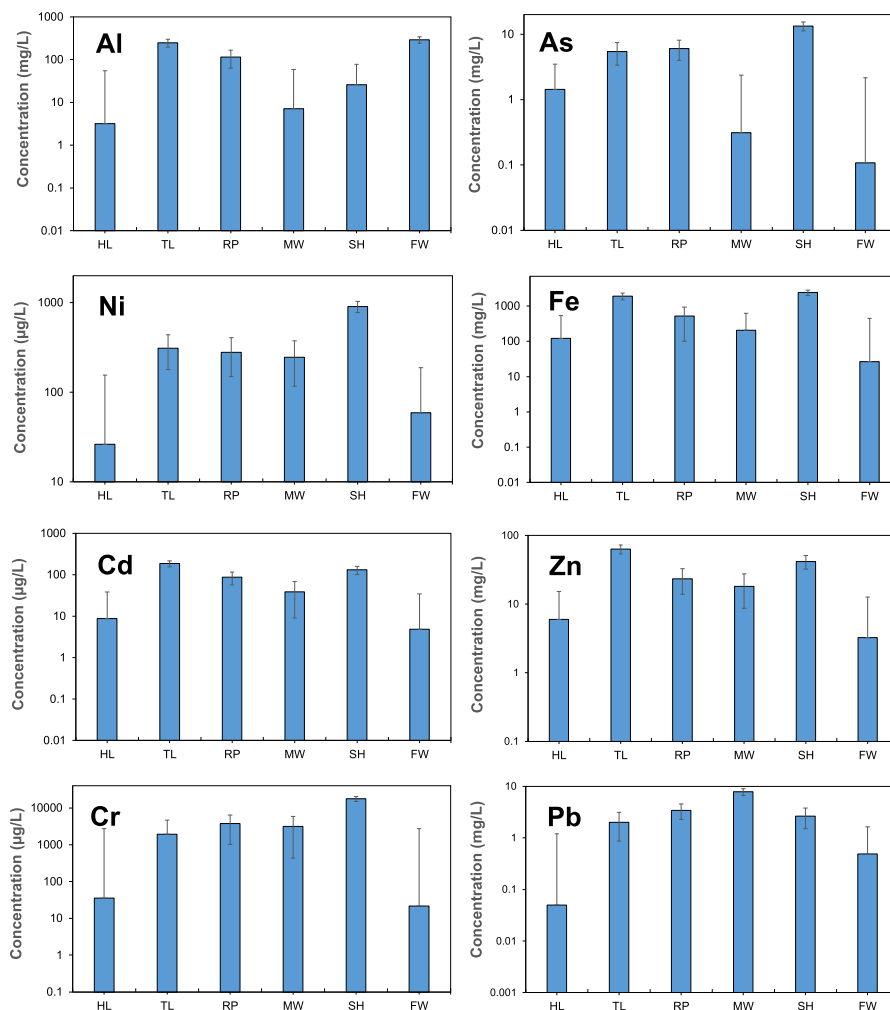


Fig. 2. Concentration of some metals/metalloids during the EN 12457-2 leaching test applied to mine wastes. HL: heap leaching wastes, TL: tailings, RP: roasted pyrite wastes, MW: metallurgical wastes, SH: spoil heap wastes, and FW: flotation wastes.

secondary salts in contact with water.

The hazardousness of these wastes could be determined according to international regulations on waste disposal based on the release of dissolved solids during the leaching test. Thus, the spoil heaps could be considered as hazardous wastes according to the European regulations (EC, 2003) due to the exceedance of threshold values for As, Cr, Cu, Sb, sulfate, and Zn (Table SM3). The tailings, which also exhibited a high reactivity (Fig. SM1) would be also considered as hazardous wastes by surpassing the values for As, sulfate, Cu, and Zn. The same character was observed for the roasted pyrite and flotation wastes, as their compositions exceeded the threshold values of hazardous wastes for As, Cu, and Zn, and sulfate and Cu, respectively (Table SM3). On the other hand, the metallurgical and heap leaching wastes appeared to pose a lower hazard than the other abovementioned wastes. In the case of the metallurgical wastes, only the threshold value of Pb for hazardous wastes was exceeded (Table SM2); the heap leaching wastes should be disposed of among non-hazardous wastes considering the elevated concentrations of As, Sb, Se, sulfate, and Zn (Table SM3). In turn, the rest of wastes should be treated (i.e., neutralized, encapsulated, etc.) before disposal in order to mitigate environmental risks.

The potential release of metalloids from wastes in contact with water could be quantified considering their total content in mine wastes (Figs. SM2 and SM3). Despite the high Fe concentrations of mine wastes, Fe release was below 10% for most wastes, except for the metallurgical ones, which released around 47% of the total Fe contained within them.

Other metals hosted within the wastes such as Mn, Cu, Zn, Ni, Cr, and Cd were released in considerable amounts upon contact with water, with values ranging from 18 to 52% for Cu, 13–44% for Mn, 14–41% for Zn, 20–42% for Ni, 19–46% for Cr, and 20–31% for Cd (Figs. SM2 and SM3). In contrast, the heap leaching wastes exhibited a noticeably lower release (below 7%) of all metal/loids. A low release of metal/loids such as As, Pb, Mo, Sb, Sn, and Se was observed for the studied mine wastes. For example, the release of As did not exceed 6%, with the highest values recorded for the roasted pyrite and heap leaching wastes (Fig. SM2). In the case of Pb, the release rate was even lower, with values below 0.35%. The low mobility of both of these metal/loids in the secondary minerals of sulfide wastes has been widely reported in the literature (e.g., Roussel et al., 2000). Low release rates were also observed for Sb and Mo (with only 4% of release for spoil heaps; Figs. 2 and 3), Sn (release below 0.1% of the total content), and Se (below 3%). On the other hand, it is remarkable that despite the low concentrations of V, Tl, or U found in these wastes (Table SM2), these elements were released in significant amounts from some wastes; up to 19% of the total V from spoil heaps, 15% of Tl from metallurgical wastes, and around 20% of U from spoil heaps and roasted pyrite wastes (Figs. SM2 and SM3).

3.3. Bioaccessibility of metals through oral and respiratory routes

Although some metals such as Co, Cu, Cr, Fe, and Zn are considered essential for humans in trace amounts, the enhanced absorption of these

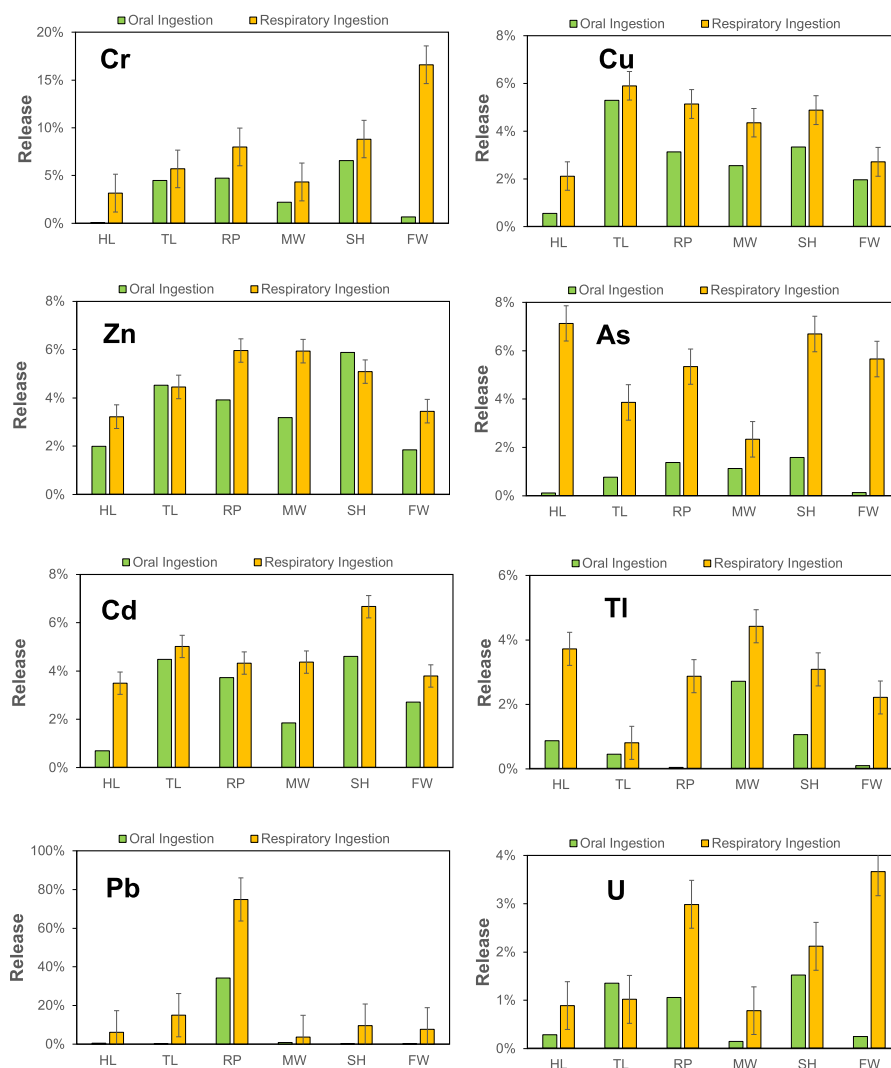


Fig. 3. Bioaccessibility fraction (BAF) of selected metal/loids hosted in mine wastes ingested via digestive and respiratory routes. HL: heap leaching wastes, TL: tailings, RP: roasted pyrite wastes, MW: metallurgical wastes, SH: spoil heap wastes, and FW: flotation wastes.

metals may lead to serious health problems. In turn, other metal/loids such as As, Cd, Pb, or Tl are not essential and may have toxic effects in humans even at low concentrations (Plumlee and Ziegler, 2003). Table SM4 shows the bioaccessibility of selected metal/loids through different routes (i.e., digestive and respiratory) according to their toxicity or abundance in mine wastes. Regarding the digestive route, enhanced absorptions of Cu and Zn were observed, with values ranging from 2.9 mg/kg to 57 mg/kg and from 5.0 mg/kg to 84 mg/kg, respectively; the maximum values represent the concentrations of metal/loids released from tailings samples and to a lesser extent spoil heaps. High concentrations of Pb (from 3.3 mg/kg to 383 mg/kg) and As (1.3–30 mg/kg) were also observed in the solutions mimicking stomach and intestine fluids. While As was preferentially released from spoil heaps and tailings, Pb was chiefly liberated from metallurgical and roasted pyrite wastes. Spoil heaps also liberated significant concentrations of Cr (25 mg/kg) in the simulated digestive fluids, with a moderate release from tailings, roasted pyrite, and metallurgical wastes (from 2.2 to 4.5 mg/kg; Table SM3). A lower absorption was observed for other metal/loids such as Cd, Tl, and U, with most values not exceeding 1 mg/kg. While most metal/loids were preferentially absorbed during the gastric phase of digestion, the intestinal phase could also be important during the potential absorption of some metals/metalloids such as As, Tl, or Cu (31–48% of digestive ingestion; Fig. SM4). It is worth noting

that the metal/loids released during the gastric phase together with those released during the intestinal phase can potentially be absorbed into the blood system within the intestinal tract (e.g., Ruby et al., 1996; Tharankan et al., 2010).

In the case of the respiratory route, the metal/loids exhibiting a higher potential absorption in lung fluids were Pb and As. The highest potential absorption of Pb was observed for tailings (1801 mg/kg) and metallurgical wastes (1731 mg/kg), followed by spoil heaps (1009 mg/kg), roasted pyrite (479 mg/kg), heap leaching (135 mg/kg), and flotation wastes (91 mg/kg). A similar potential absorption trend was observed for As, but with significantly lower concentrations (from 103 mg/kg to 28 mg/kg). Tailings (63 and 84 mg/kg, respectively), and to a lesser extent spoil heaps (31 mg/kg and 70 mg/kg, respectively) and roasted pyrite (36 mg/kg and 35 mg/kg, respectively) wastes also released significant concentrations of Cu and Zn when in contact with lung fluids. However, lower amounts were liberated from heap leaching, metallurgical, and flotation wastes (from 2.0 to 22 mg/kg of Cu and from 5.0 to 16 mg/kg of Zn). The potential absorptions of Tl, Cd, and U were also low throughout the respiratory route with values below 1 mg/kg, except for Tl derived from spoil heaps (1.83 mg/kg). Regarding the potential absorption between lung tissues, the potential absorption was predominant in the extracellular tissues of the lungs, with values between 80 and 100% for most metal/loids (Fig. SM4). The potential

absorption by intracellular lung tissues was only predominant for As originating from heap leaching (77%) and metallurgical wastes (55%), and for U from flotation and metallurgical wastes (66 and 62%, respectively).

On the other hand, the potential capacity of a waste to be assimilated by the human body may be established by comparing the absorption of metal/loid with their total contents in the waste. Fig. 3 shows the bio-accessible fraction (BAF) of selected metal/loids passing through the digestive and respiratory routes according to their toxicity or abundance in each waste type. In general terms, the potential absorption of metals hosted in wastes through both the digestive and respiratory routes was low relative to their total contents in the wastes, with values generally not exceeding 8% of the total concentration for most metal/loids (e.g., Cu, Zn, As, Cd, Tl, or U). However, some metals exhibited a significantly higher absorption potential, especially through the respiratory route. For example, the release of Cr from flotation wastes passing through the respiratory route reached a value of 17% of the total. In the case of Pb, around 75% and 34% of the total Pb contained in the roasted pyrite wastes were liberated through the respiratory and digestive routes, which highlights the high bioaccessibility of Pb in this type of waste. For the oral ingestion route, the following order of potential metal/loid absorption was observed: Cr (1.8–5.9%) > Zn (1.8–5.9%) > Cu (0.7–5.3%) > Cd (0.7–4.6%) > Tl (0.1–2.7%) > U (0.2–1.5%) ~ As (0.1–1.6%) > Pb (0.2–0.8%); for the latter however, a high value of 34% was observed when originating from roasted pyrite wastes, as previously indicated. This contrasts with the different bioaccessibility patterns observed by Helsler et al. (2022) who studied sulfidic wastes and distinguished different potential absorption values for the following metal/loids: Cd (13–100%) > Zn (9–69%) > Pb (4–67%) > Cu (8–41%) > Ni (1–37%) > As (1–11%) > Cr (1–9%). These differences may be related to the mineralogy of the mine wastes as pointed out by Schaidler et al. (2007), who studied the mobility and bioaccessibility of Cd, Zn, and Pb in mine wastes at the Tar Creek Superfund Site (USA). These authors observed a high bioaccessibility of Cd, Zn, and Pb (60–100%) through the oral ingestion of carbonate-rich particles, and a very low one for sulfide-rich particles (0–3%).

In the case of the respiratory route, the following order of metal/loid absorption potential was observed: Pb (3.7–74%) > Cr (3.1–17%) > As (3.8–7.1%) > Cd (3.5–6.7%) > Zn (3.2–6.6%) > Cu (2.1–5.9%) > Tl (0.8–4.4%) > U (0.9–3.7%). These values are lower than those reported by Schaidler et al. (2007) for Zn (26–70%) and Cd (45–64%), but higher for Pb (6–16%). However, when compared only with sulfide-rich wastes, the bioaccessibility reported by these authors was lower (e.g., 1.4% for Zn and 0.4% for Pb) than that reported in our study.

3.4. Potential impact of wastes on human health

Table SM5 shows the average daily intake (DI) values calculated for each metal/loid in the bioaccessible fractions of each waste and their comparison with tolerable daily intake (TDI) values, defined as the highest dose that can be ingested on a daily basis for a long time with no observed adverse effects on animals (USEPA, 2021). According to these results, up to 89 µg Pb kg⁻¹ of BW d⁻¹, 10 µg Zn kg⁻¹ of BW d⁻¹, 6.0 µg Cu kg⁻¹ of BW d⁻¹, 24 µg As kg⁻¹ of BW d⁻¹, 2.1 µg Cr kg⁻¹ of BW d⁻¹, 0.33 µg Tl kg⁻¹ of BW d⁻¹, 0.04 µg Cd kg⁻¹ of BW d⁻¹, and 0.013 µg U kg⁻¹ of BW d⁻¹ could be ingested by children following incidental hand to mouth action. In the case of incidental respiratory ingestion, the DI reached values below 0.001 µg kg⁻¹ of BW d⁻¹. Considering the TDI values (Boisa et al., 2013), the DI values for Pb and As through oral ingestion significantly exceeded the established threshold values (1.9 µg Pb kg⁻¹ and 0.30 µg As kg⁻¹, respectively). In the case of pulmonary ingestion by inhalation, the DI values remained below the recommended tolerable limits.

To perform a toxicological evaluation of the studied mine wastes based on the metal (loid) toxicity and their bioaccessibility, the hazard quotient (HQ) was estimated according to Helsler et al. (2022):

$$HQ_{bio} = \frac{(DI \cdot RBA)}{RD}$$

where DI is the daily intake, RBA is the relative bioaccessibility via digestive or pulmonary routes, and RD are the reference doses for metal/loids established by U.S. Environmental Protection Agency (2021) and Hu et al. (2011). Thus, this quotient considers not only the metal/loid daily intake but also its relative bioaccessibility. Fig. 4 shows that despite the high metal/loid concentrations measured in the wastes, most HQ for individual metal/loids exhibited values well below 1, with the highest HQ values found for As (0.08–0.55) and Pb (0.03–3.74). Considering the summation of all studied metal/loids, only the accidental ingestion of roasted pyrite waste particles would lead to non-carcinogenic effects (HQ > 1), mainly due to the contribution of Pb and to a lesser extent As. In the case of the inhalation of particles through the respiratory system, the HQ values were well below 0.001, indicating a low risk of non-carcinogenic effects following the accidental inhalation of these particles.

3.5. Influence of waste mineralogy on the mobility and bioaccessibility of metal/loids

Mineralogy appears to control the release of metals in sulfide mine wastes subjected to weathering conditions (e.g., Cánovas et al., 2019; Jamieson et al., 2015; Molina et al., 2013). Thus, some metal/loids such as Fe, As, Sb, Tl, Pb, or Sn, which are mainly associated with oxides and sulfide phases, showed low release potentials during their contact with

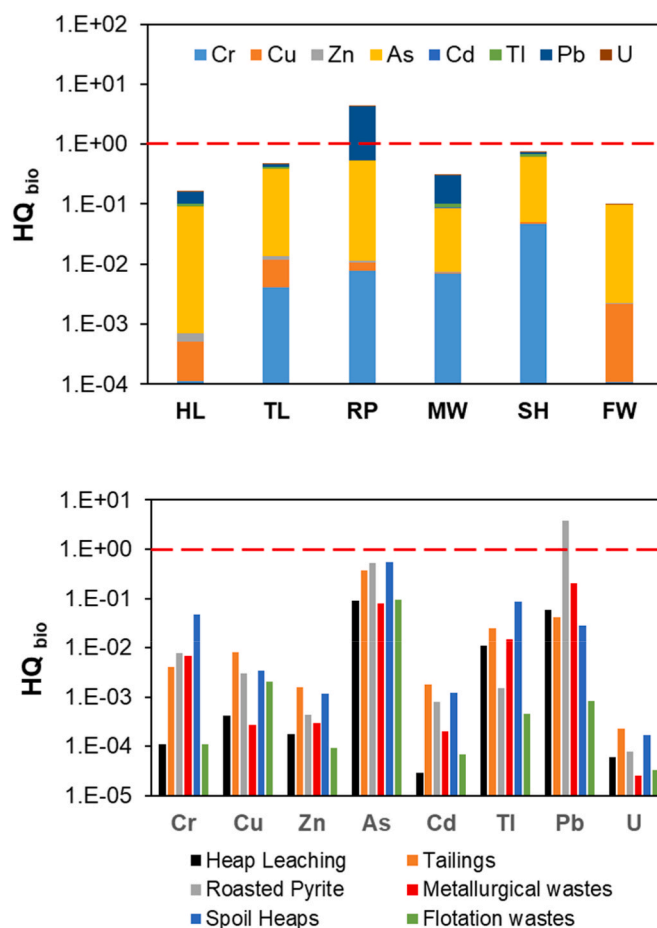


Fig. 4. Human health risk assessment of non-carcinogenic risk for oral ingestion in children (2–6 years old). The samples that pose a potential non-carcinogenic risk (HQ > 1) exceed the dashed line. HQ: hazard quotient.

water (Figs. SM2 and SM3). In turn, some other metals such as Mn, Zn, Cu, Cd, Ni, Co, or Cr were released in significant amounts (20–60%) when in the presence of water (Figs. SM2 and SM3). This fact was also observed by Loredo-Portales et al. (2020), who reported a higher release rate and bioaccessibility of Zn than As and Pb. The release of these metals from sulfide mine wastes appears to be controlled by the dissolution of highly soluble evaporitic sulfates that mainly release Fe, which precipitates in AMD-affected sites (e.g., Buckby et al., 2003; Cánovas et al., 2019; Keith et al., 2001). These minerals are formed through the evaporation of AMD, incorporating other metal/loids such as Cu, Zn, Co, Cr, Mn, or Ni as impurities. Although these minerals were scarcely identified by XRD (except in flotation wastes; Table SM2), a detailed examination of the samples by SEM-EDS allowed the identification of a variety of Fe sulfates (Fig. SM5). The presence of amorphous Fe minerals was also observed by SEM-EDS, and their poor crystallinity may indeed enhance the release of metal/loids. This same conclusion was obtained by Thomas et al. (2018), who linked the higher release efficiency of metal/loids from sulfide tailings to the percentage of soluble sulfates, soluble Fe bearing solids, and the abundance of poorly crystalline Fe minerals. Previous events of mine waste weathering may also enhance the potential release and bioaccessibility of metals/metalloids (Molina et al., 2013; Thomas et al., 2018).

Remarkably, the most mobile metals in wastes, such as Cd, Zn, Cr, and to a lesser extent Ni, Cu, and Mn, displayed a high correlation between total and soluble contents in the studied wastes (R^2 of 0.65–0.99); the least mobile metals/metalloids (e.g., Fe, As, Pb, Al, or U) showed poor or non-existent correlations between both phases (Fig. SM6). The abundance of these secondary minerals in the studied wastes controlled the release of metal/loids upon weathering. Thus, the heap leaching wastes with the presence of alkaline minerals such as calcite and the absence of soluble sulfate salts, released lower amounts of metal/loids than other wastes such as spoil heaps, tailings, and roasted pyrite wastes (Fig. 2; indeed, the intense oxidation of sulfides in the latter waste types led to the formation of high quantities of soluble secondary minerals).

The correlation between the total and bioaccessible concentrations of metal/loids has previously been described by Nathanail et al. (2005). However, these correlations are not necessarily linear since bioaccessibility in soils and wastes may be influenced by metal speciation and the nature of sorption to the soil/waste constituents (Boisa et al., 2013). Thus, bioaccessible metals in mine soils and wastes would be associated to non-mineral bound forms or easily soluble minerals, while less bioaccessible metals would typically be incorporated into the mineral structure of stable minerals. The same conclusion was obtained by Helsler et al. (2022), who reported a high bioaccessibility of Pb through the easy dissolution of cerussite from sulfide mine wastes and a lower bioaccessibility in samples where sulfide minerals predominated. In the studied samples, iron oxides and sulfides predominate over the more soluble minerals, which may limit the metal/metalloid bioaccessibility. Figs. SM7 and SM8 show a comparison between the total and bioaccessible (i.e., oral and respiratory) metal/loid concentrations, revealing a similar pattern for the soluble metal/loid fraction. Thus, high correlations were observed between the total and bioaccessible Cd ($R^2 = 0.91–0.94$), Zn ($R^2 = 0.86–0.93$), Cr ($R^2 = 0.90–0.93$), and Cu ($R^2 = 0.65–0.77$), while lower or no correlations were observed for As and U. However, Tl and Pb exhibited remarkably different behaviors; the total and bioaccessible concentrations of the former were highly correlated ($R^2 = 0.71–0.72$; Figs. SM7 and SM8), while the concentrations of the latter in lung fluids exhibited a good correlation ($R^2 = 0.63$) with respect to their total contents in the wastes (Fig. SM8). These different release behaviors of Tl and Pb within the soluble and bioaccessible fractions may be related to the complexation of both metals by organic compounds in the latter case, potentially enhancing the solubility of both metals and therefore their bioaccessibility. Another factor enhancing the bioaccessibility of metals is the crystallinity of mineral phases. In this case, Ehlert et al. (2018) reported a high solubility of As–Fe amorphous precipitates in gastric fluids. These poorly crystalline minerals were also

observed by SEM-EDS in this study.

The results obtained in this study could help fill gaps in the knowledge regarding the environmental and health hazards of metal mining wastes dumped in abandoned mines worldwide. However, the kinetic controls on metals released from the studied wastes should be further studied at each site before implementing restoration measures to limit environmental and health problems.

4. Conclusions

The main goals of this study were to investigate the response of a variety of sulfide mining wastes to weathering as well as to determine the potential bioaccessibility of metal/loids to humans through oral and pulmonary routes. The studied wastes exhibited high concentrations of trace metal/loids such as As, Pb, Cu, Zn, Sb, or Sn. The mineralogical composition of the wastes was mainly controlled by the mineral processing applied to the original ores which were dominated by Fe oxides, hydroxides and oxyhydroxides (i.e., goethite, hematite, and jarosite), sulfides (i.e., pyrite, sphalerite), quartz, and sulfates (i.e., barite, gypsum, anglesite, melanterite, szomolnokite, parabutlerite, and copiapite).

The wastes released high quantities of sulfate (6053–119,221 mg/kg) and metal/loids such as Fe (up to 24,029 mg/kg), Al (up to 2903 mg/kg), Zn (up to 632 mg/kg), Cu (up to 569 mg/kg), Cr (up to 176 mg/kg), or As (up to 133 mg/kg) upon their contact with water, with the concentrations released from most wastes exceeding the threshold legal values for some contaminants such as As, Cr, Cu, Sb, sulfate, Pb, and Zn.

The health risk assessment performed on the studied samples evidenced that despite the high metal/loid concentrations observed, their accidental ingestion through inhalation was associated with a low risk, with HQ values below 1 for most metal/loids (except Pb). However, considering the persistence of Pb in contaminated environments, its ingestion by children could result in learning disabilities and reduced growth, and therefore, restoration measures are required to minimize these risks.

Author statement

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Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.envpol.2022.120629>.

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