Environmental Science and Pollution Research (2021) 28:14054–14067
https://doi.org/10.1007/s11356-020-11473-w

RESEARCH ARTICLE

Assessment of the pollution potential of a special case of abandoned sulfide tailings impoundment in Riotinto mining district (SW Spain)

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Received: 15 June 2020 / Accepted: 28 October 2020 / Published online: 17 November 2020
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Abstract

This work describes a special case of pollution potential assessment applied to an abandoned sulfide tailings impoundment located in the Riotinto mining district (Huelva), near the Tinto River. Three overlapping levels of discharged tailings were recognized in the impoundment, from deeper to upper: pale yellow to white, red, and brownish-yellow. Mineralogical, physical, and chemical characteristics of tailings, water leachates, water, and sulfate efflorescent salts were analyzed. The total toxic element content and the leachate concentration were respectively used to calculate two indices that support potential toxicity assessment: the Index of Contamination (IC) and the Hazard Average Ratio (HAQ). According to the IC values, all tailings samples showed a high potential for contaminating soils and sediments, especially the intermediate tailings with up to As (8.6 g kg^{-1}), Pb (14.8 g kg^{-1}), and Cu (1 g kg^{-1}). Deeper tailings leachate was extremely saline and acidic, with a very high concentration of sulfates and toxic elements, exceeding the values: 2600, 980, 30, and 17 mg L^{-1} for SO_4, Fe, Al, and Cu, respectively. For this reason, these deeper tailings were linked to the saline and acid seepage, and also to the sulfate acid efflorescences formed at the dike toe. In conclusion, the studied abandoned tailings impoundment is related with a high likelihood of polluting the environment, represented by very high IC and HAQ values. However, when the Tinto River is considered the receiving water body, the severity of the potential contamination must be judged as very low.

Keywords Index of Contamination · Hazard Average Quotient · Tinto River

Introduction

Old mining waste storage facilities abandoned without rehabilitation, or where the rehabilitation has been incomplete or negligent, often represent a permanent potential risk for the population and the environment, especially when they contain potentially toxic elements. The Directive 2006/21/CE of the European Parliament and the Council (European Parliament and Council 2006), on the management of waste from extractive industries, sets down that "it is necessary for Member States to ensure that an inventory of closed, including abandoned, waste facilities located on their territory is drawn up in order to identify those which cause serious negative environmental impacts or have the potential of becoming in the medium or short term a serious threat to human health or the environment." Within this framework, the Geological Survey of Spain (Instituto Geológico y Minero de España, IGME) developed a methodology for the preliminary risk assessment of abandoned mine waste facilities (Alberruche del Campo et al. 2016). The complete methodology has been systematically applied to Spanish mining waste facilities, for the development and update of the national inventory under article 20 of the Mining Waste Directive, from 2011 to the present.

The methodology was designed to identify the most problematic tailings impoundments or mining heaps, assessing the likelihood and the severity of the consequences for various risk scenarios of contamination and physical instability. The assumption is that this risk assessment should be the first step for prioritizing abandoned mine waste facilities for rehabilitation. In addition to the site-specific factors that define the

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Responsible Editor: Philippe Garrigues

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exposure pathways and receptors, the potential contamination risks caused by mining wastes depend firstly on their chemical properties. Concerning contamination processes, the methodology judges the total content of toxic elements and the water-soluble fraction, accepting that chemical contamination of soils, sediments, and water is the result of a combination of the dispersion of particles and dissolved elements by wind and water when they act on mining waste (Arranz-González et al. 2016). When the IGME methodology was designed, it was decided to assess the hazard of water pollution linked to soluble elements of mining wastes through leaching tests because, in Spain, water affected by mining wastes can rarely be sampled, especially in dry seasons.

The purpose of this work is to investigate and evaluate the contamination potential of a special case of tailings impoundment, using part of the overall evaluation methodology designed for abandoned mining waste facilities. This selected impoundment stores three different types of tailings, perfectly distinguishable from each other. From a practical point of view, part of the tailings will be more relevant as a source of pollution linked to eroded materials, and another will be more important due to the dissolution of pollutants. This circumstance is uncommon or, at least, it is the only case found among the facilities included in the Spanish inventory. The impoundment is located in the Riotinto mining district (Huelva, Spain, Fig. 1). It is one of the numerous abandoned mining waste facilities present in the Iberian Pyrite Belt (IPB). As is known, the exploitation of metallic minerals in the IPB, since pre-Roman times, has left a huge legacy of abandoned mines and one of the world's largest accumulation of orphan mining wastes and sources of acid mine drainage (AMD) (Sánchez-España 2008). The work focuses on the application of two indices for potential toxicity assessment, which are part of the mentioned methodology: the Index of Contamination (IC) and the Hazard Average Quotient (HAQ) (Alberruche del Campo et al. 2016; Arranz-González et al. 2016). The IC index is involved in estimating the probability of erosion contamination scenarios. The HAQ index takes part in the estimation of the probability of water pollution by effluents generated in mine wastes. These indices allow obtaining a synthetic measure of the polluting potential of the mining wastes. By using these indices, this work aims to study whether the tailings stored at this facility have a great potential to contaminate nearby water bodies, even, from the perspective of the Tinto River, the severity of these effects may not be high.

Materials and methods

Site description

The study area is located in the Riotinto mining district (province of Huelva, Fig. 1), belonging to the well-known Iberian Pyrite Belt (IPB). There are several published papers that provide pertinent geological information (e.g., García-Palomero 1990; Leistel et al. 1998; Tornos 2006; Mellado et al. 2006, and references therein). The ores that have mainly mined in the Iberian Pyrite Belt consist of massive polymetallic sulfides (e.g., Leistel et al. 1998), containing pyrite (FeS_2), with minor chalcopyrite ($CuFeS_2$), arsenopyrite ($FeAsS$), sphalerite (ZnS), and galena (PbS). Another important ore exploited since very early in the IPB is gossan, which was mined for gold, copper, silver, and gold. It was formed by the weathering of massive sulfide mineralizations. Gossan appears enriched on secondary iron oxyhydroxides, oxides, and oxy-sulfates: goethite (α-FeO(OH)), hematite (Fe_2O_3), and minerals of the jarosite group.

The average annual temperature in the study area is over 17.1 °C. The average annual precipitation is 756 mm, and annual potential evapotranspiration reaches 758 mm. Despite the similarity of the two annual values, the distribution of precipitation and temperature throughout the year causes a marked dry summer, as is typical of the Mediterranean climate. This dry period, identified with the Thornthwaite water balance (Thornthwaite and Mather 1955), extends from June to September. Hydrology reflects this seasonal water balance with a marked water flow variability from summer to winter, as well as between different years. Theoretically, the original vegetation was a forest of holm oak (*Quercus rotundifolia*). Dominant land cover in the surroundings consists of spoil heaps, slag dumps, other tailings impoundments, industrial mining ruins, pine forests, and pastures.

The tailings impoundment named Represa I-II store flotation wastes from the Riotinto Mine. Recently, it was included in the inventory performed by the Geological Survey of Spain with the code 938-IV-4-003. It seems that the impoundment was operative until the beginning of the 50s. It is located in the municipality of Minas de Riotinto, within the area known as Zarandas-Naya. This area became the center of mineral processing from the 19th century until relatively recent times. The mineral-based processes carried out were three: copper concentration by flotation, concentration of gold and silver by oxidation, leaching and cyanidation, and copper cementation on iron scrap. The Zarandas-Naya area is the southernmost part of the Riotinto mining district, which is crossed by the Tinto River after passing the "Peña del Hierro" Mine at its source. Throughout this whole course, the river receives abundant inputs of sulfate, iron, metals, and metalloids from many mine adits, spoil heaps, ore stockpiles, tailings, and slags.

Represa I-II was the subject of research by Martín-Crespo et al. (2011) and Arranz-González and Cala-Rivero (2011). Likewise, it is located in the vicinity of a slag dump studied by Lottermoser (2005), and next to another abandoned tailings facility studied by Arranz-González et al. (2012). It is mostly a side-hill impoundment, although in its central part it can be considered a cross-valley type (Vick 1990) because it sits over

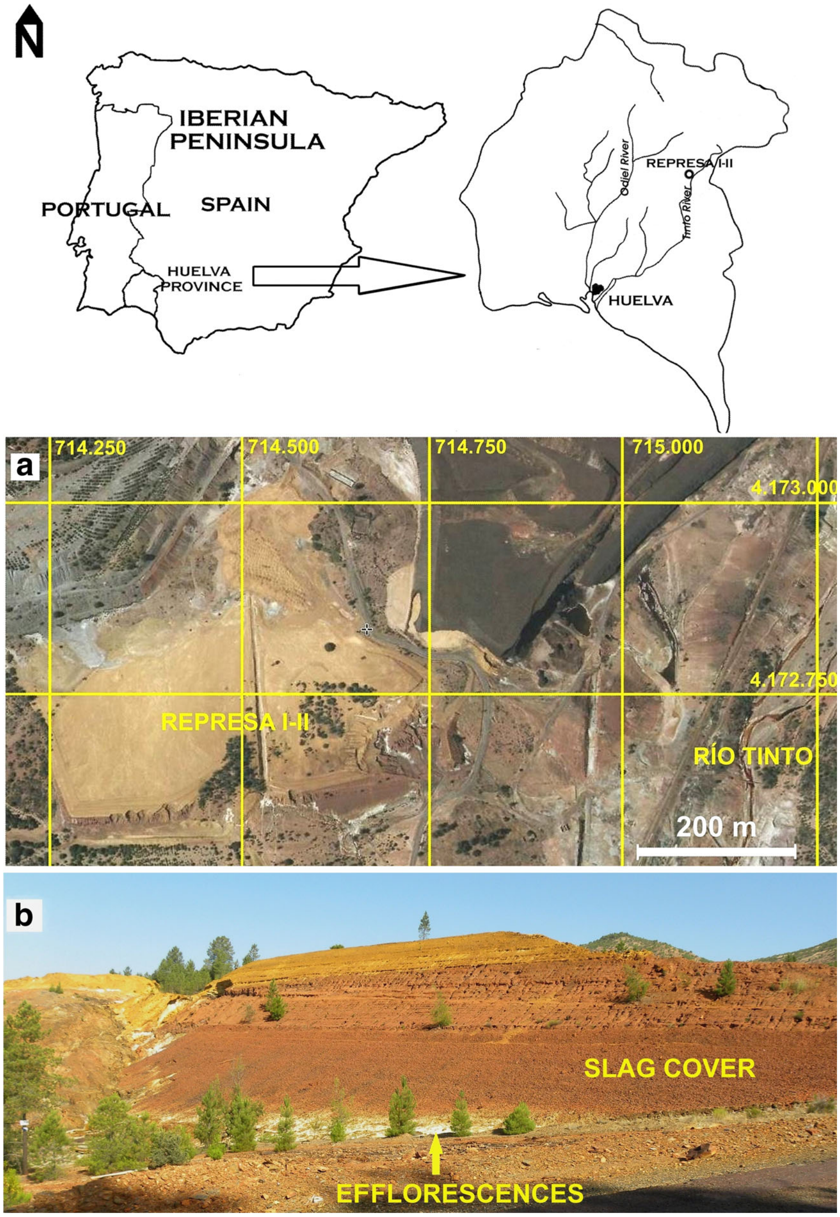

Fig. 1 Simplified location map and images of the Represa I-II impoundment. **a** Aerial image. Modified from an image downloaded from the web page http://sigpac.mapa.es/fega/visor/. Superimposed numbers refer to UTM coordinates (ETRS89/UTM zone 29N). **b** Front view of the tailings impoundment, showing the three types of mining waste stored, and the sulfate efflorescences associated with seepage

the bed of an ephemeral creek. This ephemeral stream runs for about 350 m until joining the stream named Barranco del Pie de la Sierra, and the waters of both converge with the Tinto River about 200 m downstream. The impoundment can also be qualified as an upstream raised embankment (Vick 1990), formed with the thickest fractions of the tailings. Decant towers were installed inside the impoundment but are non-functional, probably for a long time. At the top, centered from north to south, a large trench was dug to drain any water that might be accumulated on the surface. The foot of the dam is located about 280 m above sea level, and the maximum height reaches about 26 m. The impoundment stores about 350,000 m^3 of three different types of tailings, perfectly distinguishable from each other. This circumstance is uncommon or, at least, it is the only case found among the facilities included in the cited inventory. In the eastern half of the facility are recognized three thick overlapping levels (Fig. 2): (a) pale yellow to white tailings, located at the bottom and covered with a slag cover, like a stone mulch (deeper tailings, DT); (b) red tailings in the middle (intermediate tailings, IT); and (c) brownish-yellow tailings at the top (upper tailings, UT). The two deeper layers are no longer observed approximately from the buried creek of the central part to the west, that is, the upper layer overlies the middle layer at the eastern half and the natural terrain at the west. The dam sits on impermeable bedrock formed mainly by Devonian shales. At present, the slope of the dam is heavily eroded, except for the lower layer covered with slag. However, the slag cover is broken in the area overlying the stream, where the white tailings are apparent (Fig. 1 and Fig. 2).

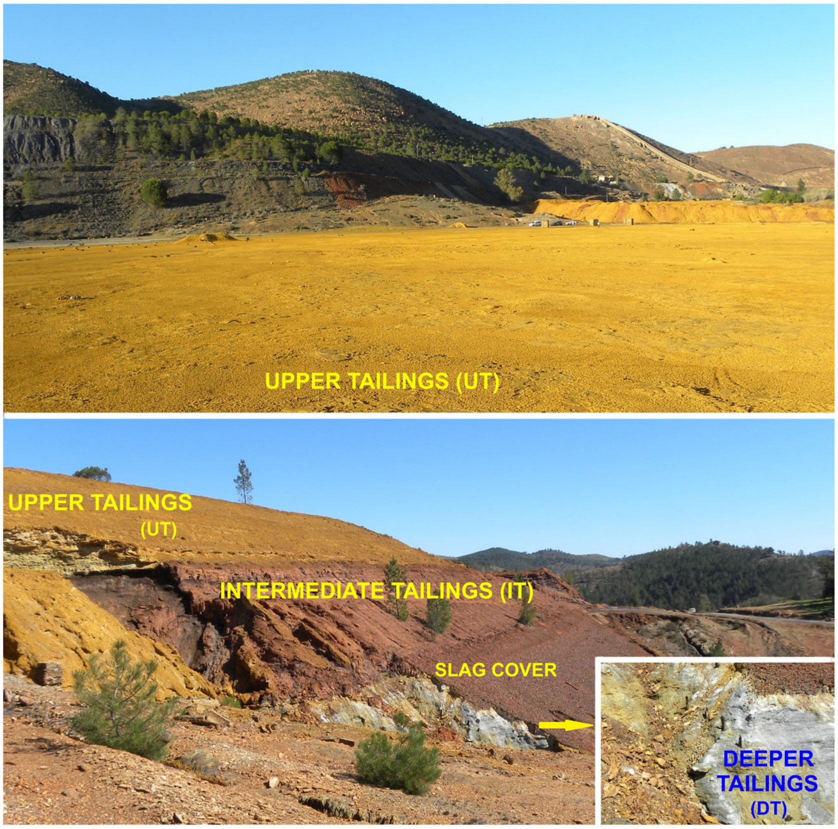

Fig. 2 Side view of Represa I-II impoundment showing the three types of stored tailings

There is no specific information available about the treatment processes from which derived such old mining wastes. Everything seems to indicate that, in this case, UT and DT consist of flotation wastes due to its small particle size (see below), even in the samples taken on the dike (DT). The intermediate tailings (IT) were probably produced by crushing and cyanide leaching of gossan. It seems that they are the rejects of a process that involves crushing, milling, and flotation/leaching of three different mineralizations, respectively, for DT, IT, and UT (Solomon 1976; Mellado et al. 2006; Tornos 2006): massive pyrites or massive sulfide ore (constituted by fine-grained pyrite and subordinate sphalerite, chalcopyrite and galena); gossan (a product of long-term supergene alteration of massive sulfides dominated by goethite and hematite); and stockwork (composed of anastomosed sulfide veins of pyrite, with quartz chalcopyrite and some chlorite). The history of the facility and the deposition of the layers are not well documented, but by observing old aerial photos, it follows that filling was completed before 1957. Therefore, the most superficial layers have undergone oxidation and erosion processes for more than 60 years. Although it is not possible to know the exact moment, a large drainage ditch was constructed approximately aligned with the buried channel of the creek. Similarly, during the 1990s, some of the easternmost red tailings were removed for reprocessing.

Sampling

Tailings samples were obtained in October 2013. Sampling was done following the methods described by Smith et al. (2000) and Hageman and Briggs (2000). The sampling method applied during the inventory consists of the collection of a composite sample, which is the product of the combination and mixture of 30 or more subsamples, taken following a random walk on the surface of each mine waste facility. At the top of the impoundment (Fig. 2), subsamples were obtained up to a depth of 20 cm, assuming that this surface horizon is the main source of dissolved elements and eroded particles. The composite sample was named UT. During the fieldwork, water was found emerging at the lowest point of the dam (corresponding with the bed of the buried creek). This water was extremely acid (see below). It was suspected, from the work of Arranz-González and Cala-Rivero (2011), that the upper tailings could not be responsible for this acidity. For this reason, it was also decided to take a sample of the white tailings. In order not to alter the slag cover, this sample was taken in the area of the stream, joining a total of five subsamples (Fig. 2). This sample was labeled DT (deeper tailings). During the same field visit, it was also decided to take a sample of the red tailings from the eastern intermediate section, to complete the characterization of all stored waste. This sample was identified as IT (intermediate tailings).

On new fieldwork developed in July 2014 (dry season), sulfate efflorescence formation was observed over the substrate, probably associated with seepage at the base of the impoundment dike (Fig. 2). Efflorescences of hydrated acid sulfates are produced by the evaporation of acidic waters generated from the oxidation of sulfide minerals (Hammarstrom et al. 2005). The dissolution of these efflorescent salts after the first rains following the dry period releases acidity and trace elements that can produce short-term environmental damage to water and soil (Alpers et al. 1994; Jambor et al. 2000). Four individual samples of these efflorescences were gently collected with a spatula, preserved in polyethylene bags, and immediately refrigerated in a portable fridge. The samples were named EF1, EF2, EF3, and EF4, with EF1 being the closest to the dam foot and EF4 the furthest.

In both October 2013 and July 2014, it was possible to sample water emerging at the lowest point of the dam (corresponding with the bed of the buried creek). These samples were named W1 and W2 for October and July, respectively. The flow was not measured, but was appreciably small in October and practically a droplet in July. A water sample was taken from the Tinto River in July 2014, downstream from the mining area. Another sample from the river, taken in February 2014, was also available. Water samples were divided into two parts. One part was filtered in the field with nitrocellulose filters (0.45 μm) and acidified with supra pure HNO_3 for cation analysis. The other part was carried to the laboratory for analysis of Na, K, Ca, Mg, anions, pH, and electrical conductivity. The water samples were kept for a few days in a portable fridge until they were delivered to the laboratory.

Analytical procedures

Total and soluble toxic elements present in tailings samples were analyzed, with the support of other physical, mineralogical, and chemical characterizations. The solid samples were air-dried and homogenized. Then, tailings samples were sieved using a 2-mm stainless-steel sieve, discarding the > 2-mm fraction. According to Smith et al. (2000), the use of the < 2 mm size fraction appears to be a good option because the majority of the chemically reactive potential of the weathered surface of historic mine-waste facilities is encompassed on this fraction. Before physical and chemical analysis, moisture content was measured with a standard oven drying of the solid samples at 105 ± 5 °C over a period of 24 h. Then, particle size distribution was measured by standard dry sieving (ASTM 5000 series) for 2–0.063-mm fractions, combined with a Sedigraph 5100 particle size analyzer (Micromeritics, Norcross, USA) for < 0.063-mm fractions.

Solid samples were gently ground before chemical and mineralogical analysis, except for pH, electrical conductivity, and leaching tests. Minerals were identified by powder X-ray diffraction (XRD), using an X'PertPro equipment (PANalytical®, Malvern, UK), with monochromated CuKα radiation. Data were collected scanning from 3° to 62° 2θ with a counting time of 0.5 s per step. Minerals identification was developed considering areas under the peaks and d-spacings, employing the software of the diffractometer and the ICDD database.

Major elements (Si, Al, Fe, Ca, Ti, Mn, K, Mg, and P) were analyzed using a MagiX X-ray fluorescence spectrometer (PANalytical®, Malvern, UK). Na was determined by lithium tetraborate fusion and analysis by a Varian Spectra AA 220FS atomic absorption spectrophotometer (Varian Inc., Palo Alto, USA). An Orion pH-meter (Thermo-Fisher Scientific, Waltham, USA) was used to measure pH in a 1:1 soil-water mixture (Peech 1965; Price 1997). Total sulfur (wt% S_{total}) was determined by ignition in a pure oxygen atmosphere, using an induction furnace with elemental CS-800 infrared analyzer (Eltra, Haan, Germany). The analysis of S_{sulfate} (wt%) was performed by digestion in 10% HCl, and adding an excess of precipitating reagent ($BaCl_2$) to precipitate $BaSO_4$, which was determined by gravimetry. The percent of S_{sulfide} content was obtained by the difference between S_{total} and S_{sulfate}. The potential for acidity generation (AP) (as kg of equivalent CO_3Ca t^{-1}) of wastes is obtained by multiplying the % of S by 32.25. This method may underestimate AP if jarosite or other acid-producing sulfate minerals are present. The neutralization potential (NP) of tailings was determined by digestion of 2 g of sample in hot HCl and then titrated with NaOH (Sobek et al. 1978).

The analysis of total trace elements (except Hg) was achieved by digestion with a concentrated mixture of HF-HNO_3-$HClO_4$ heated to dryness, and then dissolving the residue with HNO_3. The concentration of 22 elements was measured by ICP-MS (inductively coupled plasma-mass spectrometry), in a 7500ce equipment (Agilent®, Santa Clara, USA), or by ICP-AES (inductively coupled plasma atomic emission spectrometry), in a Vista MPX equipment (Varian Inc., Palo Alto, USA). Mercury was analyzed by cold vapor atomic absorption spectrometry (EPA 7471 method, USEPA 1994) that is: a part of each sample was digested with *aqua regia* (three volumes of concentrated HCl plus one volume of concentrated HNO_3), and $KMnO_4$ was added to maintain the metal in an oxidized state. The released Hg was measured using a continuous flow of cold vapor with the SpectrAA 220FS equipment (Varian Inc., Palo Alto, USA).

The potential solubilization of trace elements from tailings and efflorescences was evaluated using leaching extracts (in a solid-water ratio of 1:10), as described by the European standard EN 12457-2 (ECS 2002), without particle size reduction. The leachates were analyzed by ICP-MS with the above mentioned 7500ce spectrometer (Agilent®, Santa Clara, USA). A Multimeter MM41 (Crison, Alella, Spain) was employed to determine electric conductivity, Eh, and pH of the leachates.

An UV-Vis absorption spectrophotometry was used or anions determination, employing an Alliance-Integral-Plus autoanalyzer (AMS-Alliance, Frepillon, France) of continuous flow. The determination of Na, K, Mg, Ca, and Fe was performed by atomic absorption spectrophotometry (Flame) with a SpectrAA 220FS instrument (Varian Inc., Palo Alto, USA). The same analytical techniques and instruments used for leachates were applied to water samples.

All the obtained results were evaluated with an internal quality control system of the IGME labs, involving analysis of replicates, blanks, and Standard Reference Materials (SRM). For accuracy verification, the SRM employed were GBW 077103, GBW 07114, and GBW 07104 (China National Analysis Center for Iron and Steel, NACIS), for major determinations by XRF; GBW 077105 and GBW 07106 (NACIS), for Na determination by AAS; AR 4016, AR 4018, and AR 4019 (Alpha Resources, Inc.) for S determination by elemental analyzer; GBW 07103, GBW 07105, and GBW 071038 (NACIS) for trace element determinations by ICP-MS or ICP-AES; GBW 07404, and GBW 07405 (NACIS) for Hg determination by AAS; custom standards supplied by Inorganic Ventures for anions determinations with an Autoanalyzer, and Na, K, Mg, Ca, and Fe determinations by AAS; TM-9.2, and TM-62.2 (Environment and Climate Change Canada) for trace element determinations by ICP-MS (liquid samples). The maximum relative error was 10% for spectrometric analysis. All other maximum relative errors were between 1 and 5%. The limits of detection (LOD) (in μg mL^{-1}) were 1 for Al; 0.5 for Fe; 0.05 for Ca, and K; 0.025 for Na, and Mg. The LODs for trace elements were (μg L^{-1}): 0.05 for As, Co, Cr, and V; 0.2 for Cd, Cu, Mo, Pb, and Zn; and 0.5 for Ni, and Se. LOD for $SO_4{}^{2-}$ was 0.02 g L^{-1}. Other limits of detection are shown in the respective tables.

Index of Contamination

The erosion of mining wastes can affect nearby soils and sediments. When high concentrations of potentially toxic elements are present in the wastes, the potential to contaminate soils and sediments, due to the dispersion of particulate material, is best assessed by measuring the total content of these elements. This does not exclude that the mobility or bioavailability of trace elements transported in the eroded particles will depend on the pH, organic matter content, redox potential, and temperature of the deposition site (Alloway 2013). The assessment of the potential for contamination of particulate matter emitted from mining waste facilities was based on the examination of potentially toxic elements concentration in waste. As, Cd, Co, Cr, Cu, Hg, Mo, Ni, Pb, V, and Zn were the studied potentially toxic elements (PTE), according to European Commission Decision 2009/359/EC (European Commission 2009), to which Se was added. The methodology for the regular classification of abandoned mining waste facilities in Spain (Alberruche del Campo et al. 2016; Arranz-González et al. 2016) employs an aggregation data procedure called Index of Contamination (IC), which is proposed as a measure of the potential of mining waste to contaminate soils and sediments due to erosion processes. It is determined by the average of the relationship between total concentrations measured in a mining waste and the regional soil background:

$$\mathrm{IC} = 1/n \times \sum_{i=1}^{n} [X]i/\mathrm{BLx}$$

where X is the measured total metal concentration in the mining waste, BL_X is the geochemical background value for the X element, and n is the number of elements in which concentration measured in mining waste is higher than BL_X. The value of this index is always higher than 1. According to Arranz-González et al. (2016), the greater the value of IC, the greater is the likelihood of pollutants emission to nearby soils and sediments. Therefore, the values obtained from the index, together with the assessment of other circumstances specific to each case, can provide the first element of judgment to establish a ranking of the potential for contamination of different types of mining waste.

Hazard Average Quotient

Knowledge about the total contents of potentially toxic elements is not sufficient to assess the hazard of mining wastes. The chemical speciation present in mining waste is more determinant of mobility than the total concentration of the toxic elements (Arranz-González and Cala-Rivero 2011). Accordingly, leaching tests are helpful for geochemical characterization of the soluble constituents that can be mobilized from mining wastes (Hageman and Briggs 2000). With a view to water pollution likelihood, the methodology of the Spanish Geological Survey (Alberruche del Campo et al. 2016; Arranz-González and others Arranz-González et al. 2016) focuses on the elements included in European Commission Decision 2009/359/EC, but adding Al and Se. Another index, named “Hazard Average Quotient” (HAQ) was created to assess the potential toxicity factor for water due to the presence of soluble PTEs in abandoned mining wastes. The reference values were selected levels for the toxic elements, Al, As, Cd, Co, Cr, Cu, Hg, Mo, Ni, Se, Pb, V, and Zn, obtained from various water quality standards (Alberruche del Campo et al. 2016; Arranz-González et al. 2016). This set of values is very conservative, both from the perspective of the health of aquatic ecosystems and for any other possible use of water. The HAQ is calculated as:

$$\mathrm{HAQ} = 1/n \times \sum_{i=1}^{n} [X_{\mathrm{LEACH}}]i/\mathrm{WQL_x}$$

where $[X_{\mathrm{LEACH}}]_i$ is the concentration of the ith element in the leachate, $\mathrm{WQL_x}$ is the water quality standard for the element X, and *n* is the number of elements for which the resulting fractions are greater than one. WQL is a demanding standard, formed by the lowest concentration values among those contemplated by European Council (1998), USEPA (2002), USEPA (2012), and Puura and D'Alessandro (2005).

It is interesting to note that, apart from the use of these indices for the evaluation of abandoned mining waste facilities inventoried in Spain, their application has also inspired other recent works (Del Rio-Salas et al. 2019; Peña-Ortega et al. 2019, Guzmán-Martínez et al. 2020).

Results and discussion

Grain size and mineralogy

The particle size fraction below 2 mm was 100% for IT and DT, and 99.54% for UT. The sand (2–0.063 mm) content of the samples was 44.5, 55.2, and 60.17% dry weight, respectively, for UT, IT, and DT samples. UT was more clayey with (20%), compared to 10.4% for DT and 8.1% for IT.

Table 1 shows the mineralogical composition obtained by powder XRD. For the comments that follow, it has been considered that the term primary refers to the minerals probably present in the fresh tailings stored in the impoundment, and secondary refers to the minerals originated by the weathering processes (Jambor 1994). As mentioned, tailings of the upper part of the impoundment (UT) have been subjected to weathering for a long time. Therefore, these materials offer the typical appearance of weathered pyritic tailings, with a brownish yellow color (Munsell notation 10YR 6/8), which is characteristic of the presence of secondary minerals like jarosite and goethite. Jarosite precipitates at low pH, high SO_4^{2-} ion concentration, high levels of Fe^{3+}, and oxidizing environments (Jambor 1994). Goethite is the most stable secondary Fe mineral and is mostly formed under slightly acidic conditions, or it may also form through the transformation of less stable oxyhydroxides and hydroxysulfates (Murad and Rojik 2005). No other secondary minerals were detected by XRD analysis in the UT sample due probably to their low crystallinity. The presence of quartz and chlorite in these tailings indicates the probable origin of the exploited material: stockworks. The exploited stockworks of Riotinto Mine were composed of anastomosing veinlets of quartz with disseminated sulfides (Nehlig et al. 1998). The quartz-sulfide veins of stockworks fit on chloritized host rocks. The mineralogical results were consistent with those obtained by Martín-Crespo et al. (2011) for mostly oxidized UT samples taken in a profile located in the face of the central trench. These authors found some pyrite and sphalerite only at 2.5 m depth.

IT red tailings (Munsell notation 10R 4/4), quartz, goethite, jarosite, and hematite were identified. All of these minerals could be primary. Indeed, the IPB gossans are dominated by goethite and hematite, with quartz and some members of the jarosite group, like jarosite, plumbojarosite, or beudantite (García-Palomero et al. 1986).

The residues at the base of the impoundment (DT) were pale yellow to very light greenish-gray in the field (Munsell notations 5Y 8/1 to 10Y 8/1). In the DT sample, the identified minerals were quartz, jarosite, pyrite, elemental S, and a not well-identified phyllosilicate (probably chlorite). This combination of minerals is likely to result from the alteration of massive sulfides. The presence of other secondary hydroxides or Fe-sulfates cannot be ruled out since the XRD technique is not sensitive enough to detect low concentrations of these minerals, or because they may be minerals of low crystallinity.

All efflorescence samples were complex sulfate assemblages. The presence of quartz on EF2 and EF3 may be explained by the presence of substrate particles carried-ever during sampling, or because quartz grains provided sites for sulfate mineral formation, and were thus inevitably included during sampling (Grover et al. 2016). Except for gypsum, all the

Table 1 Mineralogical constitution of tailings samples obtained by powder X-ray diffraction. *X*, detected mineral

	Theoretical chemical formula	UT	IT	DT	EF1	EF2	EF3	EF4
Quartz	SiO_2	X	X	X			X	X
Chlorite	$(Mg,Fe)_3(Si,Al)_4O_{10}(OH)_2\bullet(Mg,Fe)_3(OH)_6$	X						
Pyrite	FeS_2			X				
Jarosite	$K\,Fe^{3+}{}_3(SO_4)_2(OH)_6$	X	X	X				
Goethite	α-FeO(OH)	X	X					
Hematite	Fe_2O_3		X					
Gypsum	$CaSO_4\bullet2H_2O$				X	X		
Hexahydrite	$MgSO_4\bullet6H_2O$					X		
Rozenite	$Fe^{2+}SO_4\bullet4H_2O$				X	X		
Pickeringite	$MgAl_2(SO_4)_4\bullet22H_2O$					X	X	X
Copiapite	$Fe^{2+}Fe^{3+}{}_4(SO_4)_6(OH)_2\bullet20H_2O$				X	X	X	X

detected secondary minerals in efflorescences are highly soluble (Hammarstrom et al. 2005). Copiapite was detected in all the efflorescence samples. This is the most common iron-sulfate mineral associated with oxidized mine wastes (Blowes et al. 2004). According to Jambor et al. (2000), in the field, the paragenesis indicates an evolutive sequence from the formation of the divalent salts of iron (rozenite) to minerals containing both ferrous and ferric iron (copiapite). Indeed, rozenite is only present in the two samples closest to the dam foot. Pickeringite was also present in three samples. This sulfate is formed mainly at low pH, by the oxidation of pyrite or other sulfides that are found together with Al-rich minerals. Other divalent cation minerals detected in efflorescent salts were gypsum and hexahydrite. It is reasonable to think that the flow of acidified water through the slag cover can also influence the subsequent precipitation of these minerals, as Lottermoser (2005) showed in his study of a nearby slag dump.

Bulk chemical composition

The major oxides analysis indicated that UT and DT tailings were characterized by a high percentage of SiO_2, and a relatively important concentration of Fe_2O_3 (Table 2). The Al_2O_3 percentage was much lower in both materials, although slightly more significant in UT. About 18% in DT and 6% in UT corresponded to Loss on Ignition (LOI). Other oxides present in these materials were negligible. Unlike the previous ones, IT was dominated by Fe_2O_3, with a certain percentage of SiO_2, and lower amounts for the remaining oxides. LOI was intermediate in this sample. SiO_2 content follows the order UT > DT > IT, like in the expected sequence: stockworks > massive sulfides > gossan. The Fe_2O_3 content follows the order IT > DT > UT, like in the expected sequence: gossan > massive sulfides > stockworks.

The efflorescent salts were dominated clearly by Fe_2O_3, with similar values than DT. As stated above, the presence of relatively more silica content in two of the salts can be interpreted as contamination, or by the inclusion of quartz grains into the efflorescences (Grover et al. 2016). The content of MgO was also significant. The magnitude reached by the LOI was remarkable, exceeding 63% in all cases, which is mainly attributable to water from hydrated minerals.

In general, the chemical composition agrees quite well with the mineralogy. The efflorescence salts concentrate Mg compared to the three types of mine wastes. As set out below, the DT residue provided the largest measure of soluble Mg. In the EF2 sample, the presence of hexahydrite would explain this. In the other samples, this mineral may be present in a concentration that makes it undetectable. It is also possible, as mentioned, that the acidic water emerging from the impoundment toe solubilizes some Mg when passing through the slag cover. This element can substitute Fe in melanterite and copiapite. Regarding pH values, the extraordinary acidity of the DT sample, as well as such of all the efflorescences, should be highlighted. This fact can be interpreted as the first evidence of the relationship between the chemical characteristics of DT tailings and the seepage water, which is the origin of the efflorescences.

Table 3 gives the results of the sulfur forms and the calculation of the acid-base account ABA based on Sobek et al. (1978). Total S ranged from 0.24 wt% in UT to 19.3 wt% in DT. Total sulfur measured in efflorescence samples ranged from 14.1 to 18.8%. Whereas a material can be considered as acid-generating when its net neutralization potential (NNP) is lesser than -20 $kgCaCO_3$ equivalent/t (Ferguson and Morin 1991), neither UT nor IT can be qualified as acid-generating wastes. Nevertheless, the calculated net neutralization potential for DT was strongly negative as a consequence of the acid generation caused by the sulfide oxidation, and the lack of suitable acid-neutralizing minerals. To this, it

Table 2 Composition of major elements by oxide composition (wt%) of the studied tailings and efflorescences. *LOI*, loss on ignition at 950 °C. pH measured in a 1:1 soil-water mixture

	Limits of detection	UT	IT	DT	EF1	EF2	EF3	EF4
SiO_2	0.5	72.16	6.29	54.4	< 0.5	< 0.5	2.46	6.51
Al_2O_3	0.5	3.56	0.63	1.13	0.80	1.31	2.64	2.60
Fe_2O_3	0.2	16.15	72.80	23.00	21.38	23.19	15.55	22.60
MnO	0.05	< 0.05	< 0.05	< 0.05	0.66	0.76	0.52	0.21
MgO	0.5	0.96	0.22	< 0.50	6.84	7.82	5.71	3.51
CaO	0.6	< 0.60	0.12	< 0.60	0.60	0.65	< 0.60	< 0.60
Na_2O	0.08	< 0.067	< 0.067	< 0.067	< 0.067	< 0.067	< 0.067	< 0.067
K_2O	0.4	< 0.40	< 0.40	< 0.40	< 0.40	< 0.40	< 0.40	< 0.40
TiO_2	0.3	< 0.3	< 0.3	< 0.3	< 0.3	< 0.3	< 0.3	< 0.3
P_2O_5	0.045	< 0.045	< 0.045	< 0.045	< 0.045	< 0.045	< 0.045	< 0.045
LOI		6.34	10.84	17.77	67.69	63.91	71.58	63.70
pH		5.47	6.54	0.99	1.20	1.06	0.62	1.08

Table 3 Sulfur forms and acid-base account. Neutralization potential (NP), acid potential (AP), and calculated net neutralization potential (NNP=NP-AP) in kg $CaCO_3$ equivalent/t solid sample. AP was estimated multiplying wt% $S_{sulfide}$ by 31.25. The limit of detection of S by the elemental analyzer was 0.05%

Sample	wt% S_{total}	wt% $S_{sulfate}$	wt% $S_{sulfide}$	NP	AP	NNP
UT	0.24	0.19	0.05	− 4	1.6	− 5.6
IT	0.83	0.82	0	2.1	0.01	1.8
DT	19.3	3.5	15.8	− 29.4	493.8	− 533.2

must be added the unevaluated presence of secondary acid-generating minerals, such as jarosite.

The total contents levels of toxic elements measured in waste samples are shown in Table 4. IC values were calculated taking into account these total element concentrations, and adopting as reference the background soil levels established by Junta de Andalucía (2004) for the Sud-Portuguese Zone (ZSP). The IPB is located in this big geologic dominium. For comparison purposes, the values obtained in the profile studied by Martín-Crespo et al. (2011) are also used. Thinking about the evident erosion of the slopes of UT and IT tailings layers, and the subsequent emission of sediments to watercourses, the results were also compared to some data from the Tinto River sediments, taken in the final section of the mining area (Galán et al. 2003).

There were neither regional background values for Mo and V, but the measured contents were not of great concern: Mo (3.2–16.1 mg kg^{-1}) and V (1.8–23.6 mg kg^{-1}). For Se, while no references are provided in Table 4, the results obtained for the three tailings types are considered very high (21–67.1 mg kg^{-1}) according to RCT (1988), which admits a maximum of 3 mg kg^{-1} for suitable surficial materials on mine-soils. Cr and Ni concentrations measured in all samples were below the soil background level, and Cd concentration was under the detection limit. The Zn content was high in DT and IT samples, above the values accepted by RCT (1988). Co was high only in DT, and Hg in the other tailings samples. According to RCT (1988), Hg was unacceptable in DT and IT samples. The total contents of As, Cu, and Pb were higher than the background levels. Especially remarkable were the values achieved in the IT sample: 8689 mg kg^{-1}, 1012 mg kg^{-1}, and 14,822 mg kg^{-1}, for As, Cu, and Pb, respectively. The total contents of Pb and As measured in this sample are much higher than those measured in sediments from the Tinto River taken in the final part of the mining area as ochreous precipitates. This is a clear consequence of the origin of IT, which undoubtedly derived from gossan. For example, the iron content of gossan was around 50% in Cerro Colorado, with 0.7 of arsenic (Williams 1934). The contents of iron and arsenic in the IT sample are 50.5% and 0.86%, respectively. The contents of Pb also point in this direction.

According to the IC values, all the tailings samples exhibit a high potential to contaminate surrounding soils and sediments, especially IT. The calculated IC for IT sample (237.8) is the highest ever published (Arranz-González et al. 2016; Arranz-González et al. 2017; Arranz-González et al. 2019; Del Rio-Salas et al. 2019; Peña-Ortega et al. 2019; Fernández-Naranjo et al. 2020; Guzmán-Martínez et al. 2020). When assessing the pollution due to eroded tailings dispersion (by water or wind erosion processes), the exposed tailings surface must be taken into account, which is maximum for UT and minimum for DT. Besides, the slag cover over the slope formed in DT tailings would reduce the possibility of erosion to almost zero. In addition to the climatic characteristics of the area, all these considerations should be taken into account to evaluate the likelihood of pollution by the emission of eroded particles from this impoundment. But it should be borne in mind that, in the IGME methodology, the comparison of the contents of potentially toxic elements of mining wastes with the corresponding soil background levels constitutes the primary yardstick for assessing the pollution

Table 4 Total concentration (mg kg^{-1}) of trace elements measured in tailings samples and other references. *BDL*, below detection limit. *IC*, Index of Contamination (Alberruche del Campo et al. 2016). *LOD*, limit of detection

Material	As	Cd	Co	Cr	Cu	Hg	Ni	Mo	Pb	Se	V	Zn	IC
LOD	0.1	0.5	0.2	2	0.5	0.1	1	0.5	2	1	0.2	2	
UT	606	< 0.5	2.1	2.0	280	0.7	< 1	3.2	449	21	11.2	76.2	13.7
IT	8669	< 0.5	1.5	10.6	1012	6.9	1.3	6.1	14,822	48.7	23.6	373	237.8
DT	281	< 0.5	106	0.9	609	3.7	1.5	4.3	974	67.1	1.8	321	15.2
Soil background levels[a]	20		16	85	31		27		31			72	
Profile samples[b]	191–674		3–62	5–13	306–4511				51–222			50–260	6.3–35.4
Tinto River sediments[c]	3090	23		52.2	2650		30.1		870			6730	

[a] Junta de Andalucía (2004)

[b] Martín-Crespo et al. (2011)

[c] Galán et al. (2003)

potential connected with erosive processes. Nevertheless, in this special case, if the Tinto River is seen as the main final receptor, the contamination risk would be much lower, as can be recognized from the sediment data (Galán et al. 2003). Even so, it would still be appreciable for As and Pb coming from intermediate tailings (IT). The real effect on the river can only be known by studying the sediments or precipitates along the entire pathway from the impoundment.

Leaching behavior

Tailings and efflorescences were subjected to the leaching test according to European standard EN 12457-2. Leaching results are shown in Table 5, which also includes water data from the seepage and the Tinto River. The values measured in the Tinto River samples were in general agreement with those published by de la Torre et al. (2011) and Cánovas et al. (2014), for the final segment of the river within the Riotinto mining district, somewhat further south than the Zarandas-Naya area.

The waste material type, influencing the solubility of elements, dictated the pH of the leachates. In general terms, it is worth mentioning that there was very limited solubilization of all the elements into the leachates of UT and IT samples. Only the percentage of soluble aluminum in UT is remarkable (23.5). The soluble percentage is between 0 and 4.7 for the rest of the elements. For the UT sample, only the values obtained for Al, Cu, Pb, and Zn exceed the standard. For IT, only Al, Hg, Se, and Zn exceed it. It should be remembered that this is a very demanding water standard. Only Hg is prominent in IT tailings. According to Arranz-González et al. (2019), the Hazard Average Quotient (HAQ) values obtained for these samples can be qualified as very low, which represents a low likelihood of contaminating water in the short term.

Thinking specifically of the Tinto River, which will sooner or later be the receptor of the dissolved elements, it does not seem likely that the input of soluble elements it might receive from these wastes will affect it. Even Hg, which has the potential to dissolve appreciably, appears below the detection limit in both seepages and efflorescences, which could mean attenuation through precipitation or sorption reactions in the tailings impoundment themselves. On the other hand, the soluble Fe, Al, Cu, Zn, and sulfate contents measured in these tailings cannot be the origin of the concentrations measured for the same parameters in seepage and efflorescence samples.

Certain very high levels of total elements in the UT and IT samples were not reflected in the corresponding leachates. This is the case for As, Se, and Pb. In particular, the negligible Pb content in the leachate of the IT sample is striking, despite the very high total content. A plausible explanation for the reduced solubility of As and Se could be the incorporation of arsenate and selenate by SO_4^{2-} substitution in jarosite, and the retention in goethite. On the other hand, it is possible the incorporation of Pb in jarosite, resulting in a solid solution of jarosite-plumbojarosite (Fendorf et al. 1997; Dutrizac and Jambor 2000; Savage et al. 2000). Furthermore, the presence of undetected anglesite ($PbSO_4$) and/or beudantite $PbFe_3(SO_4)(AsO_4)(OH)_6$ (a typical mineral in gossan) cannot be excluded.

On the other hand, the leachate of the DT sample was, by far, the highest concentrate on sulfate and all the elements studied. Leachates were extremely saline and acidic, (EC = 2.64 mS cm^{-1} at 25°, and pH 1.57). The elements Al, As, Cu, and Zn were particularly high (Table 5). The percentages that represent the soluble concentrations of Al, As, Co, Cr, Cu, Fe, Ni, and V are moderate, exceeding 5%. The percentages that represent the soluble concentrations are low for the rest of the elements. The soluble concentrations of Ca (7 mg L^{-1}) and Mg (6.22 mg L^{-1}) were also significant, being much higher than those measured in the other two tailings samples. It was considered interesting the comparison of the total release results (expressed in mg kg^{-1}) with the waste acceptance criteria for landfills. The results obtained for the DT sample were 40 mg kg^{-1} and 174 mg kg^{-1} of As and Cu, respectively, which are above the limits for hazardous waste (25 mg kg^{-1} for As, and 100 mg kg^{-1} for Cu). According to Arranz-González et al. (2019), the HAQ value obtained for the DT (237.8) can be qualified as very high, showing a very high potential for emitting contaminating effluents to water. However, reviewing the literature providing data for this index, calculated with the same leaching method, it is possible to find up to 11 wastes from metal and coal mining that exceed the value obtained for DT (Arranz-González et al. 2016; Arranz-González et al. 2019; Guzmán-Martínez et al. 2020).

As expected, in the case of efflorescence samples, the percentages of soluble elements were very high for almost all elements. However, the elements As, Cr, Pb, Se, and V were less soluble, with percentages between 14.8 and 79.7. They are probably associated with minerals of the jarosite group, which were not detected. The percentage of Mo could not be calculated in three of the four samples, and Hg was practically insoluble in all of them.

Seepage water samples have pH values ranging from 2.44 to 2.76. As expected, the concentrations of seepage samples were greater than in DT leachate, and higher in the dry season (July) than in October for all the elements and sulfate, except for As and Se. The most abundant elements in solutions produced by leaching the efflorescent salts were Fe, Al, Cu, and Zn. On the other hand, the formation of efflorescent minerals removed SO^{4-} and metals from the solution. It is reasonable to think that infiltration water (and seepage) from the waste repository is the main contributor to efflorescences nature. Assuming that seepage data from July can be quite directly related to those obtained for the efflorescences closest to the foot of the impoundment, the ratios between the concentrations of potentially toxic elements in efflorescence leachates and those in the seepage were calculated. The ratios were as

Table 5 pH, electrical conductivity (EC), sulfates, and selected trace elements measured in leaching tests at 1:10 solid/water ratio (EN 12457-2). CPP was calculated for metals included in European Commission Decision 2009/359/CE, plus Al and Se. wt% soluble was calculated as a percentage of the content obtained by acid digestion. *m.d.*, mistake data

	Water standard	UT	wt% soluble	IT	wt% soluble	DT	wt% soluble	EF1	wt% soluble	EF2	wt% soluble	EF3	wt% soluble	EF4	wt% soluble	W1 (Oct.)	W2 (Jul.)	Tinto (Feb.)	Tinto (Jul.)
Fe (mg L^{-1})		0.04	≈ 0	0.015	≈ 0	984	6	13,578	90.7	13,714	84.5	9927	91.2	10,630	67.2	3712	5720	1647	2408
Al (mg L^{-1})	0.05[a]	0.8	23.5	0.002	1.5	30.7	5.1	426.8	100	569.3	82.5	1077	86.3	1199.5	88.2	328	284.3	539	1603
As (μg L^{-1})	10[a,b]	0.52	≈ 0	1.32	0.004	4002	14.2	573	37.2	259	14.8	8296	94.8	20,343	24.1	1733	114	5464	3901
Cd (μg L^{-1})	0.25[c]	0.33	n.c.	0.4	n.c.	12.4	n.c.	208	93.3	207	70.6	309	86.1	215	79	115	125	528	1037
Co (μg L^{-1})	20[d]	2.65	1.2	1.94	1.3	661	6.2	26,452	90.3	27,031	79.7	22,601	99.1	12,282	95.2	4358	10,593	2700	7479
Cr (μg L^{-1})	50	0.05	0.025	0.1	0.009	14.3	15.9	107	32.1	102	42.7	431	61	341	56.6	83.9	60.1	76.7	130
Cu (μg L^{-1})	10[c]	177	1.58	1.54	0.001	17,453	28.7	27,857	98.4	24,947	84	64,951	99.5	75,799	84.1	17,000	21,747	155,819	393,019
Hg (μg L^{-1})	1[b]	< 0.01	< 0.014	6.95	1	3.7	1	< 0.01	< 1	< 0.01	< 0.5	< 0.01	< 0.33	< 0.01	< 0.3	< 0.01	< 0.01	< 0.01	< 0.01
Mo (μg L^{-1})	70	< 0.2	< 0.063	< 0.2	0.033	2.2	0.5	< 0.2	n.c.	< 0.2	n.c.	9.9	n.c.	16	66.8	< 0.2	< 0.2	13.4	4.02
Ni (μg L^{-1})	20[b]	1.79	n.c.	0.6	0.461	21.2	14.3	2275	84.3	2434	78.5	2557	99.5	1368	91.8	384	792	750	1475
Pb (μg L^{-1})	10[b]	50.2	0.112	0.43	≈ 0	1069	1.1	1445	51.6	714	20.3	4303	30.1	3690	25.2	467	300	283	m.d.
Se (μg L^{-1})	1[b]	1	0.047	1.9	0.04	60.4	0.9	161	79.7	155	55.6	105	56.5	231	19.4	22.3	34.4	85.3	160
V (μg L^{-1})	6	< 0.05	< 0.004	< 0.05	≈ 0	9.7	5.4	91	81.25	66.8	66.8	155	32.6	105	22.1	21	39.9	59.7	79.5
Zn (mg L^{-1})	0.12[c]	0.36	4.7	0.16	0.42	6.9	0.02	1058.8	100	1092.3	84.31	717.6	97.1	255.2	91.9	114	293.2	128.5	246.8
pH	6.5–8.5[a]	4.04		5.21		1.57		1.58		1.63		0.94		1.12		2.76	2.44	2.43	2.42
EC μS cm^{-1} 25°		93		115		2900		29,500		20,800		16,490		28,100		11,380	27,880	12,680	23,960
SO_4^{2-} (mg L^{-1})	250[b]	29		21		2640		46,942		49,014		46,024		39,850		5600	13,800	7100	11,500
HAQ		8.8		2.9		279.4													

[a] USEPA (2012)

[b] European Council (1998)

[c] USEPA (2002)

[d] Puura and D'Alessandro (2005)

follows: Se (4.6) > As = Pb = Zn (3.6) > Ni (2.9) > Co (2.5) > Fe (2.4) > V (2) > Al ≈ Cd (1.7) > Cu (1.2). As and Pb were more concentrated in most distal efflorescent salts, probably incorporated to solid-solution of copiapite, a typical mineral of hyper-acid environment (pH 0.94–1.12). In any case, starting from a solution that could resemble DT leachate, the result of efflorescence salts formation is an important enrichment of elements. This is difficult to explain because efflorescence formation involves a series of complex processes: dissolution, seepage through the base of the dike, soaking of the substrate and interaction with it, drying, and mineral precipitation. The final consequence is that the soluble concentration of SO_4^{2-} was very high on all the dissolved salts (up to 39,000 mg L^{-1}), and soluble Fe, Al, Zn, As, Cu, and Co were extremely high. Indeed, these efflorescent salts are solid solutions that incorporate a variety of ions (e.g., Hammarstrom et al. 2005) and scavenge these elements during precipitation. However, this retention is brief because it is well known that the dissolution of metal-sulfate salts during storm-runoff events causes an abrupt increase in dissolved metal and sulfate concentrations, even as the water flow increases (Dagenhart Jr 1980). Undoubtedly, the quality of the waters that intermittently flow through the small stream buried by the impoundment has been affected for decades. However, looking at the seepage data, and not considering the probable dilution and attenuation from the sampling points to the confluence with the Tinto River, only Fe, Pb, and perhaps Co content would be slightly increased.

It should be emphasized that the sampling of water and efflorescences is not always feasible when carrying out inventories, as it depends on the season, the weather, and the nature of the mining waste. In Spain, water and efflorescent salts associated with waste facilities have rarely been sampled. In this sense, when the methodology was designed, it was decided to assess each potential for water pollution by leaching tests, even if the existence of other data would facilitate understanding and judgment. From the perspective of the inventories and assessments made, the HAQ has proved valuable. However, in the exceptional case studied, it was considered necessary to assess the hazard based on leaching data for deeper tailings (DT) rather than those dominating in volume and surface area exposed (UT).

Conclusions

The tailings impoundment named Represa I-II represents a special case among the abandoned mining waste facilities in Spain. It stores three very different types of waste: UT, IT, and DT. Erosion processes have produced and will continue to produce the emission of toxic elements (As, Pb, and Cu) linked to the eroded particles. The application of a multi-pollutant index, named Index of Contamination (IC) to the total content data, allows characterizing the toxicity of these tailings as very high. The IC calculated for IT sample is the highest ever published. Furthermore, decades of tailings weathering have generated surficial oxidation. As a result, the surface layers of wastes are enriched in readily soluble weathering products such as sulfate and toxic elements, which are also present in seepage water. The solubility of some metals in leachates obtained by the European Standard EN-12457-2 was very high, especially for Al, As, Cu, Pb, and Zn for deeper tailings (DT). Regarding soluble elements, an additional index named Hazard Average Quotient (HAQ) was applied to leachates data, resulting very high for DT tailings.

Finally, Represa I-II embodies a high hazard for soils, sediments, and water contamination, represented by very high IC and HAQ values. Other information on pathways and receptors is necessary for assessing the risk of this facility: distance to water bodies, water uses, people’s presence and access, nearby land uses, etc. However, if the Tinto River is considered the main receiving water body, the severity of the effects of this potential contamination must be judged as very low. In this sense, for remediation priorities, this abandoned tailings impoundment cannot be regarded as a priority, especially when the exceptional characteristics of the Tinto River have made it worthy of protection in its current state. This does not detract that Represa I-II is undoubtedly one of many abandoned mining facilities that have contributed to making the Tinto River what it is today. Similar studies could be extended to the many other abandoned facilities in the Riotinto mining district, to obtain a clearer idea of the influence of historical mining on the Tinto River nature.

Acknowledgments The authors acknowledge the support provided by Jesús Reyes de Andrés for the chemical analysis. The authors are also grateful to two anonymous reviewers for helpful comments on the manuscript.

Author Contributions Julio César Arranz-González: Conceptualization, sampling, methodology, writing-original draft, formal analysis, and investigation. Virginia Rodríguez-Gómez: Sampling, methodology, writing-review and editing, formal analysis, and investigation. Francisco Javier Fernández-Naranjo: Sampling, methodology, and writing-review and editing. Lucas Vadillo-Fernández: Supervision.

Funding This research was funded by the Instituto Geológico y Minero de España (Geological Survey of Spain) within the internal project Support and actions in environmental impact assessment, risk assessment, and mining waste management (Code: 78.5.00.01.00).

Data availability The datasets used during the current study are available from the corresponding author on reasonable request.

Compliance with ethical standards

Ethical approval, consent to participate, and consent to publish Not applicable.

Competing interests The authors declare that they have no competing interests.

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