



Pyrite ore cargo spills as a source of soil pollution and ecological risk along the abandoned railway corridors of the Tharsis and Rio Tinto mines (Spain)

Laura Gallego · Juan Carlos Fernández-Caliani

Received: 27 September 2022 / Accepted: 1 November 2022 / Published online: 11 November 2022
© The Author(s), under exclusive licence to Springer Nature Switzerland AG 2022

Abstract Abandoned mining railways are a prominent legacy environmental issue facing many metaliferous regions with a long mining history. However, there is a general lack of information on potentially hazardous trace elements occurring in soils alongside railroad lines as a result of hazmat cargo spills. This paper explores for the first time the effects of pyrite ore transportation on soil pollution along the old railways of Tharsis and Rio Tinto, two historical mining districts of world-class importance in the Iberian Pyrite Belt. The railroad-side topsoil was found to be extremely acidic in reaction and contains abundant pyrite, spilled on the tracks during transit, and its oxidation products (jarosite, iron oxyhydroxides, and efflorescent sulfate minerals). Compared to local background concentrations, highly elevated levels of Pb, Zn, Cu, As, Hg, Sb, Bi, Cd, Ag, and Tl were detected in both railroad lines, indicating serious anthropogenic contamination. Exposure to soil contaminants, notably Pb, As, and Tl, could pose hazards

to human health and the environment. Accordingly, a specific-site risk assessment is needed before the mining railway lines are converted into recreational trails.

Keywords Pyrite · Hazmat cargo spills · Mining railway · Soil quality index · Iberian Pyrite Belt

Introduction

Railway transport is the most environmentally friendly mode of motorized transportation in terms of greenhouse gas emissions and environmental footprint (Szmaglinski et al., 2021), although it may be a potential source of soil pollution. A number of studies have found a connection between rail transport operations and hazardous soil pollutants, among which polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), oil-derived products, and heavy metals are the most commonly reported (Chen et al., 2014; Jian-Hua et al., 2009; Samarska et al., 2020; Seda et al., 2017; Stancic et al., 2022; Stojic et al., 2017; Szmaglinski et al., 2021; Wierzbicka et al., 2015; Wilkomirski et al., 2011, 2012; Zhang et al., 2012, 2013). These chemicals derive from different emission sources, such as locomotives and rolling stock, wood preservatives used for railroad ties, or from any leakage of fuel or cargo (Wilkomirski et al., 2012; Metrak et al., 2015; Vaiskunaite & Jasiunien, 2020). Heavy metal emissions arise mainly from frictional interaction between steel rails and wheels of running trains,

Supplementary Information The online version contains supplementary material available at <https://doi.org/10.1007/s10661-022-10715-3>.

L. Gallego
Dept. Geology, Tharsis Mining, 21530 Tharsis, Spain
e-mail: lauragallego@tharsismining.com

J. C. Fernández-Caliani (✉)
Dept. Earth Sciences, University of Huelva, 21071 Huelva,
Spain
e-mail: caliani@uhu.es

with Fe, Mn, Cr, Ni, and V being the main metals of concern emitted to the environment during transit (Bukowiecki et al., 2007; Burkhardt et al., 2008; Liu et al., 2009; Samarska et al., 2020; Wierzbicka et al., 2015; Zhang et al., 2012). Elevated concentrations of arsenic in surface soils of railway corridors may result from repeated applications of As-based herbicides to control grass growth (Smith et al., 2006).

All these studies have focused on conventional railway lines, but seldom dealt with heavy metal contamination within the vicinity of former mining railroads and their effects on the soil environment. Interestingly, there is a general lack of data on potentially hazardous trace elements (PHEs) occurring in soils near mining railway tracks as a result of hazmat cargo spills. In recent years it has been observed an increasing interest to convert disused railway lines into multipurpose trails and greenways (e.g., Quattrone et al., 2018; Zhang et al., 2018). Hence the importance of assessing the degree of contamination with PHEs in nearby soils, which could pose a potential threat to public health and the natural environment.

With about 500 km of abandoned mining railway lines, the Spanish sector of the Iberian Pyrite Belt provides a rail network suitable for assessing soil contamination by PHEs and their potential ecological hazard along the old mining railway corridors. The rail lines that linked the world-renowned mines of Tharsis and Rio Tinto to the Huelva estuary, on the Atlantic coast of southwestern Spain, are the two major and most representative mining railways in the region (Romero-Macías, 2006). They are no longer operational due to a lack of use and were abandoned or dismantled over decades ago. When active, these private narrow-gauge lines were crucial to become mining operations for copper and pyrite economically viable, providing mineral transport services over a century from the mining districts to the port of Huelva for export overseas. The mining railways also served as a secondary mode of transportation of people and freight.

The railway traffic and the operations performed during mineral loading and transportation had caused a visible impact on the local soil environment. In both mining railway corridors, anywhere along the length of the lines, one can see large quantities of pyrite ores that have spilled from the mineral wagons by the side of the tracks when transported. In addition, track ballast is another potential source of contaminants in the mining railway system, because as much as four

million tons of Roman slags containing significant amounts of Cu, Pb and Ag were used as ballast for the rails (Salkield, 1987).

This paper reports for the first time the legacy effects of railway traffic on soil heavy metal pollution along the former railway lines of Tharsis and Rio Tinto mines. Specifically, the study was aimed at determining the current status of soil contamination and the potential risk to human and ecological receptors by different methods of index calculation. Due to growing interest from regional and local stakeholders to transform the abandoned railroad lines into recreation trails for biking and walking, the results from this research would help in developing strategies to minimize potential exposures to soil contaminants.

Material and methods

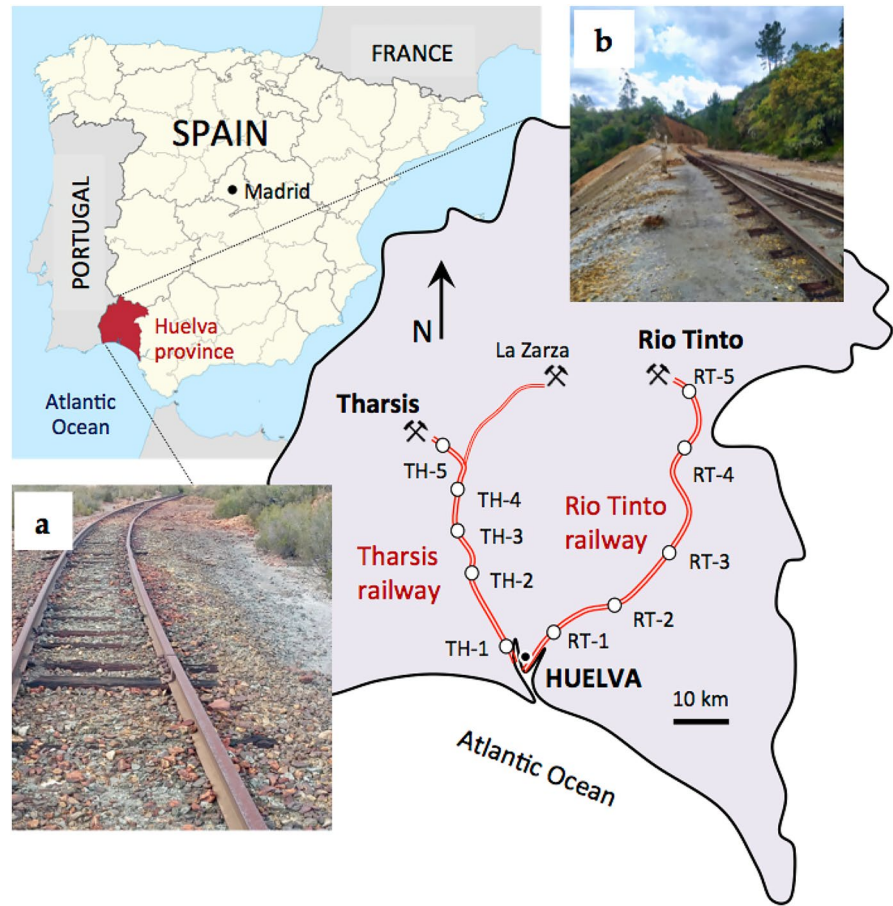
Mining railway description and sampling locations

The former railway corridors of Tharsis and Rio Tinto mines are located in the Huelva province of southwestern Spain (Fig. 1). The mining railway lines ran through two distinct regions with different physiographic features. From north to south, the landscape changes noticeably from gentle mountains covered with Mediterranean forest to fertile farmlands and salt marshes across a coastal plain. Leptosols and Cambisols are the most extensive group of soils in the northern hills while Vertisols and Solonchaks dominate most of the land in the coastal area (soil classification according to World Reference Base for Soil Resources, WRB, 2015).

The Tharsis mining railway (Fig. 1a) was opened in 1871 with the aim of transporting the pyrite ores extracted by the Tharsis Sulphur and Copper Co. Ltd. from the mines of Tharsis and La Zarza to Huelva, where the mining company had its own loading dock on the river Odiel. When the mines closed in the late 1990s, the railway and rolling stock were abandoned after being in service for more than a century (Romero-Macías, 2006). The main line was 47 km in length from Tharsis to river Odiel of narrow-gauge track (1220 mm). Parts of the railroad tracks have been removed and recycled as scrap.

The Rio Tinto-Huelva railway (Fig. 1b) was built in 1875 by the Rio Tinto Co. Ltd. to connect its mines

Fig. 1 Location map of the sampling localities along the old mining railway corridors of Tharsis (a) and Rio Tinto (b), and field pictures of the soil adjacent to the rusted rail trucks



with the port of Huelva. This leading world company also had its own pier on the river Odiel to facilitate the exportation of mineral on a large scale. The main line consisted of 84 km of narrow-gauge track (1067 mm) following nearly the course of the river Tinto. In the 1970s the old railway did not meet modern requirements and it was gradually falling into disuse until its closure in 1984 (Romero-Macías, 2006). It is estimated that as much as 150 million tons of ore were transported by rail and shipped from the Rio

Tinto pier (García-Mateo & Prieto, 2012). Currently, much of the railway line has been dismantled for scrap, although a restored 11 km section was opened for tourism in 1994.

The extent of soil contamination was studied in five sampling locations of each mining railway corridor (Table 1), in which other anthropogenic disturbances apart from rail transport seemed to be negligible. Although sampling strategy was conditioned by accessibility, the sampling locations were chosen

Table 1 Geographical coordinates of the sampling localities

Tharsis mining railway			Rio Tinto mining railway		
Sample	North	West	Sample	North	West
TH 1	37° 16' 22"	06° 59' 05"	RT 1	37° 17' 36"	06° 53' 42"
TH 2	37° 25' 45"	07° 03' 28"	RT 2	37° 21' 19"	06° 41' 34"
TH 3	37° 29' 11"	07° 04' 33"	RT 3	37° 27' 06"	06° 34' 15"
TH 4	37° 32' 35"	07° 04' 19"	RT 4	37° 35' 18"	06° 33' 06"
TH 5	37° 35' 35"	07° 05' 43"	RT 5	37° 40' 18"	06° 33' 45"

at roughly equidistant positions along the paths of the railroads. At each sampling locality, soil surface samples (0–5 cm depth) with similar slope and drainage conditions were randomly collected in at least three different sites scattered in an area of about 100 m². The samples were taken in the immediate vicinity but outside the toe of railway embankment (Fig. 2). In addition, a control soil covered with natural vegetation was established at more than 50 m far away from the tracks. At the control sites, trace element content there was set as local background concentration. All topsoil samples were taken using a stainless steel trowel, bulked to form a composite sample of about 1 kg representing the site, and then stored in airtight polyethylene bags.

Analytical methods

The soil samples were dried at room temperature, gently ground, passed through a 2-mm stainless-steel sieve, and thoroughly mixed to ensure optimal homogenization. Soil pH was measured with a digital pH meter (Crison Instruments), previously calibrated with two buffer solutions at pH 4 and 7, in a

soil to deionized water suspension of 1:2.5 (w/v), after shaking for 15 min and left to stand for 30 min.

Mineral composition was determined by X-ray powder diffraction (XRD) with a BRUKER AXS D8-Advance diffractometer, using monochromatic Cu-K α radiation under standard instrumental conditions: from 3 to 65° 2 θ , with a step size of 0.02° and a counting time of 0.6 s per step, at 30 mA and 40 kV. Relative mineral abundance was estimated by empirical intensity factors weighting integrated peak area values of distinctive reflections in combination with the 100% approach (Khale et al., 2002). To ensure accurate identification of accessory minerals and poorly crystallized phases, the samples were examined by field emission scanning electron microscopy (FESEM) using a JEOL JSM-IT500HR instrument coupled to an energy-dispersive spectrometry (EDS) microanalytical system (X-Max detector, Oxford Instruments). Back-scattered electron (BSE) images and EDS spectra were acquired at 20 kV accelerating voltage to assist in the mineral identification of accessory heavy metal-bearing particles. The FESEM-EDS study also enabled the observation of morphological features and textural relationships among the various phases.

Pseudo-total concentrations of fourteen PHEs (Ag, As, Bi, Cd, Co, Cr, Cu, Hg, Ni, Pb, Sb, Tl, V, and Zn)

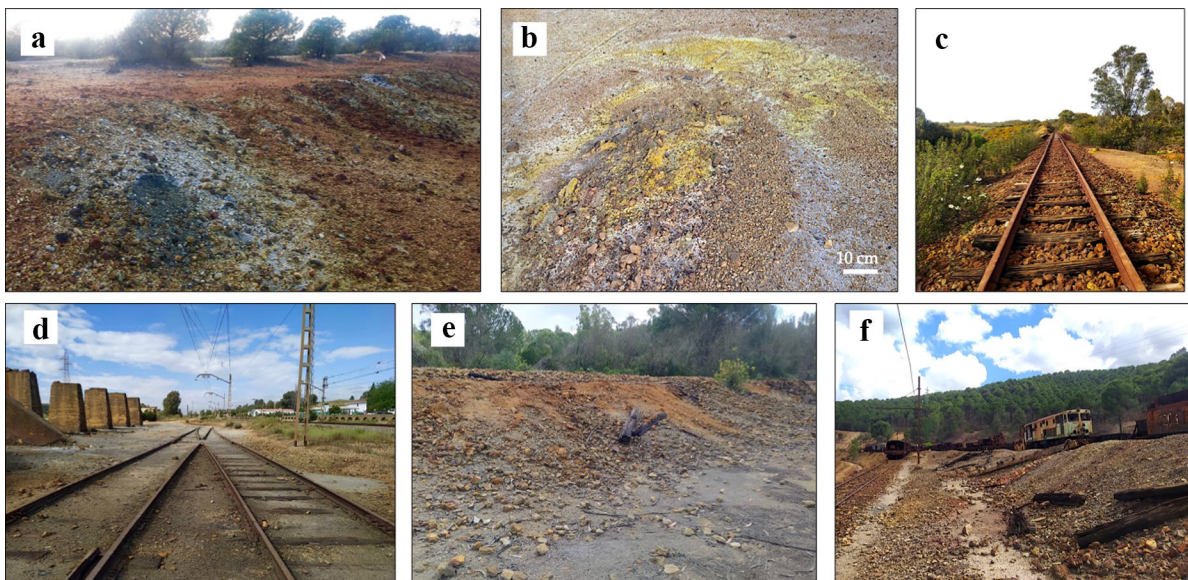


Fig. 2 Field pictures of some sampling locations showing: (a) pyrite ore concentrate spilled from the wagons while being transported to the port of Huelva (sampling location TH-1); (b) sulfate salt deposits left on surface soil by evaporation of acid waters derived from oxidizing pyrite (RT-1); (c) railway tracks

and wooden ties on a ballast bed of crushed ancient slags (TH-3); (d) Double-track railway at the old Las Mallas station (RT-2); (e) disused railway embankment and adjacent soil (RT-3); (f) rusting rolling stock abandoned in the Rio Tinto mining area (RT-5)

in soil samples were determined by inductively coupled plasma optical emission spectrometry (ICP-OES), after digestion with aqua regia. This partial digestion uses a combination of concentrated hydrochloric and nitric acids (3HCl:1HNO₃) to leach sulfides, some oxides and some silicates. Most base and noble metals are usually dissolved in the aqua regia-extracts. The analyses were conducted at Activation Laboratories (Ontario, Canada), which is accredited to the ISO/IEC 17,025 standard (ISO, 2005). Detection limits of the analyzed PHEs and laboratory quality control report are provided in Supplementary Table S1. Quality control was accomplished through the analysis of reagent blank samples, certified reference materials (OREAS series), and replicate samples. Relative deviation standard (RDS) values were less than 10% for most analyzed PHEs.

Data analysis

A two-tailed equal variance t-test was used to determine if there was significant differences in average values of PHEs concentration between the two groups of samples (railroad-side soil and control soil). The critical level of significance was set at $\alpha=0.05$ (95% confidence interval). Principal component analysis (PCA) was carried out on the log-transformed data to distinguish between different sources of PHEs in soil (Boruvka et al., 2005). Statistical analysis was performed with the Statistica 10.0 and MS Excel 2016 software packages. For the purpose of trend testing, censored data were replaced with detection limit values.

Soil contamination was assessed by calculation methods that relate the concentrations of PHEs in soil alongside railway and their local background concentrations, providing simple comparative means for assessing soil quality (e.g., Cai et al., 2015). Thus, a quantitative evaluation of multielement contamination degree (*Cd*) was determined using the formula:

$$C_d = \frac{\sum_i^n C_f^i}{n}$$

where *n* is the number of PHEs under investigation (*n*=14 in this study) and *C_f* is the contamination factor for a given element (*i*), which is a single pollution index defined as follows:

$$C_f = \frac{C_s}{C_b}$$

where *C_s* is the concentration of a trace element measured in the soil affected by rail transportation, and *C_b* is the measured concentration in the control soil (local background concentration).

Based on the contamination degree index, Abraham and Parker (2008) divided the contamination level into seven grades ranging from nil to very low contamination (*Cd*<1.5) to ultra-high degree of contamination (*Cd*≥32).

The Nemerow pollution index (NPI) was calculated by the following equation (Nemerow, 1985):

$$NPI = \sqrt{\frac{(C_f^i)_{avg}^2 + (C_f^i)_{max}^2}{n}}$$

where *C_f* is the contamination factor as previously defined, *C_{f_{avg}}* and *C_{f_{max}}* are the average and maximum values, respectively, of *C_f* among all the trace elements of concern, and *n* is the number of trace elements. According to NPI values, five classes of soil quality can be distinguished: no pollution (≤0.7), warning limit (0.7–1), slight pollution (1–2), moderate pollution (2–3), and heavy pollution (≥3).

The method developed by Hakanson (1980) was used to determine the potential ecological risk index (RI) of multiple trace elements, using the *C_f* values of the most concerned PHEs occurring in soil:

$$RI = \sum_i^n Er^i = \sum_i^n Tr^i \times C_f^i$$

where *Er* is the potential ecological risk factor for the trace element *i* and *Tr* is a toxic-response factor for the given pollutant (Hg=40; Cd=30; As=10; Cu=5; Pb=5; Cr=2; and Zn=1). Based on the RI values, the following grades were used to describe the potential ecological risk: low risk (RI<150); moderate risk (150≤RI<300); considerable risk (300≤RI<600); and very high risk (RI≥600).

Results and discussion

Soil mineralogy

The topsoil samples collected in the close vicinity of the railroads are similar in mineral composition (Table 2), although there are noticeable differences in relative abundance of major crystalline phases, as

determined by XRD. They are made up of a mixture of common soil minerals (quartz, mica, kaolinite, and feldspars) and highly variable proportions of contaminant metal-bearing minerals, mostly pyrite and jarosite.

The results achieved from FESEM-EDS analysis confirmed the mineral composition determined by XRD, and allowed us to identify some fragments of the ancient slag that was used as track ballast, as well as accessory minerals of environmental significance, such as iron oxyhydroxides and a variety of secondary sulfates (Fig. 3).

Pyrite usually occurs as well-formed cubic crystals showing clear signs of alteration, such as deep striations and dissolution pits and channels on surfaces (Fig. 3a, b), as a result of oxidative weathering by well-known reactions (Rimstidt & Vaughan, 2003). The oxidative dissolution of pyrite provided an acidic and oxidizing environment suitable for jarosite precipitation. Under FESEM examination, jarosite was found as fine aggregates of pseudocubic-shaped crystals ranging between 1 and 2 μm in size (Fig. 3c). Other weathering products of sulfide oxidation included amorphous or poorly crystallized iron oxyhydroxides consisting of micron-sized particles that often appear aggregated into granules. Moreover, clusters of elongated prismatic crystals of gypsum over 50 μm in length (Fig. 3d) and epitaxial overgrowths of anglesite on barite (Fig. 3e) were observed in some samples, as well as hydrated sulfate minerals (Fig. 3f) occurring as yellow-white efflorescent crusts on the surface soil. This secondary mineral assemblage is consistent with that derived from sulfide weathering processes in mine soils of the Iberian Pyrite Belt (Fernández-Caliani et al., 2009), and

resembles the mineralogy of alluvium contaminated by mining in the Rio Tinto area (Hudson-Edwards et al., 1999).

Soil acidification

The topsoil samples influenced by mining railway activity are ultra-acidic, with mean pH values of 2.9 in both corridors (Table 3). This average value is significantly lower than those of background soil at the control sites ($p < 0.05$). The control samples with the highest degree of acidification were collected at sites closest to the mining areas (pH=4.0 at Tharsis and pH=4.6 at Rio Tinto), so it is plausible that these soils not only reflect direct pollution from rail traffic but also from mining activities. Results of soil reaction contrast markedly with those of other authors (e.g., Wilkomirski et al., 2012) who have reported mean pH values in the range of 7.3–8.0 in soil samples along inactive railway tracks elsewhere.

Sulfide oxidation has become a major driver of soil acidification, which in turn can have critical effects on PHEs release and toxicity. In fact, the soil immediately adjacent to the rail tracks was almost entirely devoid of vegetation and showed evidence of land degradation at all sampling locations due to acid produced from pyrite weathering. The efflorescent sulfate salts provide another potential source of acidity upon dissolution by rainfall (Grantcharova & Fernández-Caliani, 2022; Valente & Gomes, 2009).

Trace element concentrations

All pseudo-total concentrations of PHEs measured in both soil potentially contaminated by cargo spills and

Table 2 Semi-quantitative estimates of mineral composition (wt %), as determined by XRD, of the soil samples located in the immediate vicinity of the railways tracks and potentially contaminated by ore transportation

Railway	Sample	Quartz	Clay min	Feldspars	Pyrite	Jarosite	Gypsum
THARSIS	TH 1 – A	15–20	15–20	<5	50–55	<5	5–10
	TH 2 – A	40–45	50–55	<5	<5	5–10	–
	TH 3 – A	30–35	20–25	5–10	5–10	10–15	5–10
	TH 4 – A	25–30	45–50	5–10	5–10	15–20	–
	TH 5 – A	15–20	30–35	<5	15–20	30–35	–
RIO TINTO	RT 1 – A	40–45	20–25	5–10	<5	15–20	5–10
	RT 2 – A	5–10	55–60	<5	55–60	15–20	5–10
	RT 3 – A	5–10	5–10	<5	30–35	30–35	10–15
	RT 4 – A	10–15	5–10	<5	5–10	15–20	–
	RT 5 – A	20–25	25–30	<5	10–15	30–35	–

Clay minerals: mica and kaolinite

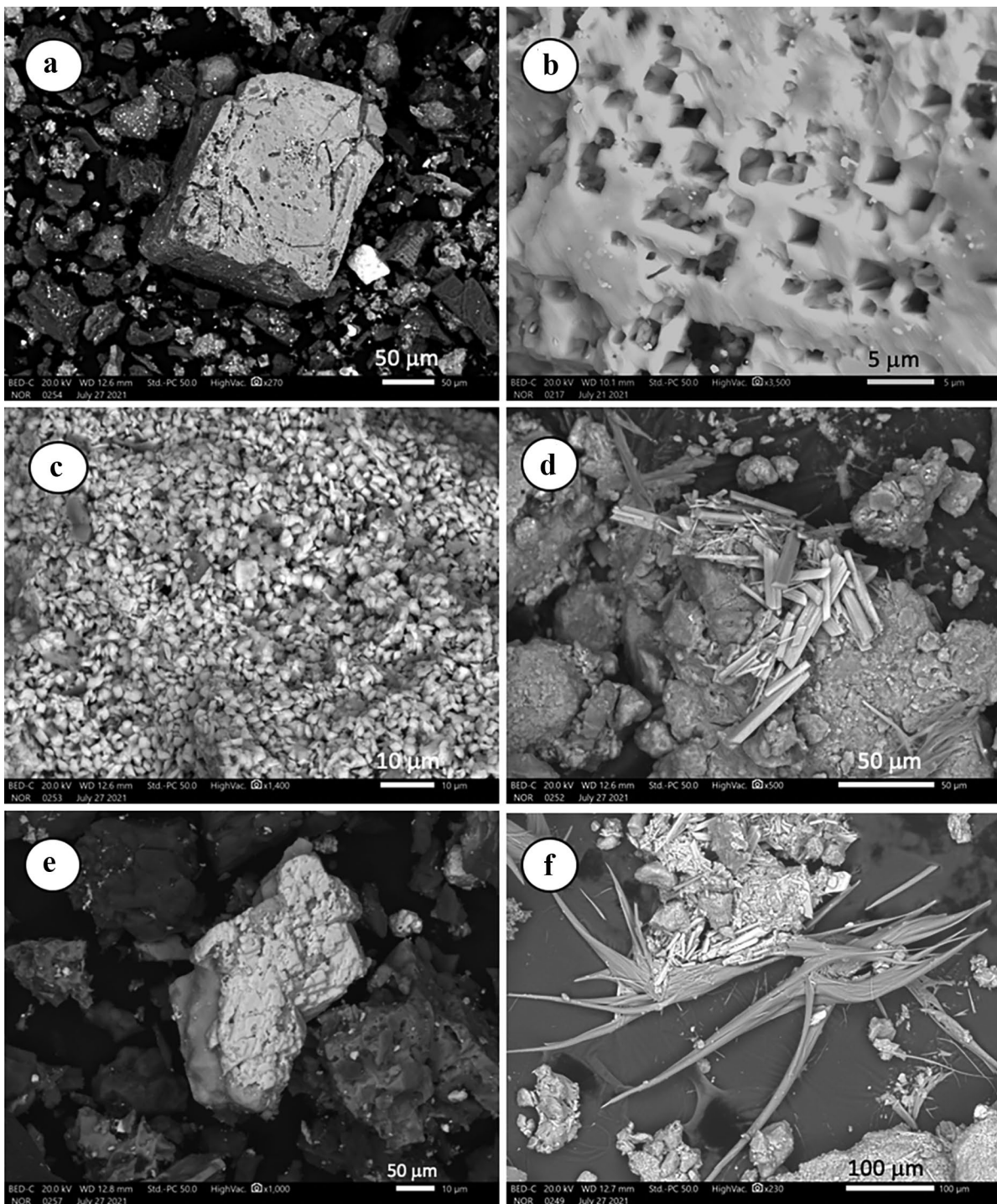


Fig. 3 FESEM-BSE images showing: a cubic crystal of pyrite (a) with dissolution pits on surface (b); an aggregate of micron-sized crystals of jarosite (c); a cluster of prismatic

crystals of gypsum (d); and epitaxial overgrowth of anglesite on barite (e); and fibrous masses of hydrated sulfate of iron and aluminium, probably halotrichite (f)

Table 3 Soil pH (in water) comparison between samples potentially contaminated by ore transportation and control samples from the two mining railway lines

	Tharsis railway	pH (in water)	Rio Tinto railway	pH (in water)
Potentially contaminated soil	TH 1 – A	2.26	RT 1 – A	2.98
	TH 2 – A	3.30	RT 2 – A	2.88
	TH 3 – A	3.35	RT 3 – A	4.61
	TH 4 – A	3.35	RT 4 – A	1.93
	TH 5 – A	2.39	RT 5 – A	2.15
Mean value		2.93 ± 0.55		2.91 ± 1.05
Control soil	TH 1 – B	5.50	RT 1 – B	5.88
	TH 2 – B	5.30	RT 2 – B	6.18
	TH 3 – B	5.35	RT 3 – B	5.94
	TH 4 – B	6.12	RT 4 – B	5.49
	TH 5 – B	4.04	RT 5 – B	4.63
Mean value		5.26 ± 0.76		5.54 ± 0.59

control soil are reported in Table 4, including those below the detection limit and over-range values.

Most PHEs in soil affected by long-term ore transportation varied widely within and between the mining railway corridors, depending on the element involved and the sampling location. Exceptionally high concentrations of Pb (over 5000 mg kg⁻¹), Zn (up to 7370 mg kg⁻¹), Cu (up to 2660 mg kg⁻¹), and As (up to 1990 mg kg⁻¹) were detected across all sampled sites of both railroad lines. These levels are nearly two orders of magnitude above the regional geochemical baseline (Galán et al., 2008), and are comparable to those reported in strongly contaminated mine soils of the Iberian Pyrite Belt (Fernández-Caliani et al., 2009; Mourinha et al., 2022). Other contaminants of concern like Sb (up to 754 mg kg⁻¹), Hg (up to 163 mg kg⁻¹), Bi (up to 149 mg kg⁻¹), Ag (up to 75 mg kg⁻¹), Tl (up to 47 mg kg⁻¹), and Cd (up to 30.6 mg kg⁻¹) were far outside the normal ranges of the European and Spanish soils (Locutura et al., 2012; Salminen, 2005). The large spatial variability of these chalcophile contaminants in soil alongside railways is clearly related to the widespread occurrence of pyrite ores, in varying amounts, due to the falling off loads while trains were running. The fragments of ancient slag used as track ballast is likely an additional source of Ag, Pb and Cu (Salkield, 1987).

Pseudo-total concentrations of Ag, As, Bi, Cu, Hg, Pb, Sb, and Tl in the soil samples collected in the vicinity of the railways tracks were significantly higher ($p < 0.05$) than those of the control soil

samples (Fig. 4). In contrast, the contents of Cr, Ni, and V were significantly below the control soil levels used as local baseline reference values ($p < 0.05$). However, there no was significant differences ($p > 0.05$) in the contents of Co, Zn, and Cd between both group of samples. Interestingly, some control soil samples (e.g., sample RT-4B) had abnormally high concentrations of PHEs despite their apparently natural trait. This could be due to unforeseen contamination caused by atmospheric deposition of wind-blown dust from the railway tracks.

By projecting the data onto the PCA diagram (Fig. 5), two distinct clusters characterized by strong and opposite scores can be visually identified. A group with large positive loadings for Cr, Ni, and V on the first principal component, which is statistically dominant, being interpreted as the component of natural element concentration; and another one comprising the chalcophile PHEs on the negative side of the same principal component. These pedogeochemical associations have been interpreted as formed by geogenic and sulfide-related anthropogenic elements, respectively (Fernández-Caliani et al., 2009).

Soil contamination assessment

The current status of soil contamination can be inferred on the basis of soil quality indices that relate the concentrations of PHEs in affected soil and their concentrations measured in control samples, at sites assumed to reasonably represent the local natural background including diffuse anthropogenic inputs.

Table 4 Pseudo-total concentrations (aqua regia soluble) of potentially hazardous trace elements (in mg kg⁻¹) in soil samples exposed to railroad contamination and control soil samples from the abandoned railways of the Tharsis and Rio Tinto mines

Trace element (mg kg ⁻¹)	Tharsis mining railway										Rio Tinto mining railway									
	Potentially contaminated soil					Control soil					Potentially contaminated soil					Control soil				
	TH-1A	TH-2A	TH-3A	TH-4A	TH-5A	TH-1B	TH-2B	TH-3B	TH-4B	TH-5B	RT-1A	RT-2A	RT-3A	RT-4A	RT-5A	RT-1B	RT-2B	RT-3B	RT-4B	RT-5B
Ag	75.3	2.6	12	12.8	40	0.4	<0.2	1.4	0.3	1	20.5	43.7	58.9	45.8	53.8	2.6	<0.2	0.6	9.1	3.8
Cd	5.2	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	0.9	<0.5	<0.5	7.6	9.7	30.6	3.5	3.1	4.1	<0.5	<0.5	1.9	<0.5
Cu	361	137	306	300	1300	260	26	435	108	503	849	2660	1880	439	2090	878	75	97	1170	241
Ni	4	15	13	14	8	15	18	34	28	22	10	4	5	5	4	25	118	27	28	39
Pb	>5000	761	4720	4890	>5000	119	27	438	177	588	4470	>5000	4660	3940	>5000	551	48	159	2450	354
Zn	1510	78	75	90	331	410	65	308	94	505	1940	2290	7370	825	838	1150	100	111	513	66
As	440	433	1450	853	1300	46	19	139	76	251	1210	1370	829	1130	1990	181	88	94	811	59
Bi	97	7	30	30	80	<2	<2	3	<2	5	43	142	132	143	149	4	<2	<2	26	3
Co	29	5	4	6	16	12	12	30	18	15	7	6	32	34	3	19	35	18	20	14
Cr	7	47	30	20	19	32	33	38	27	40	26	14	5	6	11	40	99	36	28	49
Hg	163	4	14	15	56	<1	<1	1	<1	<1	9	26	30	17	17	<1	<1	<1	8	1
Sb	571	47	174	198	600	13	4	20	14	31	162	294	453	329	754	19	15	6	140	27
Tl	19	<2	6	9	18	<2	<2	<2	<2	<2	16	47	28	38	39	<2	<2	<2	3	<2
V	10	71	39	29	22	42	41	40	35	42	40	25	9	4	26	49	54	34	36	43

Fig. 4 Box-and-whisker plots comparing pseudo-total trace element concentrations in soil affected by railway ore transportation and control soil (all values are in mg kg^{-1})

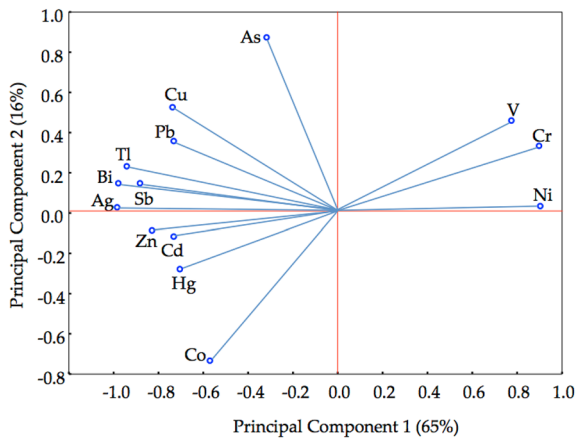
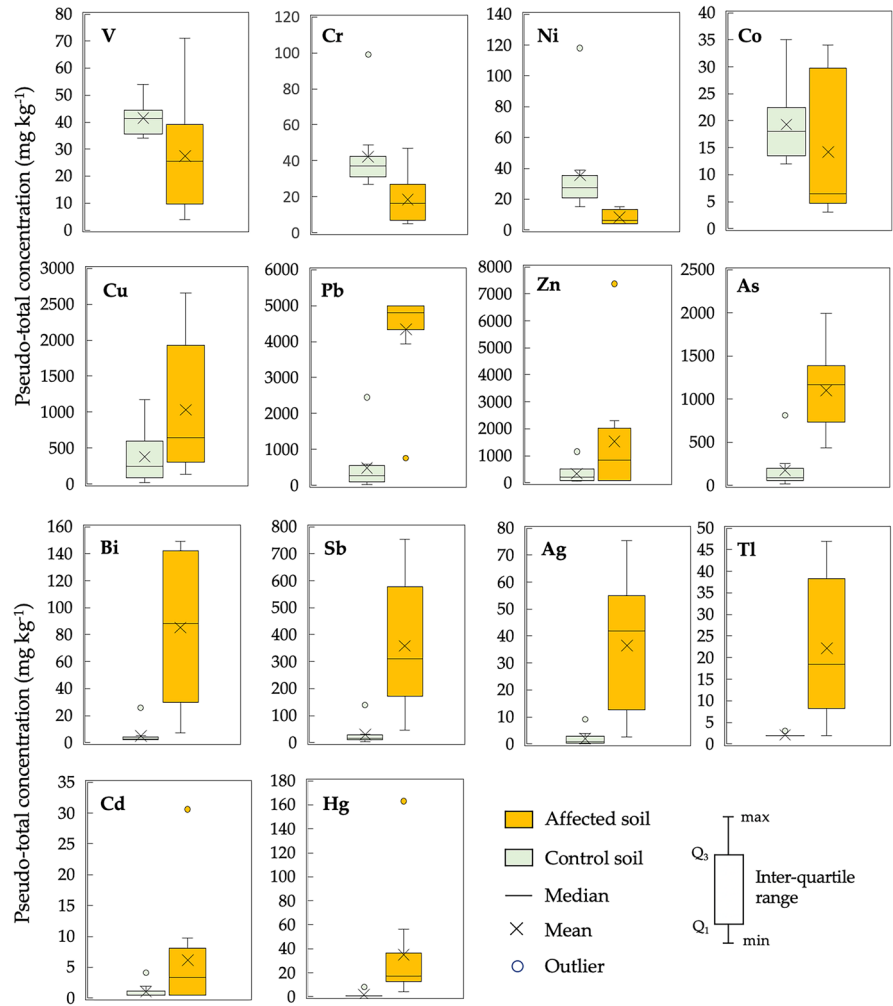


Fig. 5 Scatter plot of the principal component analysis (PCA) showing the loadings of the first two principal components for pseudo-total concentrations of trace elements of concern

Contamination factor (C_f) values of Cr, Ni, and V were below or slightly above unity in all samples, as expected for geogenic elements, which support the view that they are naturally occurring (Table 5).

In contrast, the C_f values of the sulfide-related PHEs were consistently elevated along the Rio Tinto railway line, in particular for Pb (up to 104), Sb (up to 75.5), Bi (up to 71.0), Zn (up to 66.4), and Cd (up to 61.2), as well as along the Tharsis railroad where they reached up to 163 for Hg, 48.5 for Bi, 43.2 for Sb, and 42.0 for Pb. The maximum C_f values of Cu (35.5) and As (33.7) were observed in the railway corridor of the Rio Tinto mines. Interestingly, the highest C_f values were found to be for Ag (up to 218 in the Rio Tinto railroad and up to 188 in the Tharsis railroad) due to contaminated railway ballast, as noted previously. Compared to the results reported in other studies

Table 5 Contamination factor (*C_f*) values for trace elements in soil affected by ore transportation along the former railroad lines of Tharsis and Rio Tinto mines

Railway	Sample	Contamination Factor (<i>C_f</i>)													
		Ag	As	Bi	Cd	Cr	Co	Cu	Hg	Ni	Pb	Sb	Tl	V	Zn
Rio Tinto	RT-1A	7.88	6.69	10.7	1.85	0.65	0.37	0.97	9	0.40	8.11	8.53	8.0	0.82	1.69
	RT-2A	218	15.6	71.0	19.4	0.14	0.17	35.5	26	0.03	104	19.6	23.5	0.46	22.9
	RT-3A	98.2	8.82	66.0	61.2	0.14	1.78	19.4	30	0.19	29.3	75.5	14.0	0.26	66.4
	RT-4A	5.03	1.39	5.50	1.84	0.21	1.70	0.38	2	0.18	1.61	2.35	12.7	0.11	1.61
	RT-5 A	14.2	33.7	49.7	6.20	0.22	0.21	8.67	17	0.10	14.1	27.9	19.5	0.60	12.7
Tharsis	TH-1 A	188	9.57	48.5	10.4	0.22	2.42	1.39	163	0.27	42.0	43.2	9.5	0.24	3.68
	TH-2 A	13.0	22.8	3.50	1.00	1.42	0.42	5.27	4	0.83	28.2	11.5	1.0	1.73	1.20
	TH-3 A	8.57	10.4	10.0	0.56	0.79	0.13	0.70	14	0.38	10.8	8.70	3.0	0.98	0.24
	TH-4 A	42.7	11.2	15.0	1.00	0.74	0.33	2.78	15	0.5	27.6	14.1	4.5	0.83	0.96
	TH-5 A	40.0	5.18	16.0	1.00	0.48	1.07	2.58	56	0.36	8.50	19.3	9.0	0.52	0.66

about the impact of rail transportation on adjacent soil (e.g., Chen et al., 2014, and references therein), the concentrations of these chalcophile contaminants were very high, with *C_f* values greater than 6 in most sampling locations (Table 5).

When considering the degree of multielement contamination (*C_d*), most samples were found to be very high to ultra-high contaminated with the PHEs under investigation. The *C_d* values were recorded in the range of 2.62–39.8 (Rio Tinto railway) and 4.95–37.4 (Tharsis railway), with RT-2A and TH-1A being the most contaminated samples (Fig. 6). Also, the highest values of the Nemerow pollution index (NPI) were computed in these samples (59.4 and 51.3, respectively), suggesting that there may be a severe contamination problem. The sample RT-2A was collected at Las Mallas station, where the Rio Tinto mining company had logistics facilities including a railway siding and a large rail yard, while the sample TH-1A was taken at the terminal station of the Tharsis railway, near the loading dock of Huelva. In other words, these soil samples evidence the long-term impact of increased railroad traffic. The relatively low *C_d* and NPI values observed in some samples (e.g., RT-4A) might be underestimated because the control soil may not precisely reflect the natural background concentrations due to diffuse contamination.

Potential risks to human health and ecosystems

In recent years, some sections of the old mining railway lines have been turned into greenways and now

are being used as greenways for walking and cycling, thus increasing the likelihood that soil contaminants could interact with human receptors through different exposure pathways.

For screening purposes, the PHE concentrations were compared to the threshold levels established by the Regional Government of Andalusia (Junta de Andalucía, 2015) for the assessment of contaminated soils in South Spain. The regulatory limit is defined as the concentration of a contaminant that does not result in a level of risk higher than the acceptable maximum for human health or ecosystems. The median concentrations of As, Pb, and Tl exceeded the health-based screening levels for industrial and

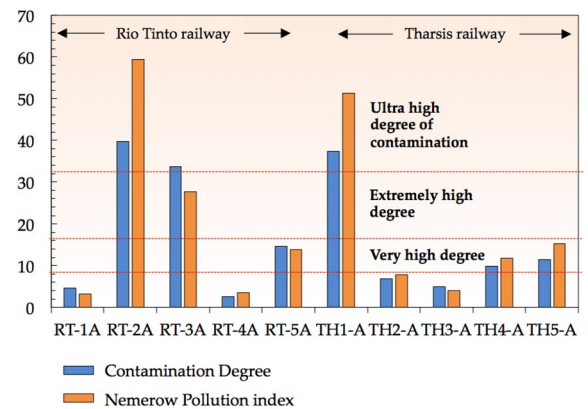
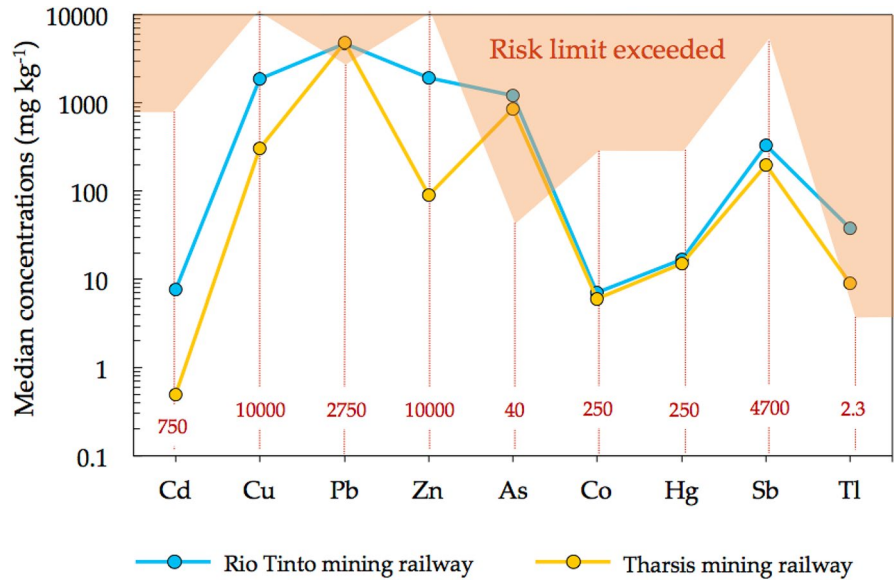


Fig. 6 Bar charts illustrating contamination degree and nemerow pollution index values obtained in soil samples from the former railway corridors of Rio Tinto and Tharsis mines

Fig. 7 Median concentrations of potentially hazardous trace elements in soil collected along the former railway corridors of Rio Tinto and Tharsis mines. The red vertical lines indicate the regulatory guidance values (in mg kg^{-1}) for industrial soils of southern Spain (Junta de Andalucía, 2015), above which adverse effects on human health and ecosystems may occur



other land uses (Fig. 7). Accordingly, soil alongside railway corridors of the Rio Tinto and Tharsis mines should be classified as potentially polluted by exposure to As, Pb, and Tl, and based on the precautionary principle, it requires a site-specific human health risk assessment.

Furthermore, the high degree of soil contamination with PHEs may pose a potential hazard to the environment. Potential ecological risk factors (Er) of As, Cd, Cu, Pb, and specially Hg along the old

railroads of Tharsis and Rio Tinto mines (Table 6) fell well above the soil quality guideline values proposed by Hakanson (1980).

The results obtained from calculation of the potential ecological risk index (RI) in both mining railway corridors (Fig. 8) are indicative of very high risk ($RI > 600$) in most sampling locations. Thus, soil contamination linked to past railway activities may represent a significant threat to nearby ecosystems and, therefore, deserve special attention.

Table 6 Potential ecological risk factors of As, Cd, Cr, Cu, Hg, Pb, and Zn in soil contaminated by ore transportation along the old railroads of Tharsis and Rio Tinto mines

Railway	Sample	Potential ecological risk factor (Er)							
		As	Cd	Cr	Cu	Hg	Pb	Zn	
Rio Tinto	RT-1A	66.9	55.6	1.30	4.83	360	40.6	1.69	
	RT-2A	156	582	0.28	177	1040	521	22.9	
	RT-3A	88.2	1836	0.28	96.9	1200	146	66.4	
	RT-4A	13.9	55.3	0.43	1.88	85	8.04	1.61	
	RT-5A	337	186	0.45	43.4	680	70.6	12.7	
Tharsis	TH-1A	95.7	312	0.44	6.94	6520	210	3.68	
	TH-2A	228	30.0	2.85	26.3	160	141	1.20	
	TH-3A	104	16.7	1.58	3.52	560	53.9	0.24	
	TH-4A	112	30.0	1.48	13.9	600	138	0.96	
	TH-5A	51.8	30.0	0.95	12.9	2240	42.5	0.66	

Potential ecological risk:
 $Er < 40$ (low); $40 \leq Er < 80$ (moderate); $80 \leq Er < 160$ (considerable); $160 \leq Er < 320$ (high); $Er \geq 320$ (very high)

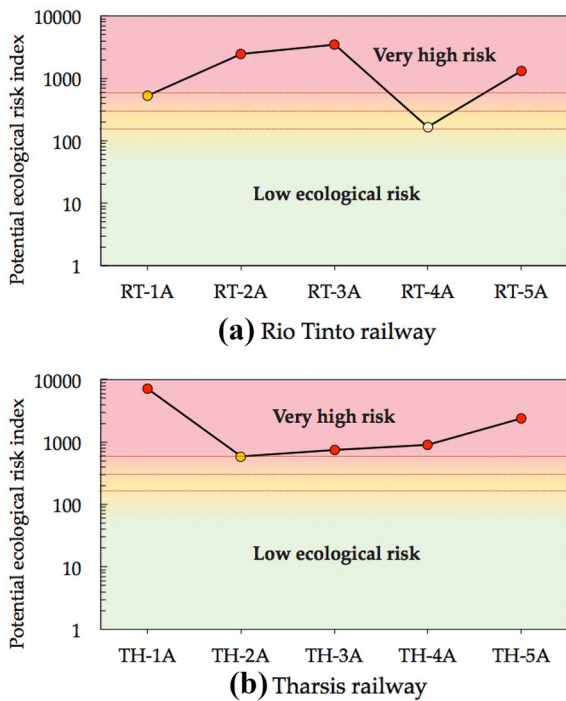


Fig. 8 Potential ecological risk index values of soil contaminated with trace elements (As, Cd, Cr, Cu, Hg, Pb, and Zn) along the former mining railway lines of (a) Rio Tinto and (b) Tharsis

Conclusions

Abandoned mining railways can be framed as a legacy environmental issue facing Southwest Spain, although it has not yet received the attention it deserves. The study carried out on representative soil sampling locations along the old mining railway corridors of Tharsis and Rio Tinto has revealed an ultra-high degree of soil contamination arising from historic railroad operations. The sulfidic material spilled on the railway tracks is an important source of soil acidification and heavy metal contamination. As a result of acid generation driven by oxidative dissolution of pyrite, the soil environment is ultra-acidic and contains exceptionally high levels of PHEs compared to local background concentrations. The contamination factors were particularly elevated for Hg, Pb, Sb, Bi, Zn, Cd, As, Cu, and Ag indicating serious anthropogenic pollution. A multivariate analysis allowed a clear distinction between these anthropogenic PHEs derived from pyrite weathering and geogenic trace elements (Cr, Ni, and V). Based on the current status

of soil contamination, certain PHEs like As, Pb, and Tl may pose an unacceptable risk to potential human and ecological receptors. In the light of these findings, a more detailed-site risk assessment should be considered to protect public health and the environment before the former mine rail lines are converted into recreational trails, and appropriate measures should be taken to minimize potential exposure to soil contaminants during trail construction.

Author contribution Laura Gallego: data curation; formal analysis; investigation; visualization; writing—original draft. Juan Carlos Fernández-Caliani: conceptualization, data curation; formal analysis; investigation; methodology; resources; supervision; validation; visualization; writing—review & editing.

Data availability The authors confirm that the data supporting the findings of this study are available within the manuscript and its supplementary material.

Declarations

Ethics approval The authors have read, understood, and have complied as applicable with the statement on “Ethical responsibilities of Authors” as found in the Instructions for Authors and are aware that with minor exceptions, no changes can be made to authorship once the paper is submitted.

Conflict of interest The authors declare no competing interests.

References

Abraham, G. M. S., & Parker, R. J. (2008). Assessment of heavy metal enrichment factors and the degree of contamination in marine sediments from Tamaki Estuary, Auckland, New Zealand. *Environmental Monitoring and Assessment*, 136, 227–238.

Boruvka, L., Vacek, O., & Jehlicka, J. (2005). Principal component analysis as a tool to indicate the origin of potentially toxic elements in soils. *Geoderma*, 128, 289–300.

Bukowiecki, N., Gehrig, R., Hill, M., Lienemann, P., Zwicky, C. N., Buchmann, B., Weingartner, E., & Baltensperger, U. (2007). Iron, manganese and copper emitted by cargo and passenger trains in Zürich (Switzerland): Size-segregated mass concentrations in ambient air. *Atmospheric Environment*, 41, 878–889.

Burkhardt, M., Rossi, L., & Boller, M. (2008). Diffuse release of environmental hazards by railways. *Desalination*, 226, 106–113.

Cai, C., Xiong, B., Zhang, Y., Li, X., & Nunes, L. M. (2015). Critical comparison of soil pollution indices for assessing contamination with toxic metals. *Water Air Soil Pollution*, 226, 352.

- Chen, Z., Wang, K., Li, W., Ai, Y. W., Li, W., Gao, H., & Fang, C. (2014). The effects of railway transportation on the enrichment of heavy metals in the artificial soil on railway cut slopes. *Environmental Monitoring and Assessment*, *186*, 1039–1049.
- Fernández-Caliani, J. C., Barba-Brioso, C., González, I., & Galán, E. (2009). Heavy metal pollution in soils around the abandoned mine sites of the Iberian Pyrite Belt (Southwest Spain). *Water Air Soil Pollution*, *200*, 211–226.
- Galán, E., Fernández-Caliani, J. C., González, I., Aparicio, P., & Romero, A. (2008). Influence of geological setting on geochemical baselines of trace elements in soils. Application to soils of South-West Spain. *Journal of Geochemical Exploration*, *98*, 89–106.
- García-Mateo, J. L., & Prieto, L. (2012). *El Ferrocarril Minero de Riotinto*. Colección Monografías del Ferrocarril, 30. Barcelona.
- Grantcharova, M. M., & Fernández-Caliani, J. C. (2022). Soil acidification, mineral neoformation and heavy metal contamination driven by weathering of sulphide wastes in a Ramsar wetland. *Applied Sciences*, *12*, 249.
- Hakanson, L. (1980). An ecological risk index for aquatic pollution control: A sedimentological approach. *Water Research*, *14*, 975–1001.
- Hudson-Edwards, K. A., Schell, C., & Macklin, M. G. (1999). Mineralogy and geochemistry of alluvium contaminated by metal mining in the Rio Tinto area, southwest Spain. *Applied Geochemistry*, *14*, 1015–1030.
- ISO -International Organization for Standardization. (2005). General requirements for the competence of testing and calibration laboratories. ISO/IEC 17025:2005. Retrieved from <https://www.iso.org/standard/39883.html>
- Jian-Hua, M. A., Chun-Jie, C. H. U., Jian, L., & Bo, S. (2009). Heavy metal pollution in soils on railroad side of Zhengzhou – Putian section of longxi-haizhou railroad, China. *Pedosphere*, *19*, 121–128.
- Junta de Andalucía. (2015). Decreto 18/2015, de 27 de enero, por el que se aprueba el reglamento que regula el régimen aplicable a los suelos contaminados. *Boletín Oficial de la Junta de Andalucía*, *38*, 28–64.
- Kahle, M., Kleber, M., & Jahn, R. (2002). Review of XRD-based quantitative analyses of clay minerals in soils: the suitability of mineral intensity factors. *Geoderma*, *109*, 191–205.
- Liu, H., Chen, L. P., Ai, Y. W., Yang, X., Yu, Y. H., Zuo, Y. B., & Fu, G. Y. (2009). Heavy metal contamination in soil alongside mountain railway in Sichuan, China. *Environmental Monitoring and Assessment*, *152*, 25–33.
- Locutura, J., Bel-Lan, A., García-Cortés, A., & Martínez, S. (2012). *Atlas Geoquímico de España*. Instituto Geológico y Minero de España.
- Metrak, M., Chmielewska, M., Sudnik-Wójcikowska, B., Wilkomirski, B., Staszewski, T., & Suska-Malawska, M. (2015). Does the function of railway infrastructure determine qualitative and quantitative composition of contaminants (PAHs, heavy metals) in soil and plant biomass? *Water Air Soil Pollution*, *226*, 253.
- Mourinha, C., Palma, P., Alexandre, C., Cruz, N., Rodrigues, S. M., & Alvarenga, P. (2022). Potentially toxic elements' contamination of soils affected by mining activities in the Portuguese sector of the Iberian Pyrite Belt and optional remediation actions: A review. *Environments*, *9*, 11.
- Nemerow, N. L. (1985). *Stream, lake, estuary, and ocean pollution*. Van Nostrand Reinhold Company.
- Quattrone, M., Tomaselli, G., D'Emilio, A., & Russo, P. (2018). Analysis and evaluation of abandoned railways aimed at greenway conversion: A methodological application in the Sicilian landscape using multi-criteria analysis and geographical information system. *Journal of Agricultural Engineering*, *49*, 151–163.
- Rimstidt, J., & Vaughan, D. J. (2003). Pyrite oxidation: A state-of-the-art assessment of the reaction mechanism. *Geochimica et Cosmochimica Acta*, *67*, 873–880.
- Romero-Macías, E. (2006). *Los Ferrocarriles de la Provincia de Huelva*. Publicaciones Universidad de Huelva, 590 pp.
- Salkield, L. U. (1987). *A Technical History of the Rio Tinto Mines: Some Notes on Exploitation from Pre-Phoenician Times to the 1950s*. The Institution of Mining and Metallurgy, 116 pp.
- Salminen, R. (2005). *Geochemical Atlas of Europe. Part 1: Background Information, Methodology and Maps*. Geological Survey of Finland, 526 pp.
- Samarska, A., Zelenko, Y., & Kovrov, O. (2020). Investigation of heavy metal sources on railways: Ballast layer and herbicides. *Journal of Ecological Engineering*, *21*, 32–46.
- Seda, M., Síma, J., Volavka, T., & Vondruska, J. (2017). Contamination of soils with Cu, Na and Hg due to the highway and railway transport. *Eurasian Journal of Soil Science*, *6*, 59–64.
- Smith, E., Smith, J., & Naidu, R. (2006). Distribution and nature of arsenic along former railway corridors of South Australia. *Science of the Total Environment*, *363*, 175–182.
- Stancic, Z., Fiket, Z., & Vuger, A. (2022). Tin and antimony as soil pollutants along railway lines. A case study from North-Western Croatia. *Environments*, *9*, 10.
- Stojic, N., Pucarevica, M., & Stojic, G. (2017). Railway transportation as a source of soil pollution. *Transportation Research Part D: Transport and Environment*, *57*, 124–129.
- Szmaglinski, J., Nawrot, N., Pazdro, K., Walkusz-Miotk, J., & Wojciechowska, E. (2021). The fate and contamination of trace metals in soils exposed to a railroad used by Diesel Multiple Units: Assessment of the railroad contribution with multi-tool source tracking. *Science of the Total Environment*, *798*, 149300.
- Vaiskunaite, R., & Jasiunien, V. (2020). The analysis of heavy metal pollutants emitted by railway transport. *Transport*, *35*, 213–223.
- Valente, T. M., & Gomes, C. L. (2009). Occurrence, properties and pollution potential of environmental minerals in acid mine drainage. *Science of the Total Environment*, *407*, 1135–1152.
- Wierzbicka, M., Bemowska-Kalabun, O., & Gworek, B. (2015). Multidimensional evaluation of soil pollution from railway tracks. *Ecotoxicology*, *24*, 805–822.
- Wilkomirski, B., Galera, H., Sudnik-Wójcikowska, B., Staszewski, T., & Malawska, M. (2012). Railway tracks - Habitat conditions, contamination, floristic settlement - A review. *Environment and Natural Resources Research*, *2*, 86–95.
- Wilkomirski, B., Sudnik-Wójcikowska, B., Galera, H., Wierzbicka, M., & Malawska, M. (2011). Railway transportation as a serious source of organic and inorganic pollution. *Water Air Soil Pollution*, *218*, 333–345.

- WRB. (2015). *World Reference Base for Soil Resources 2014, update 2015. International soil classification system for naming soils and creating legends for soil maps*. World Soil Resources Reports, 106. FAO, Rome.
- Zhang, H., Wang, Z., Zhang, Y., & Hu, Z. (2012). The effects of the Qinghai-Tibet railway on heavy metals enrichment in soils. *Science of the Total Environment*, 439, 240–248.
- Zhang, H., Zhang, Y., Wang, Z., & Ding, M. (2013). Heavy metal enrichment in the soil along the Delhi-Ulan section of the Qinghai-Tibet railway in China. *Environmental Monitoring and Assessment*, 185, 5435–5447.
- Zhang, W., Oh, S., & Hofe, R. (2018). Transforming abandoned rail corridors into multi-purpose trails: Applying a spatial hedonic approach to estimating the economic

benefits of the Little Miami Scenic Trail in Cincinnati, Ohio, USA. *Urban Rail Transit*, 4, 274–287.

Publisher's Note Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.

Springer Nature or its licensor (e.g. a society or other partner) holds exclusive rights to this article under a publishing agreement with the author(s) or other rightsholder(s); author self-archiving of the accepted manuscript version of this article is solely governed by the terms of such publishing agreement and applicable law.