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Effect of parent material and atmospheric deposition on the potential pollution of urban soils close to mining areas

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ABSTRACT

The aim of this study is to analyse the concentration and determine the sources of potentially toxic elements (PTEs) in urban soils under the influence of mining activities. To this end, topsoil samples were collected in the public parks and green areas in Minas de Riotinto (a town next to one of the largest open pit mines in the world) and Aracena (a nearby town outside the area of influence of the mine). After determining the concentrations of elements of interest —Cr, Co, Ni, Cu, Zn, As, and Pb— the values were compared in terms of the soil location and origin (*in-situ* or *ex-situ*), and with the background and regulatory levels for the region. The elemental concentrations in the fine fraction of the soils (particles <50 μm) were also measured. The concentrations of some PTEs (Cu, As and Pb), also found in the dust from nearby mines, were higher in the *in-situ* soils of Minas de Riotinto than in those of Aracena. The concentrations of PTEs in *ex-situ* soils of both towns were much lower than in *in-situ* soils, and similar between the two locations, revealing the influence of the parent material as a primary source of PTEs. However, the concentrations of As and Cu in the *ex-situ* soils of Minas de Riotinto were significantly higher than in those of Aracena, while a significant increase of these elements in the fine fraction was seen for both *in-situ* and *ex-situ* soils. These two elements are directly related to mining activity, implying that atmospheric deposition of dust from the mines contributes to the greater concentration of PTEs in the soils of Minas de Riotinto. Because these sources lead to soils with potentially dangerous concentrations of pollutants, they should be further studied in relation to their long-term influence on human health.

1. Introduction

Soil pollution is an environmental problem that goes easily unnoticed, but can have a profound impact on the functioning of ecosystems and on human health (Oliver and Gregory, 2015; Raimi et al., 2022; Rodríguez-Eugenio et al., 2018). Several processes related to soil pollution can affect people's health, including the transfer of pollutants to plants and subsequent accumulation in the food chain, which can compromise food safety (Zhang et al., 2015; Zwolak et al., 2019). However, the most direct impact that soil pollution has on health is the transference of pollutants to the human body (Rodrigues and Römkens, 2017). This is a major problem in urban soils, as nowadays most people live in cities (United Nations, 2018), where there is a high chance of exposure. Potentially toxic elements (PTEs) are harmful pollutants associated with soil particles that can enter the body through ingestion (Filippelli and Laidlaw, 2010), inhalation (Huang et al., 2016), or dermal contact (Wei et al., 2022). This exposure can lead to toxicity where a cause-effect relationship is usually difficult to establish (Bini and Wahsha, 2014), although it is known to cause acute and chronic diseases (Tchounwou et al., 2012). Moreover, children are a demographic group especially exposed to the urban soils of parks and playgrounds, and they are especially sensitive to certain toxic elements such as Pb and As, which can pose a higher risk to their health (Bini and Wahsha, 2014; Han et al., 2020; Jaishankar et al., 2014).

To prevent the risk of pollution by PTEs, governments have established legal limits for their concentrations. The regulatory levels vary depending on the soil use, but are usually strict for urban soils (Provoost et al., 2006). To properly monitor and regulate soil pollution, it is key to understand the sources and processes that lead to high concentrations. Essentially, the sources of PTEs in soils can be split into two categories:

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natural or geogenic, meaning the PTEs come from parent material; and anthropogenic, a primary contributor to the concentrations of most PTEs in soils (Zwolak et al., 2019). In urban soils, relevant anthropogenic sources of PTEs would include residential heating, traffic, industrial manufacturing, power plants, fertilizers and pesticides from nearby agriculture, smelting, and mining activities (Albanese and Breward, 2011). Industrial mining and ore processing are considered the second worst polluting industry when ranked by disability-adjusted life years, only after lead-acid battery recycling (Bernhardt, 2016). These activities release large amounts of airborne particles containing PTEs, the most important of which are Pb, Cr, As, Cd, Hg and Zn (Alloway and Ayres, 1997). The deposition of these particles affects the elemental

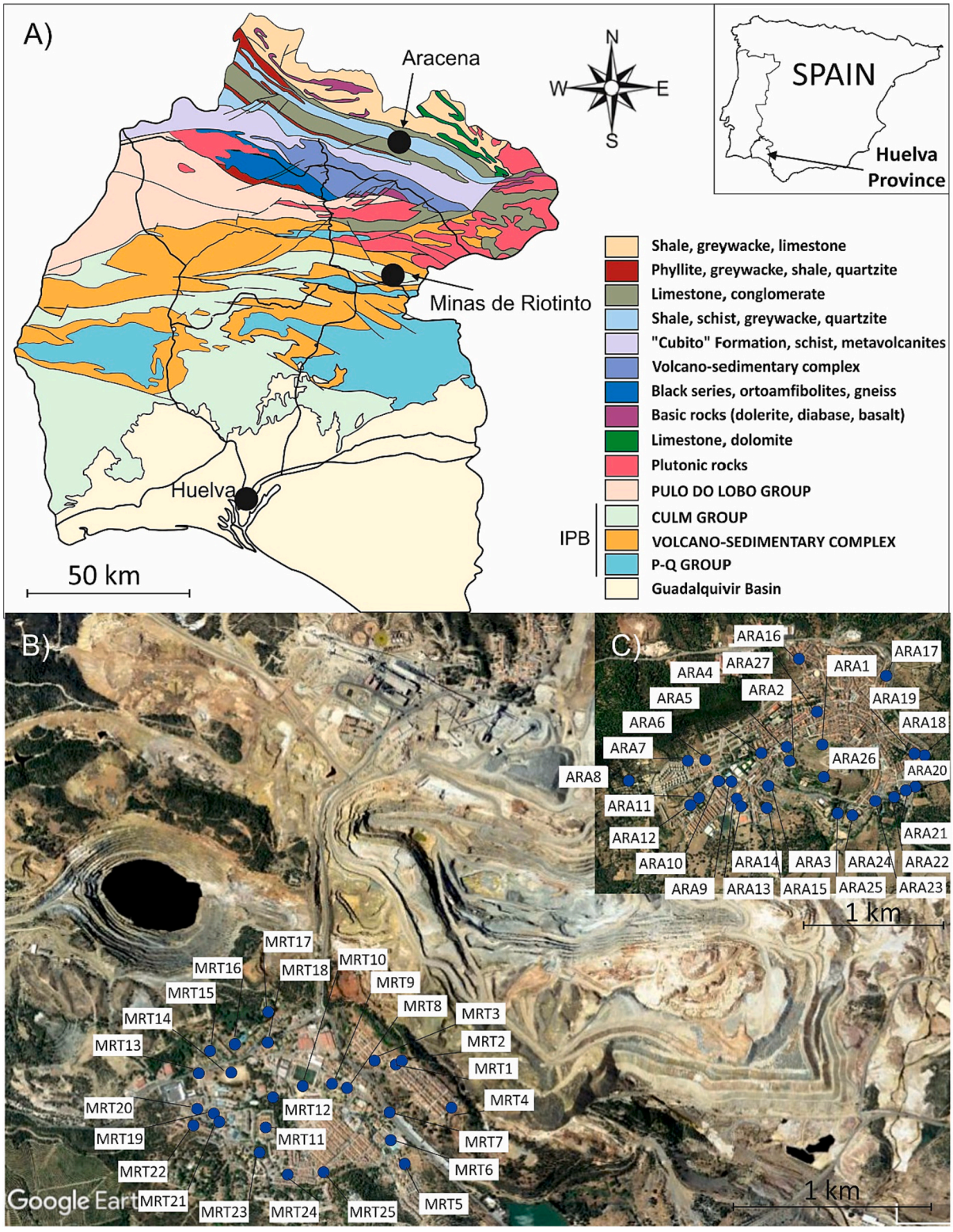

Fig. 1. A) Geologic domains of the Huelva province, and location of the studied towns. B) Aerial view of the town Minas de Riotinto, and location of the sampling points. C) Aerial view of the town Aracena, and location of the sampling points.

concentrations of surrounding soils within a radius of at least 10 km (Alvarenga et al., 2004; Bacon and Dinev, 2005; Pope et al., 2005; Rawlins et al., 2006), with smaller particles reaching farther (Csavina et al., 2012). Therefore, settlements closer to mines, especially open pit mines, are the most affected by this source of PTEs (de Araújo et al., 2022; Mireles et al., 2012).

The mining district of Rio Tinto is one of the largest and most important polymetallic areas in the world, where the historical exploitation of the mines has led to severe environmental impact. This includes alteration of the landscape by the open pit mines; deforestation due to both the use of timber for smelting and the effect of acid rain resulting from smelting sulphurous minerals; and the pollution of soils, rivers and atmosphere caused by the mine waste dumps exposed to water and wind erosion (Fernández-Caliani, 2008; Fernández-Caliani and Galán, 1996). PTE concentrations in the soils around the mines has increased in a radius of 5–7 km (Chopin and Alloway, 2007), as the particulate matter deposited around the mining site contains elevated PTE-bearing minerals including chalcopyrite [$CuFeS_2$], sphalerite [ZnS], galena [PbS], and arsenopyrite [FeAsS] (Castillo et al., 2013; Fernández-Caliani et al., 2013). One town affected by this pollution source is Minas de Riotinto, located a few hundred meters away from the mine. In a previous study we analysed the presence of PTEs in the soils of this town and their association with minerals (Parviainen et al., 2022), but the distribution of PTEs in the soils of this town, and how they are affected by different sources, had not yet been studied.

The aim of this study was to analyse the concentrations of PTEs and other elements (focusing on Cr, Co, Ni, Cu, Zn, As, and Pb) in the urban soils of Minas de Riotinto, and to compare them with the ones in a nearby town of similar characteristics but further beyond the influence of the mining area. This work sheds light on the sources of the concentrations of these potential pollutants in the area, a first step in risk assessment for humans in towns nearby mining activities.

2. Material and methods

2.1. Study area

The study area includes the towns of Minas de Riotinto and Aracena in the province of Huelva, in southwestern Spain. Our main focus is on Minas de Riotinto, a town of *ca.* 4000 inhabitants (INE, 2018) situated less than one km away from the open cast operations of the Rio Tinto Mining District. This town lies in a geologic domain known as the Iberian Pyrite Belt (IPB), containing one of the world's largest volcanogenic massive sulphide deposits, estimated to have 1700 Mt. of metallic sulphides (Sáez et al., 1999; Fig. 1A). The deposits belong to the South-Portuguese region and are found among magmatic and sedimentary rocks with associated stockwork, composed mainly of pyrite [FeS_2], with lower amounts of sphalerite [ZnS], galena [PbS], chalcopyrite [$CuFeS_2$] and tetrahedrite [$(Cu,Fe)_{12}Sb_4S_{13}$], along with other rarer minerals (Fernández Rodríguez and Díaz Azpiroz, 2008; Sáez et al., 1999). This mining district underwent intense activity, especially during the Roman domination (1st and 2nd centuries AD), when it was exploited to extract metals like copper and silver (Nocete et al., 2014; Rothenberg and Gracia Palomero, 1986); and then again from the end of the 19th century to the middle of the 20th, when the English corporation Rio Tinto Company Ltd. extracted copper and sulphur (Fernández-Caliani, 2008; van Geen et al., 1997). Large open cast mines, such as Corta Atalaya and Corta Cerro Colorado (the former being one of the largest open pit mines in the world) were abandoned when the mining activity ceased in 2001. The Cerro Colorado deposit is currently being exploited, since 2015, to obtain copper. The ground over this geologic environment consists of poorly and moderately developed soils, respectively Regosols and Cambisols (I.A.R.A., 2005).

As a control site we selected Aracena, a town of *ca.* 8000 inhabitants, *ca.* 30 km to the north of Minas de Riotinto, outside the area of influence of Rio Tinto mines. From a geologic standpoint, Aracena is located in the Ossa-Morena Zone. The Aracena Metamorphic Belt is made up of medium to low and highly metamorphosed rocks, including marbles, schists, gneisses and quartzites (Azpiroz et al., 2004; Fernández Rodríguez and Díaz Azpiroz, 2008). The dominant soils in the area are Leptosols and Luvisols (I.A.R.A., 2005).

2.2. Sampling

The urban soil sampling was carried out in public parks, playgrounds, and other green areas in the towns of Minas de Riotinto (MRT) and Aracena (ARA). In each sampling location, a composite sample of roughly 1 kg was collected from the uppermost 2 to 3 cm of the soil from 3 to 4 random points in a 10 m radius. The samples were collected with the help of a shovel and pickaxe of stainless steel that were washed in between samples with alcohol. A total of 52 soil samples were collected, 25 from Minas de Riotinto and 27 from Aracena (Fig. 1B). For each sampling location, the coordinates were noted, as well as the soil use and origin of the parent material. The soil use was classified in three categories: public parks, playgrounds, and vacant lots. Based on the origin of the parent material, the soils were grouped in two visually different types with contrasting properties: *in-situ* soils, formed from the underlying parent material and mainly containing siliceous minerals, without any carbonate content; and *ex-situ* soils, made up of different aggregate materials including calcareous sand or gravel, in most cases having a relevant carbonate component (Parviainen et al., 2022). The samples that were mixtures of natural soils and aggregate materials were classified as *in-situ* soils due to their *in-situ* component.

2.3. Processing and analysis

In the laboratory, the samples were dried at room temperature, homogenized, sieved through a 2 mm stainless steel sieve, and stored in plastic bags. This fraction is considered as the total fraction (<2 mm). Then, approximately 30 g of each sample was sieved again using a 50 μm mesh to obtain the fine fraction (<50 μm), more likely to be affected by atmospheric deposition.

The pH and electrical conductivity (EC) of the total fraction of the soils were measured in a soil:water suspension 1:2.5 with a Metrohm 914 pH/Conductometer. Both total and fine fractions were acid digested for chemical analyses. The microwave-assisted aqua regia acid digestions (HCl and HNO_3 in a ratio of 3:1) were performed at Centro de Edafología y Biología Aplicada del Segura (CEBAS-CSIC, Murcia, Spain). The elemental concentrations (Al, V, Cr, Mn, Co, Ni, Cu, Zn, Rb, Sr, As, Cd, Ba, Tl, Pb, Th and U) were determined using an Agilent 8800 TripleQuad Inductively Coupled Plasma-Mass Spectrometer (ICP-MS) at Instituto Andaluz de Ciencias de la Tierra (UGR-CSIC, Granada, Spain). In this study, we focus on Cr, Co, Ni, Cu, Zn, As, and Pb as elements of interest, and Al to normalize the data.

The quality control of the analyses was done by using certified reference material (RTC-CRM052, loamy clay), and procedural blanks were analysed to counter possible contributions from the digestion procedure. The results of the certified elements can be found in Table S1.

2.4. Data analysis and comparison with background and regulatory levels

The statistical analyses were carried out with SPSS software v. 20.0 (SPSS Inc., USA). Group comparisons were made by means of the Mann-Whitney *U* test and Kruskal-Wallis test to check statistical differences between them; the significance threshold used for all tests was $\alpha = 0.05$.

To assess the dispersion of the dataset, we applied the coefficient of variation (CV). The higher the coefficient of variation, the greater the level of dispersion around the mean.

The contamination factor (*CF*) was calculated as the quotient of the concentration of each element in soil by the background values for the same element in the region (Rehman et al., 2018).

The background values for each location were defined as the 95th

percentile of the soils considered unpolluted for each geological domain (South-Portuguese for MRT or Ossa-Morena Zone for ARA) (Galán Huertos and Romero Baena, 2008), according to the regulatory levels established by the government of Andalusia (Junta de Andalucía, 2016) (Table S2).

3. Results

3.1. Total concentration of PTEs in bulk soil

The total concentrations of all analysed elements are presented in Table S3. Our focus, however, is on certain elements of interest, whose total concentration is shown in Table 1. The concentrations of Cu, As and Pb are significantly higher in the soils of Minas de Riotinto, whereas Cr, Co and Zn are significantly higher in Aracena. The heterogeneity of the concentrations is estimated by the coefficient of variation (CV). For all elements, the CV for *in-situ* soils in MRT is higher than in ARA, with extremely high values (over 50 %) for Cu, As and Pb, indicating highly heterogeneous concentrations for these three elements in Minas de Riotinto.

The total concentration of the elements of interest for *ex-situ* soils is similar in MRT and ARA. In this case, we found extremely anomalous values in two samples, mainly for Pb concentrations (Fig. S1): MRT17, soil from a historical site next to a mine waste dump, and ARA09, soil from a parking lot. Hence, the statistical comparison between locations was made without considering these two samples. The concentrations of most elements for *ex-situ* soils are not significantly different between the studied locations; only Cu, As and Pb have significantly higher concentrations in Minas de Riotinto than in Aracena (Table 1).

The total concentrations measured for *in-situ* soils were also compared with the geochemical background values in both areas, South-Portuguese region for MRT and Ossa-Morena region for ARA (Fig. S2). In the case of MRT, 54 % of *in-situ* soils exceed the geochemical background for Pb, 38 % for Cu and As, and 31 % for Zn; whereas in the case of ARA, none of the *in-situ* soils exceed these values for Cu and As, but 32 % do for Pb and 50 % for Zn. The total concentrations for *ex-situ* soils were also compared with the geochemical background values measured in materials from the Guadalquivir basin (the original source of most of the *ex-situ* materials used in public parks in southwest Andalucía) (Fig. S2). In the case of MRT, 73 % of *ex-situ* soils exceed the geochemical background for As, as well as 27 % for Cu, 18 % for Pb, and 9 % for Zn. In the case of ARA, none of the *ex-situ* soils exceed these values for Cu and Pb, and just 25 % for Zn and As. According to these background values, we calculated the Contamination Factor (*CF*) as the ratio between the mean element concentrations in the sample and the geochemical background of each soil type and location (Fig. 2).

The elements of interest are divided in two groups according to *CF*. The values of Cr, Co, and Ni in both locations (MRT and ARA) and in both soil types (*in-situ* and *ex-situ*) are below 1; but *CF* values above 1 are found in MRT for Cu, Zn, As, and Pb, with higher values for *in-situ* than *ex-situ* soils. In ARA, $CF > 1$ is found only for Zn and Pb, for both *in-situ* and *ex-situ* soils.

In view of the regulatory levels establishing what constitutes a polluted soil in Andalusia, no *in-situ* soil in MRT exceeds these levels for Cu and Zn, but 38 % for Pb and 69 % for As would exceed the levels indicating pollution, with maximum concentrations of 10,000 and 3655 mg/kg, respectively. For ARA *in-situ* soils, the regulatory levels are not exceeded by Cu, Zn, or As, whereas 27 % exceed the limit for Pb, with a maximum concentration of 773 mg/kg. No *ex-situ* soil in MRT exceeds the regulatory levels for Cu, Zn, and Pb; but 9 % for As would mark the sample as polluted, with a maximum concentration of 52 mg/kg for this element. For ARA *ex-situ* soils, regulatory levels are not exceeded in any case for any of the elements of interest.

3.2. Total concentration of PTEs in fine fraction (<50 μm)

The content of the elements of interest in the fine fraction of *in-situ* soils is different in MRT than in ARA, showing a similar relationship to the total concentration in bulk soil. The concentrations of Cu, As and Pb are significantly higher in the soils of Minas de Riotinto, whereas Cr, Co and Zn are significantly higher in the soils of Aracena (Table 2). For *ex-situ* soils, most elements of interest exhibit similar values in the fine fraction of both towns, and only the concentrations of Cu and As are significantly higher in the soils of Minas de Riotinto (Table 2).

The total concentration of PTEs in the fine fraction of the soils was also studied by means of the fine/total (F/T) ratio (Table 3). In all cases the mean values are higher than 1, yet despite the high values obtained for some elements (mainly Cu, As, and Pb in MRT *in-situ* soils), there are no significant differences between locations nor soil type. Extremely high values for the F/T ratio of at least one element of interest are found in 14 samples from MRT (56 % of sampled soils) and in 5 samples from ARA (18 % of sampled soils), both for *in-situ* and *ex-situ* soils.

According to the differences in the concentrations of the fine fraction and the F/T ratios, we applied normalized data to compare the impact of

Table 1
Descriptive statistics of total concentration of elements of interest in bulk soils in both locations (Minas de Riotinto: MRT, and Aracena: ARA) and both soil types (*in-situ* and *ex-situ*), expressed in mg/kg. CV = coefficient of variation.

MRT	*In-situ*					*Ex-situ*				
	Median	Mean	CV	Min.	Max.	Median	Mean	CV	Min.	Max.
Cr	17.2	20.2	13.1	2.75	41.8	15.0	13.6	7.51	2.30	26.2
Co	2.94	3.72	2.3	1.07	8.59	2.15	2.69	1.47	1.09	6.47
Ni	9.02	11.0	6.98	1.56	27.1	3.43	4.74	3.34	2.21	13.8
Cu	77.4	345	834	7.49	3100	16.4	26.5	20.5	5.88	62.0
Zn	92.5	136	131	25.2	430	35.7	67.1	102	11.9	381
As	61.1	551	1020	2.64	3650	22.8	32.3	40.8	5.79	156
Pb	154	1489	2770	16.2	10,000	15.7	53.1	107	8.74	389
Al	10,600	12,000	6370	5350	26,600	3300	5560	3980	2120	12,200
ARA	*In-situ*					*Ex-situ*				
	Median	Mean	CV	Min.	Max.	Median	Mean	CV	Min.	Max.
Cr	44.5	45.5	24	7.56	92.9	10.5	13.5	6.54	3.47	24.9
Co	10.8	9.96	4.16	1.49	18.0	1.59	2.47	1.76	0.93	4.49
Ni	15.0	15.4	6.,54	0.00	28.2	3.50	4.20	2.75	1.47	8.98
Cu	31.1	33.6	18.2	3.84	81.3	4.90	6.00	2.69	1.51	10.6
Zn	240	405	403	16.14	1650	52.6	110	129	18.8	333
As	9.07	12.7	8.91	3.41	33.7	6.39	8.37	6.31	3.47	17.6
Pb	50	162	222	0.00	773	7.54	71.9	143	1.67	327
Al	20,400	18,800	6620	5450	28,600	2620	6790	6850	3700	18,200

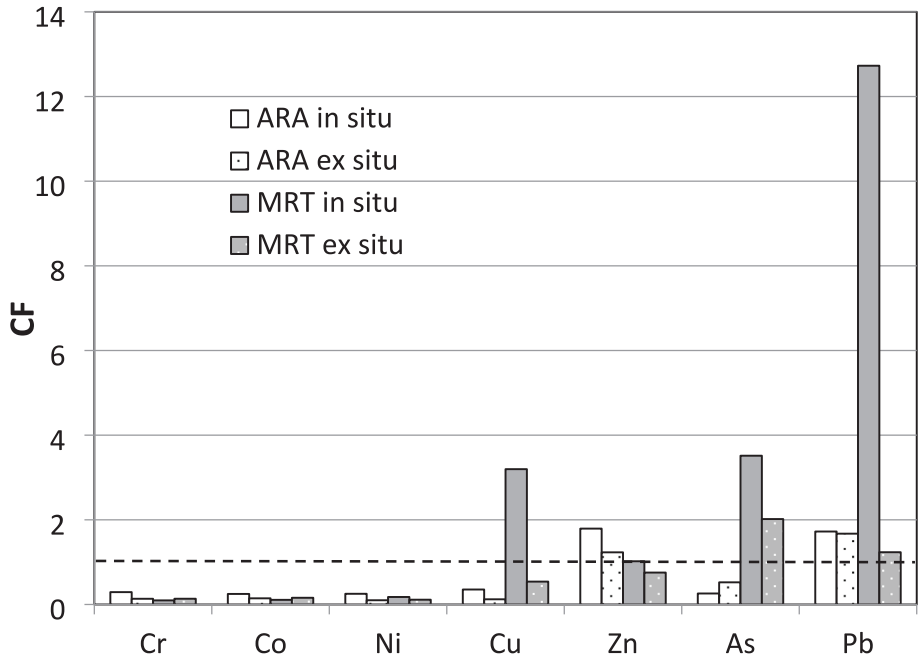

Fig. 2. Contamination Factor (*CF*; mean values) of main elements of interest in both locations (Minas de Riotinto: MRT, and Aracena: ARA) and both soil types (*in-situ* and *ex-situ*); dashed line indicates $CF = 1$.

Table 2
Descriptive statistics of total concentration of elements of interest in soil fine fraction (<50 μm) in both locations (Minas de Riotinto: MRT, and Aracena: ARA) and both soil types (*in-situ* and *ex-situ*), expressed in mg/kg. CV = coefficient of variation.

MRT	*In-situ*					*Ex-situ*				
	Median	Mean	CV	Min.	Max.	Median	Mean	CV	Min.	Max.
Cr	41.6	40.7	14.7	6.06	58.2	37.5	33.1	12.4	9.10	49.6
Co	7.90	6.97	2.37	1.47	9.63	5.52	5.46	2.20	2.55	11.2
Ni	24.0	21.9	8.6	3.33	32.8	11.8	12.3	3.85	5.94	19.8
Cu	226	408	592	55.2	2260	53.2	64.9	52.3	18.1	176
Zn	161	190	101	24.7	346	52.6	104	156	31.5	594
As	262	572	812	43.1	2660	44.4	42.7	74.3	17.2	79.8
Pb	598	1960	2880	81.5	9740	26.7	45.9	218	17.1	137
Al	40,500	44,800	25,100	22,300	120,700	18,300	23,000	14,500	8200	49,700

ARA	*In-situ*					*Ex-situ*				
	Median	Mean	CV	Min.	Max.	Median	Mean	CV	Min.	Max.
Cr	68.4	71.2	29.8	24.6	130	33.7	36.6	12.3	24.7	54.3
Co	12.9	13.7	4.26	6.55	22.9	5.52	5.80	2.49	3.84	8.34
Ni	26.9	27.9	9.73	13.8	54.4	13.2	14.5	4.12	11.6	20.0
Cu	52.5	59.6	37.5	21.1	188	17.8	19.3	8.89	11.0	30.6
Zn	397	604	593	89.2	2370	75.4	80.6	258	43.8	127
As	15.8	19.6	13.1	3.97	53.0	13.8	14.8	9.95	3.54	28.3
Pb	91.5	285	353	27.0	1180	19.9	23.0	294	10.4	41.8
Al	58,300	57,900	15,200	19,900	86,500	22,700	31,100	23,800	11,200	67,900

potential pollution of soils and to assess the influence of atmospheric deposition due to the proximity to the mine in Minas de Riotinto, as opposed to Aracena (beyond the influence area of the mine). In this study Al was used as a normalizing element, and the results are presented in Fig. 3.

The Al-normalized data of the elements of interest indicate no significant differences between locations (MRT *vs.* ARA) for Cr, Co, and Ni in both soil types. Normalized data for Zn show a significant increase for *in-situ* soils in ARA in relation to MRT, but no significant differences are found for *ex-situ* soils. In turn, normalized data for Cu, As and Pb show a significant increase in MRT in relation to ARA, both for *in-situ* as *ex-situ* soils.

4. Discussion

4.1. PTE distribution in soils and potential risk of pollution

In-situ soils in both locations of study showed significant differences in the total concentrations of certain elements. MRT soils presented higher Cu, As, and Pb than ARA soils, which matches with the main elements usually described for the mine and surrounding areas (Davis et al., 2000). This finding is also consistent with previous studies on the local geochemistry, reporting that the area of Minas de Riotinto has high natural concentrations of Cu, Zn, As and Pb (Chopin and Alloway, 2007). Moreover, in the case of these four elements the concentrations that we obtained in MRT are higher than the local background values for one or

Table 3
Fine/Total (F/T) ratio of main elements of interest in both locations (Minas de Riotinto: MRT, and Aracena: ARA) and both soil types (*in-situ* and *ex-situ*). CV = coefficient of variation.

		MRT		ARA	
		Mean	CV	Mean	CV
Cu	*in-situ*	4.9	6.6	2.0	1.4
	ex-situ	3.1	1.7	3.4	2.2
Zn	*in-situ*	2.7	2.8	1.7	0.9
	ex-situ	2.1	1.2	2.3	1.9
As	*in-situ*	14	30	1.7	1.0
	ex-situ	2.4	1.6	2.2	0.8
Pb	*in-situ*	6.9	11	2.1	2.1
	ex-situ	2.1	0.5	2.8	1.6

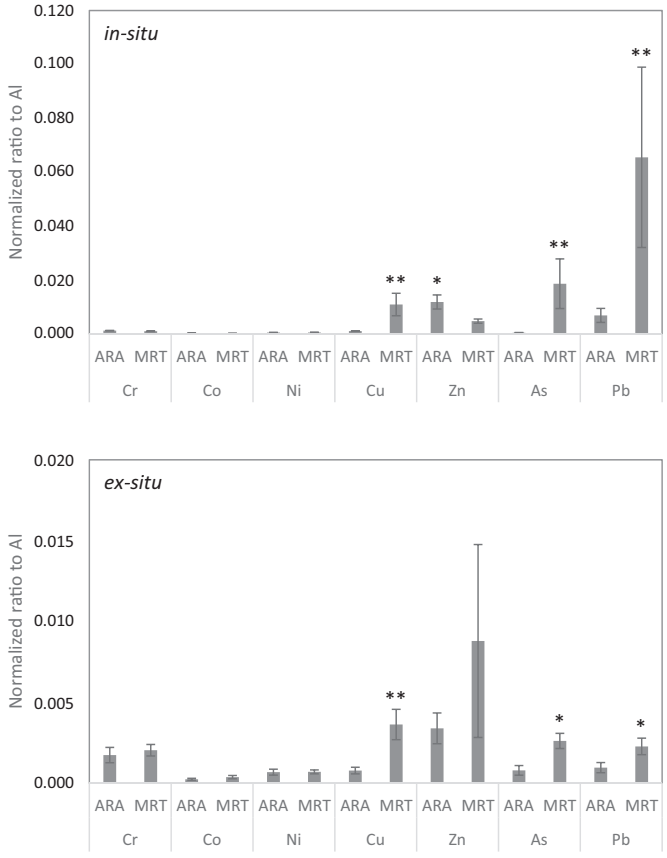

Fig. 3. Al-Normalized ratio of main elements of interest for *in-situ* and *ex-situ* soils in MRT and ARA locations (significant differences between locations are included: (*) $p < 0.1$; (**) $p < 0.05$).

more elements in 54 % of the sampled soils. In contrast, ARA *in-situ* soils have higher concentrations of Cr and Co than MRT soils, but they lie within the range of the geochemical background in the area. Higher concentrations of Zn are likewise found in ARA than in MRT soils. The concentrations of Zn and Pb in ARA soils are higher than the local background values, in line with the extremely high concentrations of these two elements found in Sierra de Aracena associated with mineralizations in the carbonate and metavolcanite parent material (Rivera et al., 2015).

Ex-situ soils at both locations are mainly composed by aggregate calcareous materials (chalky sand or gravel), for which reason we did not find significant differences in most elements —except for Cu, As, and Pb, showing higher concentrations in MRT. As these elements are directly related to the mining area, their increase in *ex-situ* soils would be related to external contributions. There are also two specific soils whose concentrations indicate extremely anomalous values of Pb: ARA09 (from a parking lot) and MRT17 (next to a mine waste dump). The high concentration of Pb is consistent with intense traffic-related activity (Albanese and Breward, 2011) at the former site.

The concentrations in the soils of Minas de Riotinto exceed the regulatory levels for As and Pb, in 69 % and 38 % of the *in-situ* soils, respectively, and in 9 % for As of *ex-situ* soils; the concentrations are higher than the range usually found in urban soils affected by pollution (Chirenje et al., 2003; Jiao et al., 2015; Luo et al., 2011; Pecina et al., 2021). One group of MRT samples, comprising *in-situ* soils that most likely developed naturally from the underlying rock (Parviainen et al., 2022), gives extreme values of Cu (up to 3100 mg/Kg), As (3650 mg/Kg) and Pb (10,000 mg/Kg).

The reported concentrations are comparable to ones obtained in other soils related to mining areas (Argyraki et al., 2018; Gamiño-Gutiérrez et al., 2013). High concentrations of these elements could be hazardous for humans due to their high toxicity, especially in the case of As and Pb, which are carcinogenic (Tchounwou et al., 2012). Still, the regulatory levels based on total concentrations do not suffice to determine the risk of pollution in a soil (Romero-Freire et al., 2015), because many factors can affect the mobility and bioavailability of PTEs in soils, so that their risk for human health can be misinterpreted. Physicochemical factors such as pH and EC, and soil constituents (*e.g.* calcium carbonate and organic carbon) are key factors controlling the mobility and potential toxicity of pollutants in soils (Izquierdo et al., 2015; Romero-Freire et al., 2015). Regulatory levels based on total concentrations in bulk soil can furthermore mask an enrichment in pollutants in the fine particles, which are the ones most likely to be re-suspended in the atmosphere (Laidlaw and Filippelli, 2008), implying an underestimation of the risk of contamination and transfer of pollutants to the exposed population.

The relatively low pH of some of these soils and the high EC (Table S3) may be related to the oxidation of sulfides in soils (Nordstrom, 2011), indicating a potential increase in their bioavailability and toxicity (Violante et al., 2010). In our study, the high concentration of PTEs (mainly As and Pb) found in MRT soils, together with the potential acidification and formation of soluble salts in some of the samples, could pose a potential risk to the health of the inhabitants of this town and should be monitored over time.

4.2. Potential sources of PTEs

The differences in the concentration of most PTEs between *in-situ* and *ex-situ* soils in the two locations indicate that the original lithology is a relevant source of these elements. In this case, *in-situ* soils from both locations have higher concentrations of PTEs than *ex-situ* soils, and this is directly related to the background concentrations of the soils in each area. The concentration of trace elements in MRT soils is consistent with the geological domain where the town is located (South-Portuguese zone) (Fernández-Caliani et al., 2009), while the concentration of trace elements in ARA is also consistent with its geological domain (Ossa-Morena zone) (Rivera et al., 2015). Aggregate materials used for *ex-situ* soils likewise show trace element concentrations similar to the source of these materials, the Guadalquivir basin (Galán Huertos and Romero Baena, 2008). However, even though the main source of trace elements found in the soils of our study is the parent material, significant anomalies found at both locations cannot be explained by this lithogenic origin.

In urban environments, common anthropogenic sources are responsible for the entry of PTEs into soils: domestic heating, traffic, mining and smelting (Albanese and Breward, 2011), and agrochemicals used in urban gardens (Pecina et al., 2021). They are difficult to discriminate from lithogenic origin in towns having high geochemical background concentrations. In our study, the presence of the open pit mines of Rio Tinto a few hundred meters from the MRT location is a potential anthropogenic source whose impact on the urban soils of this

town has not been studied in detail to date. The contamination factor (*CF*) serves as a first indicator of potential pollution. In the case of MRT soils, we measured some samples with very high *CF* values ($>>1$) for Cu, As, and Pb (especially by the northern edge of town), showing that the concentration of these elements is much higher than the local geochemical background in the area, and indicating potential anthropogenic sources (Rehman et al., 2018) related to the mining activity in the area (Fernández-Caliani et al., 2009). The presence of these anomalous concentrations of Cu, As, and Pb both for *in-situ* and *ex-situ* MRT soils, and the significant differences with respect to ARA soils (outside the area of influence of the mine) would attest to the influence of more intense anthropogenic activities in MRT.

Aluminum is an element widely used to normalize data because it represents a major constituent of soil minerals (*e.g.*, aluminosilicates, clay minerals) (Benabdelkader et al., 2018; Birch and Snowdon, 2004). In our study, the Al-normalized data of the elements of interest underlines abnormally high concentrations for Cu, As, and Pb in MRT in comparison to ARA soils, these differences being observed both for *in-situ* and *ex-situ* soils. Such findings are consistent with the *CF* values previously mentioned, supporting the anthropogenic origin of these three elements in MRT owing to mining activity.

The concentration of PTEs in fine fractions proved to be a key factor for discriminating the potential anthropogenic origin in soils, given its ease to be transported by the air and enter the soil by atmospheric deposition. Trace metals are usually concentrated in the fine fraction (Acosta et al., 2009), because fine soil particles can accumulate higher concentrations of trace elements in secondary minerals (clay minerals, iron/aluminum oxides and hydroxides, *etc.*) and organic matter (Hardy and Cornu, 2006); but extremely high concentrations in fine fractions may be a key indicator of potential pollution related to atmospheric deposition. In our study, the fine/total (F/T) ratio was evaluated for samples with values higher than 2.5 (Luo et al., 2011). For MRT soils, all anomalous samples showed an increase in the fine fraction for Cu, including *in-situ* and *ex-situ* soils. The mine of Rio Tinto was the world's leading producer of Cu at the end of XIX century (Olías and Nieto, 2015) and its activity continues today, meaning the high increase of Cu in the fine fraction is potentially related to atmospheric deposition over time. This is coherent with the results of studies that collected atmospheric particulate matter samples around the mines: Castillo et al. (2013) showed that the particulate matter around the mines is enriched in a variety of PTEs, including Zn, Cu, Pb and As. Boente et al. (2022) linked these elemental concentrations directly to the mining activities by collecting dust samples inside the mine facilities, and they highlighted the above four elements as the most concerning. They also pointed out that despite this enrichment, the concentrations of PTEs in the atmospheric dust were not directly dangerous, which is coherent with the minor impact we detected in topsoil PTE concentrations.

In mining environments, the deposition of PTEs from airborne particles is a high source of dispersion and potential pollution of surrounding soils (Cheng et al., 2018). In our study area, Cu, As, and Pb are previously described in airborne dust derived from the mines of the Rio Tinto district (Castillo et al., 2013), increasing the concentrations of these elements in the soils within an area of 2–3 km around the mines (Chopin and Alloway, 2007), where Minas de Riotinto is located. This effect may be difficult to detect in soils with naturally high concentrations of PTEs; but the *CF* value, F/T ratio and data normalization to Al proved to be good indicators to discriminate the anthropogenic source of PTEs, *i.e.* related to atmospheric deposition from the intense mining activity close to MRT. Mine dust deposition has an impact on the concentration of these elements in urban soils that should be monitored in view of the potential risk of pollution and negative health effects on the population of this town.

Notwithstanding, the relatively low concentrations of PTEs abundant in the rocks of the mine present in *ex-situ* soils, compared with the ones from *in-situ* soils, demonstrate that the geologic origin is the mayor contributor to PTE concentrations. In contrast, results from other urban soils affected by mining activities point to the mine itself as the main source of PTEs (Ma et al., 2016; Mackay et al., 2013).

One approach to prevent the health impact of these soils would be to cover them with materials from unpolluted places. As the anomalous concentrations of PTEs appear to be mostly conditioned by the geologic origin of the soils, and atmospheric deposition has a moderate effect on the levels of pollutants in *ex-situ* soils, covering natural soils and replacing them with aggregate material could alleviate the problem.

5. Conclusions

The urban soils in the mining town of Minas de Riotinto have concentrations of Cu, As and Pb higher than the background values and, in the case of the latter two PTEs, also higher than the regulatory levels. Anomalous concentrations were found for both *in-situ* and *ex-situ* soils in Minas de Riotinto (near the mine), with significant differences regarding Aracena (outside the mine's area of influence). The selection of urban soils of different types for this study —including natural soils, here referred to as *in-situ* soils, and artificial aggregate soils *i.e., ex-situ* soils— was decisive for evaluation of the pollution sources. In addition, the use of variables such as the *CF* value and the fine/total ratio in the soil samples makes it possible to discern lithogenic and anthropogenic sources of PTEs. The increase in the fine fraction of the soils after normalizing the data with Al, together with the anomalies detected in Cu and As, allowed us to detect the effect of atmospheric deposition of dust from the mine. The difference between the concentrations in *in-situ* and *ex-situ* soils showed, however, that the underlying rock is the main contributor. The high concentrations detected in some soils and the increase in the fine fraction would indicate a potential risk of exposure to be monitored over time, so as to reduce negative impacts on human health for people living close to this or other mining areas.

CRediT authorship contribution statement

Antón Vázquez-Arias: Investigation, Formal analysis, Visualization, Writing – original draft. **Francisco José Martín-Peinado:** Conceptualization, Methodology, Formal analysis, Visualization, Writing – review & editing. **Annika Parviainen:** Conceptualization, Methodology, Writing – review & editing.

Declaration of competing interest

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

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.gexplo.2022.107131.

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