Environmental Research 206 (2022) 112514

Contents lists available at ScienceDirect

Environmental Research

journal homepage: www.elsevier.com/locate/envres

Human health risks associated with urban soils in mining areas

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ARTICLE INFO

Keywords:
Urban soil
Pollution
Arsenic
Lead
Risk assessment models
Relative cancer mortality

ABSTRACT

We studied the chemical composition of As and Pb in total (<2 mm) and fine fractions (<50 μm) of 52 urban soil samples from Minas de Riotinto (mining area) and Aracena (non-exposed area) in SW Spain. In addition to a soil phytotoxicity bioassay using *Lactuca Sativa* L., we modelled and performed carcinogenic and non-carcinogenic human health risk assessment, later comparing our data with relative cancer mortality rates reported at the municipal level.

This study demonstrates that mineralized bedrock and natural soil-forming processes affect the geochemistry of natural (*in-situ*) urban soils, which in many cases surpass the regulatory levels for As (36 mg/kg) and Pb (275 mg/kg). Fine fractions of *in-situ* and mixed urban soils —susceptible of inhalation— are significantly enriched in As and Pb with respect to fine fractions of aggregate materials (*ex-situ* soils of chalky sands and gravel) in Minas de Riotinto. The soils in Minas de Riotinto are significantly enriched in As (total and fine fractions) and Pb (total fraction) with respect to Aracena. Despite elevated bulk concentrations of As and Pb, only one *in-situ* sample exhibits phytotoxic effects of the soil-water extracts on *Lactuca Sativa* L. seeds. Health risk assessment of these towns as exposure areas indicates that the soils of Minas de Riotinto are indeed a health risk to the residents, whereas there is no potential risk in Aracena. The reported relative mortality rates in Minas de Riotinto show a greater mortality of carcinogenic tumors potentially related to As and Pb exposure, including lung cancer.

Both soil type and use must be considered when administrators or policy-makers evaluate health risks involved in urbanistic decision-making. To minimize exposure risk and adverse health outcomes, we recommend that *in-situ* soils surpassing regulatory levels for As and Pb in public playgrounds and passing areas should be covered with aggregate materials.

1. Introduction

Air pollution, including potentially toxic elements (PTEs) derived from industrial and mining activities, can have negative outcomes on human health (Bini and Bech, 2014; Jaishankar et al., 2014; Kampa and Castanas, 2008; Landrigan, 2017; Morais et al., 2012). In Spain, industrial activities are ascribed to an increased risk of cancer when compared to non-industrialized areas (Fernández-Navarro et al., 2012, 2017; López-Abente et al., 2014). Besides air pollution, concentrations of As and Cr in topsoils may play a role in cancer mortality in Spain (Núñez et al., 2016). Urban soils are a growing subject of interest when considering human exposure risk to toxic and carcinogenic PTEs (Adimalla, 2020; Li et al., 2018). People come in direct contact with urban soils in public parks, playgrounds, green areas, urban gardens, and sports facilities. Urban soil quality is influenced by the associated bedrock lithology and natural soil forming processes (Galán et al., 2008), as well as by deposition of airborne particulate matter and spills from anthropogenic activities such as mining, industrial activities, construction, demolition, domestic heating, and exhaust and non-exhaust emissions from traffic (Ettler, 2015; Guillén et al., 2012;

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https://doi.org/10.1016/j.envres.2021.112514
Received 21 September 2021; Received in revised form 23 November 2021; Accepted 2 December 2021
Available online 16 December 2021

Khan et al., 2016; Zuluaga et al., 2017). Accordingly, urban soils would be both primary and secondary sources of PTE exposure to humans (Adimalla et al., 2020; Galán et al., 2008; Li et al., 2018).

Human exposure to PTEs from urban soils occurs mainly through inhalation, ingestion, and dermal contact (Li et al., 2018). Exposure Assessment can be defined in terms of the magnitude, frequency, duration, route, or exposure to an agent in the environment (U.S.EPA, 1997). Hence, potential impacts on human health can be assessed through risk assessment models. Arsenic (As) and lead (Pb) are known to induce adverse health outcomes for human beings, even at low levels of exposure (Tchounwou et al., 2012). Their toxicity depends on factors such as dose, route of exposure, chemical species, or characteristics of the exposed individuals (age, gender, genetics, and nutritional status). The International Agency for Research on Cancer (IARC) of the World Health Organization (WHO), classifies As as potentially carcinogenic (Group 1), whereas Pb is probably carcinogenic (Group 2 A) to humans (IARC, 2012, 2006). The mobility and potential toxicity of As and Pb in soils depend on factors such as pH, redox conditions, cation exchange capacity, organic carbon content, and mineralogical composition (*e.g.*, Fe oxides, $CaCO_3$) (Romero-Freire et al., 2014, 2015).

Minas de Riotinto in SW Spain is an emblematic and historic mining town located in the vicinity of the Rio Tinto mines, encompassing open pits and vast waste storage areas. Re-suspension of wind-blown fine particulate matter from the different waste materials of historic mining facilities is known to have had an impact on the local air quality (Castillo et al., 2013; Fernández-Caliani et al., 2013; Sánchez de la Campa et al., 2011, 2020). Yet little attention has been paid to the quality of urban soils in the nearby towns; and their potential health risks to the residents is unexplored. In a recent study on the chemical-mineralogical association of the urban soils of Minas de Riotinto, we underlined how the enrichment of sulfide-associated elements in the fine fraction of the urban soils implied potential human health risk (Parviainen et al., n.d.). Our current multidisciplinary approach —entailing soil science, phytotoxic tests, health risk assessment, and epidemiological evaluation— aims to fill a knowledge gap in studies interrelating urban soils and adverse health outcomes within a mining area. The aim of the current study was therefore to assess the phytotoxicity and the potential carcinogenic and non-carcinogenic risks to humans from the urban soils of Minas de Riotinto, in addition to a control site in Aracena (without mining activity). Our study was designed to evaluate soil phytotoxicity by means of a *Lactuca sativa* L. bioassay using the soil aqueous extract, and evaluate human health risk by means of risk assessment models. Afterwards, our risk assessment results were compared with the reported municipal cancer mortality of selected malignant tumors potentially related to As and Pb exposure in Minas de Riotinto (exposed population) and Aracena (non-exposed population).

2. Materials and methods

2.1. Site description

In this study, we focus on urban soils in two towns in the Province of Huelva (SW Spain) located in contrasting geological contexts. We pay particular attention to the urban soils of Minas de Riotinto (approx. 4000 inhabitants; Fig. 1), a historical mining town erected next to the Rio Tinto mines at the end of the 19th century. Mining activities continued until 2001. In 2015, the exploitation of copper with silver as by-product began again and has future prospects, perhaps continuing until 2032 (Atalaya mining, 2018). The surrounding geology of Minas de Riotinto is dominated by volcano-sedimentary rocks of the South Portuguese zone. This zone hosts the Iberian Pyrite Belt (IPB), one of the largest non-ferrous, polymetallic massive sulfide deposits at the global level (Marcoux, 1997; Sáez et al., 1999; Tornos, 2008). The open pits and vast areas covered by mining residues are located a few hundred meters from the town. The winds of northerly directions (predominantly NE) blow from the mining area towards Minas de Riotinto town.

We chose Aracena town (approx. 8000 inhabitants; Fig. 1) as our control site. Aracena lies some 30 km north of Minas de Riotinto, in the Aracena Metamorphic Belt within the Ossa Morena Zone; it is hardly impacted by large-scale mining or related industrial activities to date (Fig. 1). The surroundings of Aracena contain metamorphic rocks including dolomitic and limestone marbles and metavolcanites.

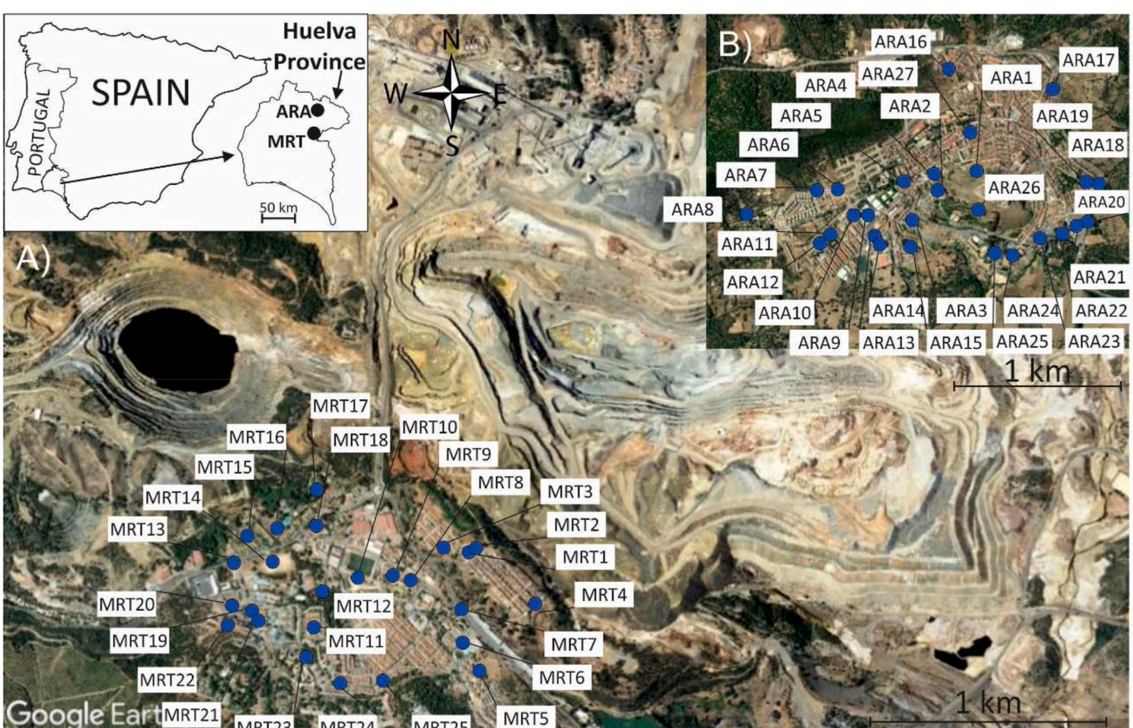

Fig. 1. Location of urban soil samples in A) Minas de Riotinto (MRT) and B) Aracena (ARA) in the Huelva Province (SW Spain).

2.2. Sampling

This study focuses on urban soil samples from Minas de Riotinto (exposed mining area) and Aracena (non-exposed control area). Twenty-five and twenty-seven soil samples were collected in November 2018, respectively from Minas de Riotinto (MRT) and Aracena (ARA), covering —to the best of our knowledge— the main public parks and green areas of these towns (Fig. 1). Composite samples (*ca.* 1 kg) of topsoil (0–3 cm) were retrieved using stainless steel spatulas from three to four points in an area of approx. 10 × 10 m, then stored in plastic bags. All sampling utensils were cleaned exhaustively in between samples with alcohol. Because the urban soils may contain natural soils that developed from local bedrock or manmade filling material (aggregates) commonly used to pave urban areas, the soil types were classified into 1) *in-situ* (natural soils); 2) *ex-situ* (chalky sand and gravel pavements); and 3) mixed (including a mixture of *in-situ* and *ex-situ* soils). The soil uses were classified as 1) playground; 2) passing area; 3) garden in public parks and residential areas; or 4) vacant lots (generally used for parking). Football courts or schoolyards were classified as playgrounds. Sample characteristics (soil type and use) are presented in Table 1; geographical coordinates are presented in the Supplementary Table S1.

2.3. Sample treatment and analysis

The soil samples were dried and periodically mixed in the laboratory at room temperature. All samples were homogenized and sieved using a 2 mm mesh, after which the gravel was discarded. Any sample <2 mm was considered as a total fraction, whereas an aliquot of approx. 30 g was sieved using a 50 µm mesh to recover the fine fraction (<50 µm).

Suspensions of soil and distilled water (1:2.5) were prepared to measure the water-soluble concentrations of As and Pb, pH and electric conductivity (EC), and bioassays. For the suspension, 10 g of soil total fraction and 25 mL of distilled water were mixed in a vial, agitated, and let to settle for half an hour, after which pH was measured. The suspension was then agitated overnight and centrifuged; and aliquots of the supernatants (5 mL each) were recovered for chemical analysis of the water-soluble concentrations of As and Pb, bioassays, as well as for EC measurements. Both pH and EC were measured using a Metrohm 914 pH/Conductometer.

The urban soil samples, including both total and fine fractions, underwent microwave-assisted *aqua regia* acid digestion with HNO_3 and HCl (3:1). The total fraction was grinded before the acid digestion. The chemical analyses of the soil samples and water-soluble fractions were performed using an Agilent 8800 TripleQuad Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) at the Instituto Andaluz de Ciencias de la Tierra (CSIC-UGR, Granada, Spain) for As and Pb. Procedural blanks and certified reference material of Loamy clay CRM052 were run by ICP-MS for quality control. The measured values of the CRM052 for As (12.8 mg/kg) and Pb (74.8 mg/kg) were found to be within the confidence limits of the certified values (14.6 and 82.6 mg/kg, respectively).

2.4. Bioassay using Lactuca sativa L

Germination and root elongation bioassays with *Lactuca sativa* L. (variety *mantecosa)* were performed following the protocol by García-Carmona et al. (2019). Filter papers were placed on petri dishes (Ø 90 mm) and soaked with 5 mL of the previously described soil-water suspensions. A control sample was prepared using 5 mL of distilled water. Subsequently, 20 seeds of *Lactuca sativa* L. were planted, the petri dishes then being introduced in an incubator at a regulated temperature of 22 ± 1 °C in the dark over five days. After this period, the petri dishes were extracted, and germination of the seeds was quantified together with the total elongation of roots and hypocotyls (exceeding 2 mm). The mean elongation of each sample was calculated based on the 15 seeds showing the longest elongation.

2.5. Human health risk assessment

For evaluation of the potential non-carcinogenic and carcinogenic exposure risks, we looked into ingestion, dermal contact, and inhalation of soils as possible exposure routes according to U.S.EPA (1997). We compared the soil concentrations with the regulatory levels of polluted soils set by the Andalusian Government (Decreto 18/2015, 2015): 36 mg/kg for As and 275 mg/kg for Pb. Based on these criteria, we identified As and Pb as PTEs for humans, for which reason their bulk concentrations were used in the exposure model. Non-carcinogenic risk could be determined using Equations (1)–(5), by calculating chronic daily intake or dose through oral ingestion (CDI_{ing}; mg/kg/d), inhalation (CDI_{inh}; mg/m^3 for non-cancer and µg/m^3 for cancer), and/or dermal contact (CDI_{dermal}; mg/kg/d) with soil particles, to generate a Hazard Index (HI) taking into account the accumulated risk of all exposure routes. The total carcinogenic risk (Rc) was calculated in view of Equations (6)–(9). The used parameters in these equations are listed in Tables 2 and 3 (Risk Assessment Information System, 2014; U.S.EPA, 2021, 2017, 2014, 2011). For non-carcinogenic risk, values > 1 indicate potential risk for human health, whereas for carcinogenic risk, values > 0.0001 imply a probability of 1/10,000 to develop cancer over the lifetime due to exposure to the studied urban soils. In addition to assessing the risk posed by each individual soil, the combined risk of a person exposed to the different soils was calculated. For this purpose, each town was considered as an exposure area, and the 95% upper confidence limit of the mean was considered the concentration level, as indicated by the U.S. Environmental Protection Agency (U.S.EPA, 1989). This value was calculated by bootstrapping.

$$CDI_{ing-nc} = \frac{C_{soil} \times IngR \times EF \times ED}{BW \times AT} \times CF \tag{1}$$

$$CDI_{dermal-nc} = \frac{C_{soil} \times SA \times AF_{soil} \times ABS_d \times EF \times ED}{BW \times AT} \times CF \tag{2}$$

$$CDI_{inh-nc} = \frac{C_{soil} \times InhR \times EF \times ED}{PEF \times BW \times AT} \tag{3}$$

$$HQ = \sum \frac{CDI_{nc}}{RfD} \tag{4}$$

$$HI = HQ_{ingestion} + HQ_{dermal} + HQ_{inhalation} \tag{5}$$

$$CDI_{ing-ca} = \frac{C_{soil} \times IngR \times EF \times ED}{BW \times AT} \times CF \times CSF_{ing} \tag{6}$$

$$CDI_{dermal-ca} = \frac{C_{soil} \times SA \times AF_{soil} \times ABS_d \times EF \times ED}{BW \times AT} \times CF \times CSF_{ing} \times ABS_{GI} \tag{7}$$

$$CDI_{inh-ca} = \frac{C_{soil} \times ET \times EF \times ED}{PEF \times 24 \times AT} \times IUR \times 1000 \tag{8}$$

$$Rc\ total = Rc_{ingestion} + Rc_{dermal} + Rc_{inhalation} \tag{9}$$

As part of the human health risk assessment, we compared cancer mortality rates at the municipal level from Minas de Riotinto and Aracena. Data on smoothed standardized mortality rates (SMRs, 1989–2014) for specific cancer locations were retrieved at municipal level from the National Mortality Atlas of Spain (ANDEES) (Corpas Burgos et al., 2020). In brief, SMRs compare the observed mortality with the expected mortality according the number of inhabitants and age (Equation (10)). SMRs take into account the size of a municipality so as to avoid extreme values in small populations.

$$SMR = \frac{\#Observed}{\#Expected} \cdot 100 \tag{10}$$

Therefore, SMR>100 for a given cause indicates an excess in risk

Table 1

Land use, soil type, pH, electric conductivity (EC), As and Pb concentrations and human health risk assessment of the urban soils of Minas de Riotinto (MRT) and Aracena (ARA). The bold numbers indicate the concentrations surpassing the threshold values for polluted soils (36 mg/kg for As and 275 mg/kg, respectively) according to the Decree of Andalusian Government on contaminated soils (Decreto 18/2015, 2015), whereas bold, italic numbers indicate samples posing carcinogenic and non-carcinogenic risk to humans. (T = total fraction >2 mm; F = fine fraction <50 μm; S = water soluble fraction; N.D. = not detected; UCL = Upper confidence limit of the mean).

Sample	Soil use	Soil type	pH	EC	Concentrations (mg/kg)				Concentrations (μg/L)		Total Carcinogenic risk (Rc)				Total Non-carcinogenic risk (HI)			
				μS/cm							Adults		Children		Adults		Children	
					As-T	As–F	Pb-T	Pb–F	As–S	Pb–S	As-T	Pb-T	As-T	Pb-T	As-T	Pb-T	As-T	Pb-T
MRT01	Playground	mixed	8.3	287	2.6	263	16	536	123	15	4.3E-07	1.3E-08	1.0E-06	3.2E-08	0.0025	0.0010	0.026	0.011
MRT02	Playground	*ex-situ*	8.4	518	5.8	42	37	37	867	144	9.3E-07	3.0E-08	2.2E-06	7.3E-08	0.0056	0.0024	0.057	0.025
MRT03	Vacant lot	*in-situ*	8.5	289	6.2	387	54	1678	636	133	1.0E-06	4.4E-08	2.3E-06	1.1E-07	0.0060	0.0035	0.061	0.037
MRT04	Passing area	*in-situ*	7.2	485	**1030**	817	**1950**	1978	2.9	N.D.	***1.7E-04***	1.6E-06	***3.9E-04***	3.9E-06	1.0	0.13	***10***	***1.3***
MRT05	Playground	*ex-situ*	8.5	191	23	48	15	27	4.6	N.D.	3.7E-06	1.3E-08	8.7E-06	3.1E-08	0.022	0.00099	0.23	0.011
MRT06	Passing area	*in-situ*	7.0	426	20	51	52	147	360	58	3.2E-06	4.3E-08	7.5E-06	1.0E-07	0.019	0.0034	0.20	0.036
MRT07	Playground	*ex-situ*	8.8	194	25	53	60	137	104	35	4.0E-06	4.9E-08	9.3E-06	1.2E-07	0.024	0.0039	0.24	0.041
MRT08	Passing area	*ex-situ*	8.5	165	**52**	80	53	120	10	12	8.4E-06	4.3E-08	2.0E-05	1.1E-07	0.050	0.0034	0.51	0.036
MRT09	Playground	*in-situ*	7.8	247	**94**	144	261	492	271	492	1.5E-05	2.1E-07	3.5E-05	5.2E-07	0.091	0.017	0.92	0.18
MRT10	Passing area	*ex-situ*	8.6	260	21	34	17	25	14	0.47	3.4E-06	1.4E-08	8.0E-06	3.4E-08	0.020	0.0011	0.21	0.012
MRT11	Playground	*ex-situ*	8.4	218	23	53	12	35	4.4	4.2	3.7E-06	9.7E-09	8.7E-06	2.4E-08	0.022	0.00077	0.23	0.0082
MRT12	Passing area	*in-situ*	5.7	65	**40**	43	83	82	460	387	6.4E-06	6.8E-08	1.5E-05	1.7E-07	0.039	0.0054	0.39	0.057
MRT13	Vacant lot	*in-situ*	8.1	577	**855**	425	**1990**	1458	38	16	***1.4E-04***	1.6E-06	***3.2E-04***	4.0E-06	0.82	0.13	***8.4***	***1.4***
MRT14	Playground	*ex-situ*	8.5	197	12	23	8.8	17	6.1	2.3	1.9E-06	7.2E-09	4.4E-06	1.8E-08	0.011	0.00057	0.12	0.0060
MRT15	Garden	mixed	8.0	309	**3660**	2656	**10,000**	9740	952	364	***5.9E-04***	8.1E-06	***1.4E-03***	2.0E-05	***3.5***	0.65	***36***	***6.9***
MRT16	Passing area	*ex-situ*	8.7	151	24	44	10	18	3.1	1.6	3.8E-06	8.4E-09	8.9E-06	2.1E-08	0.023	0.00067	0.23	0.0071
MRT17	Passing area	*ex-situ*	8.3	285	**156**	293	**389**	789	40	11	2.5E-05	3.2E-07	5.9E-05	7.8E-07	0.15	0.025	***1.5***	0.27
MRT18	Playground	*in-situ*	7.8	383	**304**	453	**1370**	2046	N.D.	N.D.	4.9E-05	1.1E-06	***1.1E-04***	2.7E-06	0.29	0.088	***3.0***	0.94
MRT19	Passing area	*in-situ*	7.4	324	**43**	53	79	132	133	175	6.9E-06	6.5E-08	1.6E-05	1.6E-07	0.041	0.0051	0.42	0.055
MRT20	Playground	*in-situ*	6.5	271	12	44	34	274	287	212	1.9E-06	2.7E-08	4.4E-06	6.7E-08	0.011	0.0022	0.11	0.023
MRT21	Vacant lot	*ex-situ*	8.0	585	6.4	17	8.7	22	447	57	1.0E-06	7.1E-09	2.4E-06	1.7E-08	0.0062	0.00056	0.063	0.0060
MRT22	Garden	*in-situ*	5.8	117	**61**	157	155	598	1680	2113	9.9E-06	1.3E-07	2.3E-05	3.1E-07	0.059	0.010	0.60	0.11
MRT23	Playground	*ex-situ*	8.0	220	17	18	16	43	63	53	2.7E-06	1.3E-08	6.3E-06	3.2E-08	0.016	0.0010	0.16	0.011
MRT24	Playground	*in-situ*	6.1	156	**1050**	1950	**3320**	6368	4308	4549	***1.7E-04***	2.7E-06	***4.0E-04***	6.6E-06	***1.01***	0.21	***10***	***2.3***
MRT25	Playground	*ex-situ*	8.4	274	23	56	11	24	44	3.5	3.7E-06	8.6E-09	8.5E-06	2.1E-08	0.022	0.00068	0.22	0.0073
MRT	UCL		–	–	**865**	–	**2358**	–	–	–	***1.4E-04***	1.9E-06	***3.3E-04***	4.7E-06	0.83	0.15	***8.5***	***1.6***
ARA01	Passing area	*in-situ*	8.0	254	4.6	4.7	74	43	10	27	7.5E-07	6.0E-08	1.8E-06	1.5E-07	0.0045	0.0048	0.045	0.051
ARA02	Passing area	*in-situ*	7.8	347	26	38	**773**	1177	41	320	4.2E-06	6.3E-07	9.9E-06	1.5E-06	0.025	0.050	0.26	0.53
ARA03	Playground	mixed	7.8	60	3.4	20	3.5	39	18	48	5.5E-07	2.8E-09	1.3E-06	6.9E-09	0.0033	0.00022	0.033	0.0024
ARA04	Passing area	*in-situ*	7.6	360	19	23	N.D.	330	28	127	3.0E-06	–	7.1E-06	–	0.018	–	0.18	–
ARA05	Passing area	*in-situ*	7.8	361	20	23	64	90	14	15	3.2E-06	5.2E-08	7.4E-06	1.3E-07	0.019	0.0041	0.19	0.044
ARA06	Passing area	*in-situ*	8.6	141	4.7	4.0	19	27	4.9	3.7	7.5E-07	1.6E-08	1.8E-06	3.9E-08	0.0045	0.0012	0.046	0.013
ARA07	Passing area	*ex-situ*	8.6	184	18	28	5.7	10	6.5	0.6	2.8E-06	4.6E-09	6.6E-06	1.1E-08	0.017	0.00037	0.17	0.004
ARA08	Vacant lot	*in-situ*	8.3	186	4.6	5.3	37	39	1.6	2.6	7.4E-07	3.0E-08	1.7E-06	7.5E-08	0.0044	0.0024	0.045	0.026
ARA09	Vacant lot	*ex-situ*	8.8	195	12	25	**327**	680	5.5	8.6	1.9E-06	2.7E-07	4.4E-06	6.6E-07	0.011	0.021	0.12	0.225
ARA10	Vacant lot	*in-situ*	8.3	244	11	15	43	79	8.2	13	1.8E-06	3.5E-08	4.1E-06	8.6E-08	0.011	0.0028	0.11	0.030
ARA11	Passing area	*in-situ*	7.9	481	11	12	**304**	360	16	77	1.8E-06	2.5E-07	4.1E-06	6.1E-07	0.011	0.020	0.11	0.209
ARA12	Passing area	*in-situ*	7.0	202	5.3	8.2	20	33	17	122	8.6E-07	1.7E-08	2.0E-06	4.1E-08	0.0051	0.0013	0.052	0.014
ARA13	Passing area	*ex-situ*	7.8	392	4.1	14	7.5	42	10	43	6.6E-07	6.1E-09	1.5E-06	1.5E-08	0.0039	0.00049	0.040	0.005
ARA14	Garden	*in-situ*	7.8	279	10	13	43	72	6.7	15	1.5E-06	3.5E-08	3.6E-06	8.7E-08	0.0093	0.0028	0.094	0.030
ARA15	Playground	*in-situ*	7.4	342	7.4	13	52	88	12	70	1.2E-06	4.2E-08	2.8E-06	1.0E-07	0.0072	0.0033	0.073	0.035
ARA16	Vacant lot	*ex-situ*	7.5	204	2.0	3.5	13	25	2.1	5.1	3.2E-07	1.0E-08	7.6E-07	2.6E-08	0.0019	0.00083	0.020	0.009
ARA17	Playground	*in-situ*	7.6	375	7.5	10	49	73	29	31	1.2E-06	4.0E-08	2.8E-06	9.8E-08	0.0072	0.0032	0.073	0.034
ARA18	Playground	*ex-situ*	8.5	171	6.4	13	6.1	14	6.9	3.3	1.0E-06	4.9E-09	2.4E-06	1.2E-08	0.0062	0.00039	0.063	0.004
ARA19	Passing area	*in-situ*	8.1	348	7.7	10	53	74	7.4	11	1.2E-06	4.3E-08	2.9E-06	1.1E-07	0.0074	0.0034	0.076	0.037
ARA20	Garden	*in-situ*	8.1	297	31	53	**473**	813	21	38	5.0E-06	3.9E-07	1.2E-05	9.5E-07	0.030	0.031	0.31	0.325
ARA21	Passing area	*in-situ*	8.2	444	34	46	**357**	689	15	29	5.4E-06	2.9E-07	1.3E-05	7.1E-07	0.032	0.023	0.33	0.245
ARA22	Passing area	*in-situ*	8.0	330	20	29	**339**	505	20	52	3.3E-06	2.8E-07	7.7E-06	6.8E-07	0.020	0.022	0.20	0.233
ARA23	Vacant lot	mixed	8.2	229	6.1	11	35	93	4.2	7.0	9.8E-07	2.9E-08	2.3E-06	7.0E-08	0.0059	0.0023	0.060	0.024
ARA24	Playground	mixed	8.1	257	8.5	20	42	124	14	14	1.4E-06	3.4E-08	3.2E-06	8.3E-08	0.0082	0.0027	0.084	0.029
ARA25	Passing area	*in-situ*	8.3	318	17	29	**626**	1098	12	74	2.8E-06	5.1E-07	6.4E-06	1.3E-06	0.016	0.040	0.17	0.430
ARA26	Passing area	*in-situ*	7.5	226	6.3	17	44	106	12	42	1.0E-06	3.5E-08	2.4E-06	8.7E-08	0.0060	0.0028	0.061	0.030
ARA27	Playground	*in-situ*	7.1	468	15	24	114	320	38	113	2.5E-06	9.3E-08	5.8E-06	2.3E-07	0.015	0.0074	0.15	0.078
ARA	UCL		–	–	16	–	254	–	–	–	2.5E-06	2.1E-07	5.9E-06	5.1E-07	0.015	0.016	0.15	0.17

Table 2
Parameters for the human health risk assessment (retrieved from Risk Assessment Information System, 2014; U.S.EPA, 2021; 2017, 2011).

Variable	Definition	Adults	Children
IngR (mg/d)	Soil ingestion rate	100	200
EF (d/year)	Exposure frequency	75	75
ED (year)	Exposure duration	26	6
BW (kg)	Average body weight	80	15
ATnc (d)	Average time for non-carcinogenic effects	9490	2190
ATca (d)	Average time for carcinogenic effects	25,550	25,550
LT (year)	Lifetime	70	70
ET (h/d)	Exposure time	1	1
CF (kg/mg)	Conversion factor	10^{-6}	10^{-6}
SA (cm^2)	Available exposed skin surface	6032	2373
AF (mg/cm^2)	Soil to skin adherence factor	0.07	0.2
InhR (m^3/d)	Inhalation rate	14.64	8.77
PEF (m^3/kg)	Particle emission factor	$1.36*10^9$	$1.36*10^9$
HQ	Non-carcinogenic risk	–x	–x
HI	Hazard index; Total non-carcinogenic risk	–x	–x
Rc	Total carcinogenic risk	–x	–x

Table 3
Parameters for As and Pb for the human health risk assessment (retrieved from U.S.EPA, 2021).

Variable	Definition	As	Pb
C (mg/kg)	Concentration in soils	–x	–x
ABS_d	Dermal absorption factor	0.03	0.001
RfD_{ing} (mg/kg/d)	Chronic oral reference dose	0.0003	0.004
ABS_{GI}	Gastrointestinal absorption factor	1	1
RfC_{inh} (mg/m^3)	Chronic inhalation reference concentration	0.0003	0.0003
CSF_{ing} $(mg/kg/d)^{-1}$	Chronic oral slope factor	1.5	0.0085
CSF_{dermal}	Chronic dermal slope factor = CSF_{ing}/ABS_{GI}	–x	–x
$IUR(\mu g/m^3)^{-1}$	Chronic inhalation unit risk	0.0043	$1.2*10^{-5}$

compared to the Spanish average, SMR<100 indicates a decreased risk, *i.e.* a lower mortality rate than expected, and SMR equal to 100 indicates a death risk similar to the one expected. Further details on the methodology for SMR estimation can be consulted in Corpas Burgos et al. (2020) and Perez Panades et al. (2020). We selected malignant neoplasms that have previously been associated with exposure to As and Pb. The tumor locations (International Classification of Diseases, ICD-10 codes) investigated include bronchus or lung (C33, C34), skin and soft tissues (C44–C47, C49; except melanoma C45.0.1.2), liver or intra-hepatic bile ducts (C22), bladder (C67), prostate (C61), and kidney, except renal pelvis (C64); in addition to these, Pb exposure has been associated with stomach (C16) and brain (C71) cancer (IARC, 2012, 2006). We included pancreas (C25), and colon (C18), as well as lip, buccal cavity, and pharynx (C00–C14) as potential tumor locations, because these cancers have been associated with elevated As concentrations in topsoil in Spain (Núñez et al., 2016).

2.6. Statistical analysis

We compared the significance of differences between soil types and study areas using the Mann-Whitney *U* test (p value < 0.05), and we performed Principal Component Analysis (PCA) to analyze the relationships among variables using IBM SPSS Statistics 24. The PCA was run using Varimax rotation. The 95% upper confidence limit of the mean for the concentrations of As and Pb in each town was calculated by bootstrapping (10,000 repetitions of random sampling with replacement) with R software, using the package boot (Canty and Ripley, 2021; R Core Team, 2021).

3. Results

3.1. Chemical characteristics of urban soils

The As and Pb concentrations in the total and fine fractions of the urban soils show trends among the different soil types (Fig. 2; Tables 1 and 4), while the influence of the soil type is observed between towns. When comparing the statistical significance of the differences between soil types, we grouped *in-situ* soils together with mixed soils (having an *in-situ* component). The comparison of median values in *in-situ* and mixed soils for the exposed and the non-exposed control area shows that the urban soils in Minas de Riotinto are significantly enriched in As (total and fine fractions) and Pb (total fraction) with respect to Aracena. The *ex-situ* soils in both towns exhibit relatively low concentrations of As and Pb. However, we observed that the *ex-situ* soils in Minas de Riotinto have significantly higher median values of As (total and fine fractions) in comparison to Aracena.

When comparing the natural and aggregate soils of each town, *in-situ* soils proved to be more enriched in As and Pb as opposed to *ex-situ* soils. The *in-situ* and mixed soils in Minas de Riotinto contain significantly higher median values of As (fine fraction) and Pb (total and fine fractions) than the *ex-situ* soils, whereas the *in-situ* and mixed soils in Aracena are significantly enriched in Pb (total and fine fractions) in comparison to the *ex-situ* soils (Tables 1 and 4).

3.2. Electrical conductivity, pH, and water-soluble As and Pb concentrations

When all soil types are pooled, there are no significant differences in pH and EC values between the urban soils of Minas de Riotinto and Aracena. However, the urban soils in Minas de Riotinto present higher ranges in the pH and EC conditions than in Aracena (Fig. 3A; Tables 1 and 4). This variation is due to a greater heterogeneity of soil properties. For instance, the soil samples with the lowest pH < 6.5 and relatively low EC values (65–271 µS/cm) correspond to *in-situ* soils of Minas de Riotinto (MRT12, MRT20, MRT22, and MRT24), whereas soil samples with elevated pH values (8.0–8.4) and the highest EC values (518–585 µS/cm) correspond to *ex-situ* soils (MRT2 and MRT21) and one *in-situ* soil sample (MRT13) of Minas de Riotinto (Fig. 3A). The pH values of *in-situ* soils (ranging from 5.7 to 8.5 with median value of 7.2) are significantly lower than the ones of *ex-situ* soils (ranging from 8.0 to 8.8 with median value of 8.5) in Minas de Riotinto. The pH values of two mixed urban soil samples in Minas de Riotinto (8.0 and 8.3) fall in between the values for *in-situ* and *ex-situ* soils. The *in-situ* soils of the exposed area also exhibit significantly lower pH in comparison to the *in-situ* soils of the control area in Aracena (ranging from 7.0 to 8.6 with median value of 7.9). On the contrary, *ex-situ* soils do not exhibit significant differences in pH values between the towns. The EC values are not significantly different among soil types nor between the exposed and control areas.

The water-soluble concentrations of As and Pb are presented in Fig. 3B. High As (up to 4300 µg/L) and Pb (up to 4550 µg/L) concentrations are detected in the urban soil samples in Minas de Riotinto, with the lowest pH values ranging from 5.7 to 6.1. These samples correspond to *in-situ* samples (MRT12, MRT22, MRT24). Additionally, one mixed (MRT15 with pH 8.0) and one *ex-situ* soil sample (MRT2 with pH 8.4) present water-soluble As concentrations close to 1000 µg/L. The *in-situ* and mixed (with *in-situ* soil component) soil samples of Minas de Riotinto present significantly higher water-soluble As and Pb concentrations than the *ex-situ* soil samples. The same trend is observed when comparing different soil types in Aracena. An intercomparison of the towns shows that the water-soluble As concentrations (ranging from 2.8 to 4300 µg/L with median value of 114 µg/L) among all soil types in Minas de Riotinto are significantly higher than in Aracena (ranging from 2.6 to 41 µg/L with median value of 12 µg/L). In contrast, the Pb concentrations in Minas de Riotinto (from below detection limit to 4550 µg/L with median of 53 µg/L) do not show significant differences with

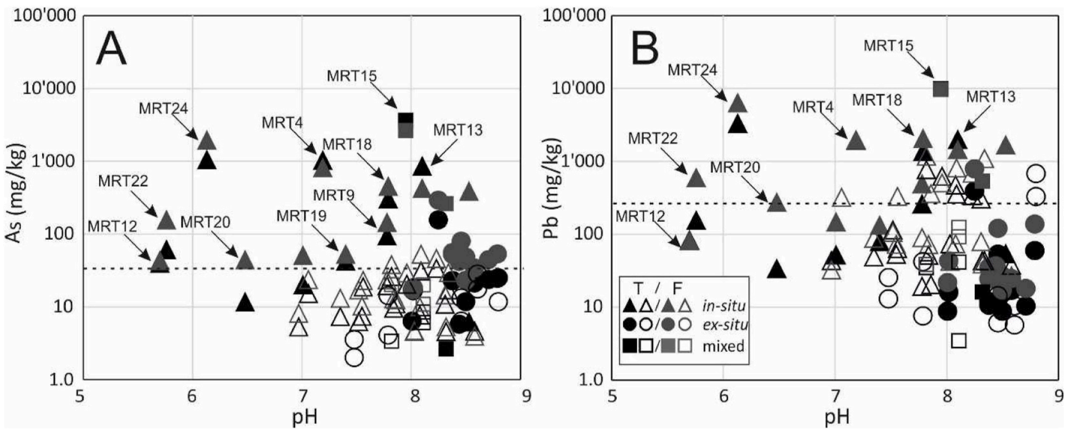

Fig. 2. Soil pH vs. A) As and B) Pb concentrations in total (T; black symbols) and fine (F; grey symbols) fractions in urban soils of Minas de Riotinto (MRT; filled symbols) and Aracena (ARA; open symbols). The dashed lines indicate the regulatory levels of polluted soils for As (36 mg/kg) and Pb (275 mg/kg), respectively, set by the Andalusian Government (Decreto 18/2015, 2015).

Table 4

Summary table presenting min., max., standard deviation (SD), mean, and median values for pH, electric conductivity (EC, μS/cm), As and Pb concentrations (mg/kg) of the urban soils of Minas de Riotinto and Aracena in both *in-situ* (including mixed samples with *in-situ* component) and *ex-situ* samples. (N = number of samples; T = total fraction >2 mm; F = fine fraction <50 μm).

	Minas de Riotinto						Aracena					
	in-situ (N = 13)						*in-situ* (N = 21)					
	pH	EC	As-T	As–F	Pb-T	Pb–F	pH	EC	As-T	As–F	Pb-T	Pb–F
Min.	5.7	65	2.6	43	16	82	7.0	60	3.4	4.0	3.5	27
Max.	8.5	577	3655	2656	10,001	9740	8.6	481	34	53	773	1177
SD	0.96	144	1017	813	2768	2877	0.40	104	8.9	13	222	353
Mean	7.2	303	552	573	1489	1964	7.9	298	13	19	170	285
Median	7.4	289	61	263	155	598	8.0	308	9.3	16	52	92
	***ex-situ* (N = 12)**						***ex-situ* (N = 5)**					
Min.	8.0	151	5.8	17	8.8	17	7.5	171	2.0	3.5	5.7	10
Max.	8.8	585	156	293	389	789	8.8	392	18	28	327	680
SD	0.24	138	41	74	107	218	0.56	92	6.5	9.9	143	294
Mean	8.4	272	32	63	53	108	8.2	229	8.5	17	72	154
Median	8.5	219	23	46	16	31	8.5	195	6.4	14	7.5	25

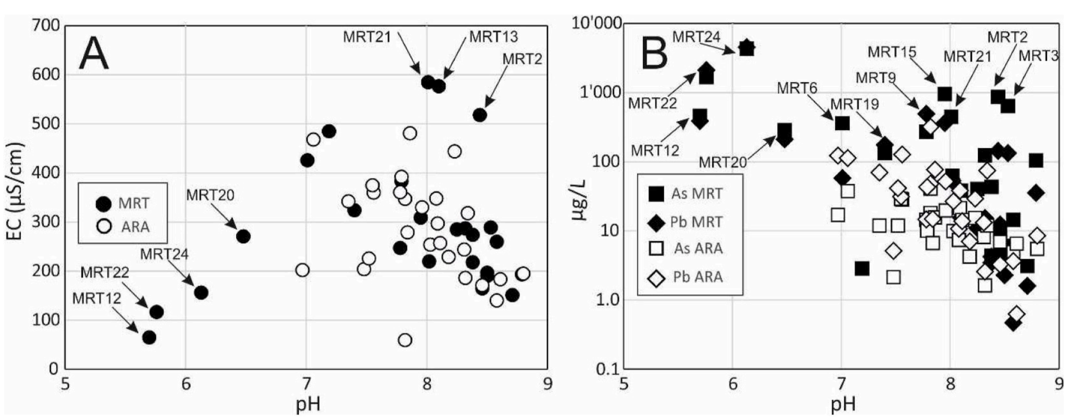

Fig. 3. Soil pH vs. A) electrical conductivity (EC) and B) concentrations of As and Pb in the water-soluble fractions in urban soils of Minas de Riotinto (MRT) and Aracena (ARA).

respect to Aracena (from 0.62 to 320 μg/L with median value of 29 μg/L). Intercomparison of different soil types between the towns shows, however, that the water-soluble concentrations of both As and Pb are significantly higher in Minas de Riotinto in the *in-situ* and mixed soils with respect to Aracena, whereas *ex-situ* soils do not show differences.

3.3. Soil bioassays

The bioassay using *Lactuca sativa* L. seeds resulted in the germination of nearly all seeds with a success rate varying from 85% to 100% (median success rate of 95% in each town). There were no significant differences between the exposed and control areas.

The results of the measured root elongation of *Lactuca sativa* L. seeds are presented in Fig. 4. The seeds grown in the soil-water extracts of urban soils of Minas de Riotinto present median elongation of 59.9 mm, whereas median elongation for the samples of Aracena is 62.2 mm. All germinated seeds are longer than the control, hence no phytotoxicity is observed, except for one sample (MRT24) presenting elongation of 39.8 mm. There are no statistically significant differences in the elongation of the seeds between the towns.

3.4. *Carcinogenic and non-carcinogenic risks of the urban soils*

The urban soil samples from Aracena do not represent a health risk for the residents, yet up to six samples from Minas de Riotinto show potential risk (Table 1; Supplementary Table S2). Arsenic is responsible for the carcinogenic risk of the urban soils, whereas As and, to a lesser extent, Pb would be responsible for the non-carcinogenic risk. The calculated cancer risk of As for adults and children was unacceptable in the *in-situ* soil samples MRT4, MRT13, and MRT24 and in mixed sample MRT15 —and additionally, for children, the *in-situ* sample MRT18 presenting values over 1/10,000. Further, a non-carcinogenic health risk of As is detected for adults and children in samples MRT15 and MRT24 (*e.g.*, surpassing up to 36 times the reference dose, RfD, value for children) and for children in the *in-situ* samples of MRT4, MRT13, and MRT18, and in the *ex-situ* sample MRT17. Lead exhibits non-carcinogenic health risk for children in samples MRT4, MRT13, MRT15, and MRT24. The risk assessment considering the whole town of Minas de Riotinto as an exposure area exhibits carcinogenic risk of As for both adults and children, whereas As and Pb present non-carcinogenic risk for children (Table 1).

3.5. *Cancer mortality*

Cancer of lip, buccal cavity and pharynx (SMR of 139 and 113 in Minas de Riotinto and Aracena, respectively), bronchus and lung (126 and 102), skin (non-melanoma; 119 and 118), liver and intra-hepatic bile ducts (121 and 113), colon (113 and 93), bladder (112 and 103), and stomach (106 and 93) exhibit increased SMRs in Minas de Riotinto and are generally higher than in Aracena (Fig. 5). The rest of the neoplasms show low SMRs and no significant differences between the towns. For instance, prostate cancer (104) exhibits only slightly increased SMR values in Minas de Riotinto, whereas kidney (97), brain (93), and pancreas (89) cancer show slight decreases in the SMR values (Fig. 5).

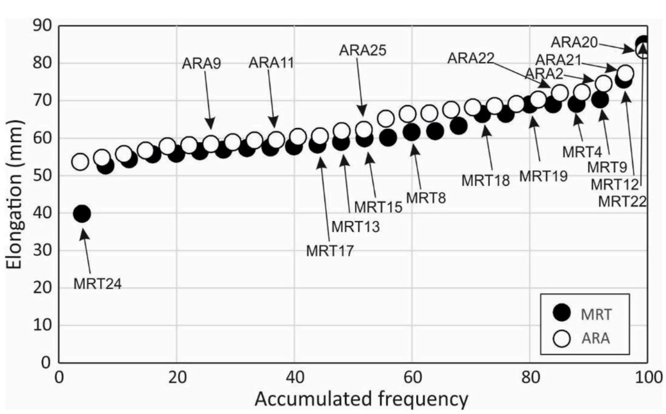

Fig. 4. Accumulated frequency curve for the measured root elongation of *Lactuca sativa* L. seeds grown in the extract of soil-water suspension of each soil sample from Minas de Riotinto (MRT) and Aracena (ARA). The soil samples exceeding the regulatory levels for polluted soils for either As or Pb in Minas de Riotinto and for Pb in Aracena are indicated (Table 1) (Decreto 18/2015, 2015).

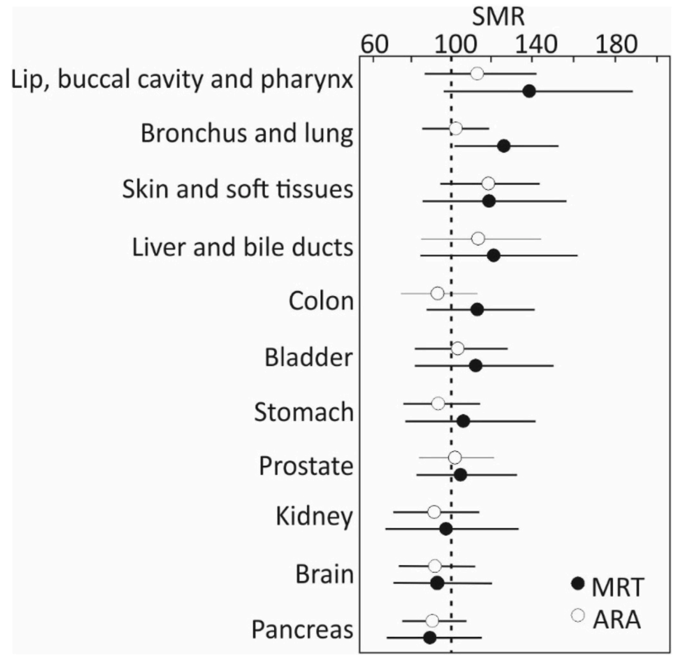

Fig. 5. Smoothed standardized mortality rate (SMR) and confidence interval (95% CI) of cancer for selected tumor locations associated with As and Pb exposure in Minas de Riotinto (MRT) and Aracena (ARA) (Source: Corpas Burgos et al., 2020).

4. Discussion

4.1. *Soil chemistry of As and Pb and their enrichment in the fine fraction*

Parent rock lithology and mineralizations are ascribed as main factors controlling the baseline geochemistry. Galán et al. (2008) established soil geochemical baseline maps for the geological units in the Province of Huelva, including the South Portuguese Zone (hosting IPB) and Ossa Morena Zone, where Minas de Riotinto and Aracena are respectively located. These authors highlight the enrichment of As, Cu, and Pb in the South Portuguese Zone and Zn in Ossa Morena Zone. Accordingly, the As and Pb enriched urban soils in Minas de Riotinto correspond principally to natural soils impacted by mineralized bedrock in the northern edges of the town, closer to the mining area. The *in-situ* soils of Minas de Riotinto present even higher median values of As (61 mg/kg) and Pb (155 mg/kg) than the baseline values of the South Portuguese Zone (25 mg/kg and 38 mg/kg, respectively; Galán et al. (2008)). Moreover, many of the urban soil samples exceed the regulatory levels of As for polluted soils (36 mg/kg; 44% of all soils and 77% of the *in-situ* soils) and Pb (275 mg/kg; 24% of all soils and 38% of the *in-situ* soils) set by the regional government (Table 1; Fig. 2; Decreto 18/2015, 2015). In Aracena, the median value for Pb (51 mg/kg) in *in-situ* soils surpasses the baseline value of Ossa Morena Zone (32 mg/kg), and seven soil samples also exceed the regulatory levels for Pb for polluted soils (Table 1; 26% of all soils and 27% of the *in-situ* soils). On the one hand, the enrichment of As and Pb in the *in-situ* soils of Minas de Riotinto can be related to the sulfide minerals (*e.g.* arsenopyrite [FeAsS], galena [PbS]) and secondary minerals formed as sulfide oxidation products (*e.g.* beudantite [$PbFe_3(AsO_4)(SO_4)(OH)_6$], arsenian plumbojarosite [$Pb_{0.59}Fe_3(AsO_4)_{0.18}(SO_4)_{1.82}(OH)_6$], and As- and Pb-bearing Fe oxyhydroxides) (Almodóvar et al., 2019; Parviainen et al., n.d.). Deposition of airborne particles derived from the adjacent mine workings may be a secondary source of As and Pb pollution in the urban soils (Sánchez de la Campa et al., 2020). On the other hand, the elevated concentrations of Pb in the *in-situ* soils of Aracena are associated with SEDEX-type mineralizations of galena and other Pb-bearing sulfosalts in the carbonate parent rocks (Rivera et al., 2015). Soil parent material was observed to be a key factor influencing the As concentrations in urban soils of Nordic cities (Tarvainen et al., 2018). For instance, in Hämeenlinna (Finland), elevated concentrations of As (up to 44 mg/kg; median 8.9 mg/kg) are attributed to the As-rich geochemical bedrock province. Yet Pb (up to 179 mg/kg; median 13 mg/kg) was associated with anthropogenic pollution (Tarvainen et al., 2018). Similarly, in a Polish study of urban soils, the concentrations and spatial distribution of Pb (up to 167 mg/kg; median 30 mg/kg) were mainly related to human activity, *i.e.* atmospheric deposition of pollutants from city traffic and power/heat production by coal combustion (Różański et al., 2018).

A decreasing grain size has been shown to increase PTE enrichment and bioaccessibility in urban soils. The urban soils of Minas de Riotinto exhibit a significant enrichment of As and Pb in the fine fraction (<50 μm) with respect to bulk soil samples (<2 mm). Additionally, our previous studies have shown that fine-grained (<10 μm) As and Pb-rich phases are abundant in the *in-situ* soils of Minas de Riotinto (Parviainen et al., n.d.). The soil fractions below <10 μm are of particular importance as they are prone to dusting and suspension in the air, and subsequently pose a risk to humans through inhalation. Similarly, PTE concentrations in different particle size fractions of dust were studied in urban areas in Oruro, Bolivia (Goix et al., 2016): the fine fractions <50 μm of soil dust samples collected from two football courts under the impact of mining and smelting activities, respectively, were severely enriched in PTEs including As, Cd, Cu, Pb, Sb, Sn, and Zn. Especially, the fractions <2 μm and 2–20 μm, which may be inhalable, were enriched in these PTEs. Madrid et al. (2008) further detected enrichment of Cr, Cu, Ni, Pb, and Zn in the fine fractions (fractions <2 μm and 2–10 μm) of urban soils of Seville, Spain.

The PCA exhibits an excellent correlation of As and Pb concentrations in the bulk and fine fractions in Minas de Riotinto, falling into the first component with factor loadings close to one (Table 5). However, elevated concentrations of As and Pb in the soil samples in Minas de Riotinto are not correlated with their respective water-soluble concentrations (component 2). The solubility of As and Pb may be explained by other soil properties and components. Generally, As solubility is reduced in soils with iron oxide and organic matter contents, whereas elevated pH and $CaCO_3$ content would have the opposite effect (Romero-Freire et al., 2014). Lead solubility is reduced in soils rich in $CaCO_3$ and organic matter (Romero-Freire et al., 2015). For instance, the samples MRT9, MRT15 and MRT24 surpass the regulatory levels of As and Pb for polluted soils (Table 1), and present elevated concentrations in the soluble fraction (271–4300 μg/L and 364–4550 μg/L, respectively). But the solubility of As and Pb is well below 1% in comparison to the total fraction, which may owe to the Fe (hydr)oxide content (Parviainen et al., n.d.; Romero-Freire et al., 2014). Other samples surpassing these regulatory levels exhibit much lower soluble concentrations of As and Pb, however (<40 μg/L and <16 μg/L, respectively). The samples exceeding the regulatory levels for Pb exhibit relatively low soluble concentrations of Pb (Table 1). Contrariwise, soil samples with lower bulk concentrations of As and Pb (*e.g.* MRT2, MRT3, MRT6, MRT12, MRT20, MRT21, MRT22; two of them slightly surpassing the threshold value for As) have high water-soluble concentrations (287–1680 μg/L and 57–2110 μg/L, respectively; Table 1; Figs. 2 and 3). These samples show higher solubility of water-soluble As, with up to 15% in MRT2 (carbonate-rich *ex-situ* soil sample). Still, there is no clear relation between these samples, because among them there are both *in-situ* and *ex-situ* samples with varying pH (from 5.8 to 8.5) and mineral composition (Parviainen et al., n.d.). According to the PCA for Aracena, the solid concentrations of As are correlated in the first component, whereas Pb solid concentrations correlate in the second component. Furthermore, the water-soluble As concentrations (component 3) in Aracena are not correlated with the solid concentrations, whereas the soluble fraction of Pb presents similar factor loadings for the second and third components. The lack of correlation between the bulk solid concentrations and water-soluble fractions in both towns may be attributed to other soil properties and components (Romero-Freire et al., 2014, 2015).

4.2. Phytotoxicity and human health risk assessment

Toxicity of the soils depends on a variety of soil properties and constituents, including pH, redox potential, calcium carbonate and organic carbon content, and concentrations of the PTEs and their mineralogical association (Izquierdo et al., 2015; Li et al., 2018; Romero-Freire et al., 2014, 2015; Simón et al., 2005). Based on the bioassay using *Lactuca sativa* L., only the *in-situ* soil sample MRT24 from a playground exhibits phytotoxicity, whereas other samples in Minas de Riotinto and Aracena do not show toxic effects. Extremely high concentrations of As and Pb (>4000 μg/L of each) in the soil-water extract

Table 5
Principal Component Analysis for pH, soil pollutants (As and Pb in total (T), fine (F), and water-soluble (S) fractions), ecotoxicity (elongation and germination of *Lactuca sativa* L.), and health risk assessment (Carcinogenic (Car) and non-carcinogenic (Tox) effect for adults (A) and children (C)) data for Minas de Riotinto (MRT) and Aracena (ARA). High positive and high negative correlations are highlighted with bold numbers.

MRT	Component			ARA	Component		
	1	2	3		1	2	3
pH	0.035	**−0.771**	−0.499		0.153	0.214	**−0.884**
As-T	**0.995**	0.072	0.036		**0.945**	0.306	0.062
As–F	**0.907**	0.380	−0.091		**0.884**	0.336	0.065
As–S	0.270	**0.931**	−0.156		0.343	0.304	**0.764**
Pb-T	**0.992**	0.115	0.018		0.476	**0.870**	0.093
Pb–F	**0.924**	0.347	−0.056		0.515	**0.836**	0.066
Pb–S	0.160	**0.961**	−0.117		0.094	0.610	**0.670**
Elongation	−0.217	−0.046	**0.886**		0.498	0.234	0.565
Germination	0.275	−0.019	**0.617**		−0.137	0.334	0.242
As-CarA	**0.995**	0.072	0.036		**0.943**	0.314	0.071
As-CarC	**0.995**	0.072	0.036		**0.943**	0.314	0.071
As-ToxA	**0.995**	0.072	0.036		**0.943**	0.314	0.071
As-ToxC	**0.995**	0.072	0.036		**0.943**	0.314	0.071
Pb-CarA	**0.992**	0.115	0.018		0.476	**0.870**	0.092
Pb-CarC	**0.992**	0.115	0.018		0.476	**0.870**	0.092
Pb-ToxA	**0.992**	0.115	0.018		0.476	**0.870**	0.092
Pb-ToxC	**0.992**	0.115	0.018		0.476	**0.870**	0.092
Eigenvalue	12.2	2.33	1.47		11.3	2.14	1.65
Variance %	71.7	13.7	8.65		66.4	12.6	9.69
Accumulated %	94.0				88.7		

of MRT24, in the absence of calcium carbonate (Parviainen et al., n.d.), were probably too hostile conditions for *Lactuca sativa* L. growth. The PCA did not show correlation between the bioassay and the concentrations of As and Pb, either in the solid fractions or in the water-soluble fraction (Table 5). The growth of the germinated seeds seems to be favored in other *in-situ* soil samples (*e.g.* MRT9, MRT12, and MRT22; Fig. 4) in Minas de Riotinto, surpassing the regulatory levels for polluted soils for As (Table 1) and with elevated concentrations of As and Pb in the soil-water extracts (Table 1; Fig. 3B). Moreover, the calcium carbonate content (Parviainen et al., n.d.), higher pH, and lower PTE concentrations of *ex-situ* soils (Figs. 2 and 3) present favorable conditions for the germination tests, but generally result in shorter root elongation of the *Lactuca sativa* L. (Fig. 4). The PCA moreover suggests that the bioassay has no relation with the results obtained by the calculations of risk assessment models. To better evaluate the potential toxicity of the soils, bioassays using other organisms than *Lactuca sativa* L. are needed.

Soil type and use are both held to be important factors when evaluating the health risks of urban soils. Our results show that the soil type is decisive in the enrichment and potential toxicity of the urban soils —highlighting natural soils as a risk factor in Minas de Riotinto— while the soil use may have an effect on the potential exposure risk. The exposure risk is highest in urban areas that are frequently transited by residents, including playgrounds and passing areas in public parks and residential areas. Other studies stress that in playgrounds and sports facilities, children are at highest risk (Różański et al., 2018). The urban soils in Minas de Riotinto presenting elevated concentrations of As and Pb —and thus posing highest carcinogenic and/or non-carcinogenic health risks to residents —are generally *in-situ* soils (Table 1). Additionally, one *ex-situ* and one mixed soil sample were found to have elevated concentrations of these PTEs. They correspond to playgrounds (MRT9, MRT18, MRT24), passing areas (MRT4, MRT17), a garden (MRT15) in public parks, and a vacant lot (MRT13). The risk assessment models take into consideration the soil bulk concentrations (PCA exhibits linear correlation; Table 5), but not the smaller fractions (*e.g.*, <150 μm as recommended by U.S.EPA, 2016) or the solubility of the samples. Bulk concentrations might underestimate the likelihood of PTE adherence to hands and incidental ingestion, consequently underrating the health risks (U.S.EPA, 2016). In this study, the water-soluble fraction of As and Pb is not directly correlated with bulk soil concentrations (Table 5). Therefore, bioavailability tests are needed to further assess the potential exposure risks, even of the samples with low bulk concentrations but with higher As and Pb solubility. Arsenic poses a major risk to children, who are especially sensitive to As intoxication, as their metabolism may take longer to expel it from their body (Bini and Bech, 2014). Since playgrounds and public parks are frequented by children, the urban soils of such public spaces are of special concern (Han et al., 2020). According to our results, As poses non-carcinogenic risk to children in six of the aforementioned soil samples, and carcinogenic risk in five of them. Additionally, Pb poses non-carcinogenic risk to children in four urban soil samples. The risk is not only because of the harmful effects of As and Pb on health (Bini and Bech, 2014; Jaishankar et al., 2014), but also because there may be a synergistic effect between them, increasing toxicity (Islam et al., 2016). Likewise, in other mining areas, urban soils have been recognized as potential exposure routes to humans. In Lanmuchang (Guizhou Province, China), the impact of outcropping sulfide mineralization and sporadic mining activity was reflected as elevated PTE concentrations in urban soils, and As posed potential non-carcinogenic and carcinogenic risk to children and adults (Ma et al., 2020). In urban areas without mining impact, other exposure routes besides soils may gain importance. For instance, in another Chinese city within Hunan Province, elevated concentrations of Pb (median 116 mg/kg) and As (median 44 mg/kg) were detected in the urban soils, though in this case ingestion of food and inhalation of particulate matter were considered to have greater non-carcinogenic and carcinogenic risk than ingestion of soils (Cao et al., 2016).

Cancer is considered a multifactorial disease that may be influenced by external aspects such as lifestyle, smoking habit, diet, occupation, and environmental exposure, as well as internal biological and genetic aspects (Institute of Medicine, 2002). Regarding the external factors, diet (including water consumption) is held to be the main exposure route of As among the general population, whereas inhalation of As from ambient air is considered a minor exposure route except in polluted areas and under occupational exposure (IARC, 2012; and references therein). Lung cancer is associated to As exposure via inhalation, for instance, due to industrial emissions, *e.g.*, Cu smelters. Additionally, a recent study showed an association between As topsoil concentrations and mortality due to cancers of the stomach, pancreas, lung, brain, and non-Hodgkin's lymphomas (men and women) (Núñez et al., 2016). Furthermore, these authors observed an association with cancers of the buccal cavity and pharynx, colorectal, renal, and prostate in men. Exposure to Pb is strongly associated with occupational scenarios such as the mining industry, including lead smelting, refining industries, battery manufacturing plants, painting and printing industries, and gasoline stations (IARC, 2006). For the general population, inhalation of Pb is considered a common exposure route, especially in the vicinity of industrial activities (IARC, 2006; and references therein). Urban soils are increasingly associated with human well-being and health; inhalation, ingestion, and dermal contact are potential exposure routes to humans (Li et al., 2018). Regardless of the statistical significance, we observed an increase in SMRs for lip, buccal cavity and pharynx, bronchus and lung, liver and intra-hepatic bile ducts, colon, and bladder cancer in Minas de Riotinto in comparison to Aracena (Fig. 5). When evaluating Minas de Riontinto as an exposure area, our study moreover shows increased carcinogenic risk for both children and adults considering all exposure routes (inhalation, ingestion and dermal contact; Table 1), which supports the increased cancer mortality rates. Still, other exposure routes cannot be disregarded. Ingestion of potentially polluted water and food, as well as inhalation of mining-derived airborne particulate matter, may influence the increased relative mortality in Minas de Riotinto, and they may have a synergic effect. For instance, the proximity of metal industries, mining facilities, and smelters has previously been reported to increase the mortality of lung cancer and digestive system cancers in exposed populations in Spain and Chile (Fernández-Navarro et al., 2012; García-Pérez et al., 2012; Ruiz-Rudolph et al., 2016). Yet these studies lack a cause-effect relationship of the cancer mortality risk and are based on the distance to the potential pollution sources. Our study highlights the potential influence of elevated concentrations of As and Pb in the urban soils of Minas de Riotinto, and subsequently elevated Rc values, upon the increased cancer mortality of many types of cancers previously associated with exposure to these carcinogenic elements. One must bear in mind that our study is highly explorative and we cannot assume a causal association, although it confirms that further research is needed on the potential carcinogenic risk in the study area.

4.3. Recommendations to minimize human exposure to polluted urban soils

Attention should be paid to the potential human health risks associated with urban soils in mining areas that may be enriched in PTEs through primary and secondary processes. For a better understanding of the potential exposure risks, bioavailability tests are needed, and should be applied even to samples with low bulk concentrations but with higher As and Pb solubility.

In Minas de Riotinto, both soil type and use must be considered when evaluating the health risks. Our study shows that the fine fractions of *in-situ* and mixed soils are significantly enriched in As and Pb in Minas de Riotinto, and in Pb in Aracena, with respect to *ex-situ* soils consisting of chalky sand or gravel aggregates. Therefore, our results imply that aggregate pavements covering the natural soils in public parks may reduce the exposure risk of As and Pb to humans. Especially those playgrounds and passing areas with natural *in-situ* soils surpassing the regulatory levels would benefit from a filling material, preventing potential exposure through inhalation, dermal contact, or ingestion of soils in the case of children owing to their hand-to-mouth habit. Chalky sands and gravel can be recommended as pavement materials, because they are generally poor in PTEs by nature.

5. Conclusions

This study focuses on the potential phytotoxicity and human health risks of urban soils, most likely polluted by As and Pb, in the historic mining town of Minas de Riotinto, Spain. The soils underlying many public parks —principally composed of natural *in-situ* soils— exceed the regulatory levels for soils polluted in these elements, thus presenting carcinogenic as well as non-carcinogenic risks for children and adults. Such soils, bearing the impact of locally metal-enriched lithology, are widely used for playgrounds and passing areas. Hence, there is potential exposure risk for residents, especially children. Yet phytotoxicity was observed only in one *in-situ* sample. Natural soil-forming processes therefore appear to control As and Pb enrichment within the urban soils of Minas de Riotinto, though an influence of airborne PM deposition cannot be ruled out.

In Minas de Riotinto, increased relative mortality rates of various types of cancers were found, previously related to As and Pb exposure. Such data underpin our findings about the potential increased cancer risk by As in the exposure area of Minas de Riotinto. However, further exposure routes (not just urban soils) cannot be disregarded, having possible synergic effects.

In the light of our findings, it may be stated that urban decision-making should strive to minimize human exposure to As and Pb from urban soils. Given the chemical and risk assessment results expounded here, we recommend covering *in-situ* soils with aggregate materials that are known to be poor in PTEs.

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.

Acknowledgements

We thank Ms. I. Martínez Segura and Mr. M.J. Roman Alpiste for their assistance in laboratory work. Additionally, Dr. A. Parviainen acknowledges the 'Juan de la Cierva–Incorporación' fellowship (grant number IJCI-2016-27412); and Dr. J.P. Arrebola acknowledges the Ramón y Cajal program (grant number RYC-2016-20155) from the Spanish Ministry of Science, Innovation and Universities. Research performed at the UGR was supported by the Project RTI 2018-094327-B-I00, funded by the Ministry of Science, Innovation and Universities. The European Regional Development Fund (ERFD) and the European Social Fund (ESF) of the European Commission (co)funded the fellowships, research and infrastructure endeavors involved in this research performed at the Instituto Andaluz de Ciencias de la Tierra (UGR-CSIC).

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.envres.2021.112514.

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