Occurrence, leaching, and mobility of major and trace elements in a coal mining waste dump: The case of Douro Coalfield, Portugal

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A R T I C L E   I N F O

A B S T R A C T

The coal mining residues from past mining activities in the Douro Coalfield are emplaced in many dumps near the mining areas, causing substantial environmental impacts. This study aims to contribute to the investigation of environmental impacts caused by the disposal of the residue in the Douro Coalfield through the determination of the geochemical composition of waste materials collected at $3 - 15$ m depth, and of the water-leachable fraction produced by percolation in these materials inside the dump. The elements with higher concentration in the leachates are Ca, Cd, Co, Mg, Mn, Na, Ni, S, and Zn, indicating that they are the most easily leached and accessible elements for percolation and mobilization into the environment. The presence of these elements in the leachates is principally attributed to their occurrence as water-soluble ions in clays and sulphides affected by natural weathering conditions, which promotes their breakdown and occurrence as exchangeable ions. The leachates are classified as acid high-metal. Natural weathering and leaching in the São Pedro da Cova waste dump are the principal paths for chemical elements to be percolated and mobilized to environment, posing risk to the soils, waters and ecosystems in the surrounding areas.

1. Introduction

Europe hosts voluminous quantities of mine waste related to past mining activities (Blengini et al., 2019). Much of these wastes were deposited when little or no concern was given to environmental issues. Consequently, the environmental legacy left by past mining is very significant. Recent EU policies assumed the rehabilitation of environmental liabilities arising from industrial mining activities a priority. Portugal has also a significant environmental legacy arising from intense past mining activities in almost all its territory and, as other EU countries, is resolving the negative environmental legacy (EDM, 2011).

The mining activity related to coal exploitation in Portugal occurred in a total of 143 mines (mostly very small). Of which, the Douro, Rio Maior, Santa Susana, and Cabo Mondego coalfields stand out for their importance (Lemos de Sousa et al., 2010). The first concession was registered in 1850, although it is known that the coal mining in the Douro Coalfield (São Pedro da Cova mine) started in 1795. Coal mining in Portugal ended in 1994, with the closure of the Pejão mine (also in the Douro Coalfield). The inventory of abandoned mining areas in Portugal includes the coal mines of Moinho da Ordem (Santa Susana Basin, SW of Portugal), Pejão, and São Pedro da Cova (both in the Douro Coalfield, NW Portugal).

The Douro Coalfield, dated from Carboniferous (Upper Pennsylvanian [Lower Stephanian C]), is the largest occurrence of coal in Portugal (53 km long; 30–250 m thick) (Eagar, 1983; Fernandes et al., 1997; Lemos de Sousa and Wagner, 1983; Pinto de Jesus, 2003). For almost two centuries, between 1795 and 1994, the anthracite A, was mined in dozens of small mines, with the São Pedro da Cova and Pejão mines standing out for their size and socio-economic importance (Custódio, 2004). From 1959 to 2004, the coal was principally used for energy production in a thermal power plant. The rejects and overburdened material from coal

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mining were deposited in many coal-waste dumps (at least 20 were identified near the mining areas), that now represent substantial environmental impacts (Ribeiro et al., 2010a; b; 2011).

Among these dumps, the São Pedro da Cova (SPC) waste dump has been the subject of several studies that revealed a case study of great scientific interest (Ribeiro et al., 2010a; c; 2012; 2017a). In recent years, two research projects focused their activities in SPC waste dump: ECOAL-MGT - Ecological management of coal waste piles in combustion; and, CoalMine - Coal mining wastes assessment, monitoring, and reclamation of environmental impacts through remote sensing and geostatistical analysis. The importance of the studies performed in SPC waste dump is related to the fact that it has been self-burning since 2005, following ignition caused by forest fires. The combustion process, identified here for the first time in dumps from anthracite The mining in Portugal, adds further to environmental and human health impacts related with waste disposal, mainly due to the emission of volatile organic compounds and particulate matter to atmosphere (Ribeiro et al., 2010a; 2017b). The SPC waste dump is close to an inhabited area and social infrastructures, which add further to effects on human health.

Previous studies on the SPC waste dump focused on the characterization of the waste material, identification of the combustion by-products (gaseous emissions, newly-formed coal fire gas minerals) and the identification of potential environmental impacts in surrounding environment, including impacts on soils, waters, ecosystems, and human health (Ribeiro et al., 2010a; c; 2012; 2017b). Fig. 1 shows the burning area in SPC waste dump with the observed emission of gases, the precipitation of neo-formed S on the surface, and burned vegetation. However, previous research dealt only with superficial samples (maximum of 50 cm in depth) and none investigated inside the waste dump at greater depths. The physico-chemical characteristics of leachates generated inside the waste dump were also never investigated.

The elements in leachates produced within a coal-waste dump can be released by percolation from the waste material to surrounding soils and water, thus posing risk to environment. Therefore, the determination of chemical composition of the leachates is essential to the prediction of the removal by leaching from waste dump and for the identification of environmental risks. In addition, the elements mobility depends on their mode of occurrence (Querol et al., 1996).

Sequential extraction methods have been widely used to investigate the leaching behaviour and mobility of elements in coal, coal-wastes and coal combustion products, with emphasis on hazardous and heavy elements (e.g. Chuncai et al., 2014; Querol et al., 1996; Zhao et al., 2008). These procedures normally include various extracting steps to obtain different fractions, including water/acid soluble and exchangeable fractions, carbonate-bound fraction, organic-bound fraction, silicate-bound fraction, and

sulphide-bound fraction. The water/acid soluble and exchangeable fractions are considered to be more mobile and easily leached to the environment (e.g. Chuncai et al., 2014; Querol et al., 1996; Zhao et al., 2008).

The main goal of this research is to contribute to the study of the environmental impacts related with the coal mining wastes disposed in the SPC waste dump. For this, the chemical composition of waste material and of the water-leachable fraction produced by percolation in these materials were determined. The outcomes will give insights to the mode of occurrence and mobility of elements in the SPC waste dump and to the identification of potential environmental impacts on subjacent and surrounding areas.

2. Samples and methods

Fig. 2A and B display the location and an aerial image of the SPC waste dump (with an elongated form and occupying nearly 28 000 m^2). A total of eight boreholes were drilled along the top of the SPC waste dump with 9–15 m depth. The boreholes were drilled by a private company with interest in the possible reuse of the material. Fig. 2C shows the topography of the waste dump and the locations of the drilling boreholes (F1 to F8).

For this study, the company kindly provided samples from two boreholes (denominated F3 and F8). Samples from those boreholes were prepared and analysed for the determination of geochemical compositions of the waste material and the leachates obtained from the same samples. Samples analysed were respectively collected at 3 m, 6 m, and 9 m depth from F3 and at 3 m, 6 m, 9 m, 12 m, and 15 m depth from F8.

The proximate analysis of samples, to determine moisture and ash yield, was performed according to ISO standards (ISO 1171, 2010; ISO 589, 2008). The coal-waste material samples were analysed through inductively coupled plasma mass spectrometry (ICP-MS) to determine the chemical composition. To establish the elements rapidly accessible for leaching within the coal-waste dump and likely being mobilized and released to environment, single batch leaching tests using deionised water as leachate (liquid-solid ratio: 10-1; agitation during 2 h) were performed. The leachate composition includes the water-soluble and exchangeable compounds from the waste material. It is intended that these leaching tests may simulate the natural percolation within the coal-waste dump and indicate the elements more easily released to subjacent and surrounding areas. The leachates were then also analysed by ICP-MS. The pH and electrical conductivity (EC) of the leachates were determined. The ICP-MS analysis were completed by Bureau Veritas Mineral Laboratories (Canada).

3. Results and discussion

3.1. Chemical composition of coal-waste material

The data obtained from proximate analysis and inorganic chemical composition of waste material collected from boreholes at different depths in the dump are presented in Table 1.

Proximate analysis reveals that samples have an ash yield varying from 75.8 wt.% to 87.4 wt.%. Of the major elements, Al, Fe, and K are the most abundant in all samples, reflecting the dominant mineralogical composition of SPC waste materials (Ribeiro et al., 2015). Considering the trace elements listed in Table 1 and illustrated in Fig. 3, elements Ba, Cr, Li, Mn, Rb, Sr, V, and Zr have concentrations higher than 100 mg/kg, while elements As, Cs, Cu, Ga, Nb, Ni, Pb, Sc, Y, and Zn have concentration between 10 and 100 mg/kg. The elements presenting concentration between 1 and 10 mg/kg are Be, Co, Hf, Mo, Sb, Sn, U, and W, and those less abundant, with concentration less than 1 mg/kg, are Bi, Cd, and Ta. The sum of

**Fig. 1.** General view of the burning area in the SPC waste dump.
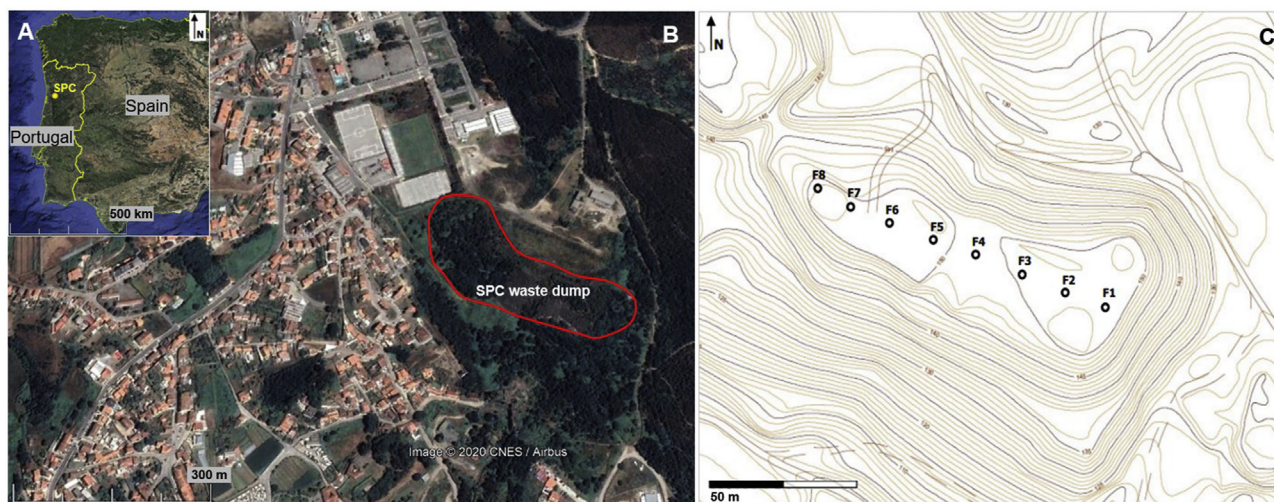
Fig. 2. A) Location of the SPC waste dump; B) Aerial image of the SPC waste dump and surrounding area (from Google Earth); C) Plain view of the SPC waste dump and locations of drilling boreholes.

Table 1
Ash yields (wt.%) and concentrations of major (wt. %) and trace (mg/kg) elementsin samples from the SPC waste dump collected from boreholes. Data from other samples from the SPC waste dump (collected in the surface), samples from other coal waste dumps in DC (DC Waste), coal (DC Coal) and bearing lithologies (DC Litho) from DC, as well as data from world hard coals (WCC) and background of black shales (BBS) were added.

	SPC (this study)								[1]SPC (n = 8)		[2]DC Waste (n = 44)		[2]DC Coal (n = 3)	[2]DC Litho (n = 3)	[3]WCC	[3]BBS
	F3-1	F3-2	F3-3	F8-1	F8-2	F8-3	F8-4	F8-5	Min	Max	Min	Max				
Ash [db]	75.8	85.5	82.0	87.4	83.2	83.1	83.6	78.6	76.4	91.2	23.0	96.5	–	–	–	–
Al	9.7	9.0	9.7	10.3	9.3	9.4	9.3	9.4	9.7	12.2	2.3	12.2	11.7	9.2	–	–
Ca	0.0	0.1	0.1	0.1	0.3	0.1	0.1	0.1	0.0	0.1	0.0	0.4	0.3	0.1	–	–
Fe	3.0	3.2	3.0	3.9	3.3	4.4	4.1	3.1	2.2	4.7	0.2	10.6	4.5	2.7	–	–
K	2.2	2.3	2.4	2.4	2.1	2.1	2.3	2.1	2.1	2.7	0.5	3.1	2.6	2.5	–	–
Mg	0.2	0.2	0.2	0.2	0.2	0.3	0.2	0.2	0.1	0.2	0.1	0.7	0.5	0.5	–	–
Na	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.5	0.5	0.0	0.7	1.0	0.4	–	–
P	0.0	0.0	0.0	0.1	0.2	0.1	0.1	0.1	0.0	0.1	0.0	0.4	0.2	0.0	0.3	0.93–2.2
S	0.3	0.1	0.2	0.2	0.2	0.2	0.3	0.3	0.2	0.4	0.0	1.1	0.1	0.1	–	–
Ti	0.4	0.4	0.4	0.4	0.4	0.5	0.4	0.4	0.4	0.5	0.1	0.6	0.6	0.4	0.9	0.93–2.2
As	32.5	21.3	25.0	22.3	25.4	25.9	24.3	48.9	33.8	79.3	19.0	114	142	11.0	9.0	10–80
Ba	645	573	633	608	523	539	598	535	547	729	182	913	1186	667	150	270–800
Be	4.0	5.0	6.0	5.0	5.0	5.0	5.0	4.0	4.0	5.0	2.0	6.0	12.0	3.3	2.0	1.0–3.0
Bi	1.0	0.8	0.8	0.7	0.8	0.7	0.7	0.7	0.8	1.5	0.2	1.8	1.8	0.2	1.1	0.0–4.0
Cd	0.2	0.2	0.2	0.2	0.2	0.3	0.2	0.2	0.1	0.2	0.1	0.9	1.1	0.1	0.2	2.0–12
Co	4.3	9.5	7.7	9.9	7.4	10.7	8.3	5.3	2.3	5.8	0.8	14.5	73.3	8.6	6.0	10–30
Cr	107	123	100	124	118	118	115	134	98.0	136	22.0	282	184	85.7	17.0	50–160
Cs	50.6	37.6	43.4	42.4	36.3	38.7	41.7	43.0	46.9	58.4	9.8	58.4	78.3	18.9	1.1	2.0–7.0
Cu	23.7	36.2	28.9	27.8	27.2	23.6	26.9	31.9	22.3	59.7	12.6	80.1	131	8.8	16.0	35–150
Ga	25.1	25.3	25.7	28.8	25.9	24.3	24.3	25.5	27.4	33.2	5.7	33.4	36.4	23.3	6.0	9.0–25
Hf	3.7	3.7	3.5	3.7	3.4	3.3	3.4	3.4	2.7	3.9	0.8	5.4	3.0	3.9	1.2	2.5–6.0
Li	260	233	238	275	374	249	228	274	174	324	11.4	324	497	155	14.0	15–50
Mn	64.0	186	157	326	146	237	235	94.0	26.0	116	6.0	1802	313	233	71.0	200–800
Mo	3.3	3.2	2.4	2.3	3.0	3.2	2.5	4.4	2.2	3.9	2.0	10.4	25.8	0.7	2.1	6.0–60
Nb	14.9	13.4	14.9	15.3	13.8	14.1	14.7	15.2	15.0	19.6	2.7	32.8	22.6	16.9	4.0	7.0–15
Ni	24.6	35.6	30.1	36.3	25.5	37.2	31.0	26.5	19.1	27.2	3.8	89.9	483	39.0	17.0	40–140
Pb	38.3	29.4	30.4	28.1	29.1	29.4	29.0	37.1	33.5	57.9	18.6	61.7	88.6	36.6	9.0	10–40
Rb	152	140	151	153	125	127	141	139	150	173	32.0	174	164	121	18.0	40–120
Sb	2.8	2.0	2.2	2.5	2.3	2.4	2.6	3.1	2.4	14.4	1.1	76.4	8.8	5.3	1.0	2.0–11
Sc	14.3	13.6	14.4	16.2	14.7	16.5	15.0	14.8	12.4	15.5	4.5	19.1	20.8	14.0	3.7	7.0–20
Sn	5.5	6.8	5.9	5.3	5.9	5.3	5.3	5.3	4.8	7.9	0.6	15.9	10.2	5.0	1.4	2.0–10
Sr	143	128	154	138	161	122	140	142	123	177	45.0	325	568	108	100	100–300
Ta	0.8	0.8	0.7	0.7	0.7	0.7	0.7	0.9	1.0	1.2	0.1	2.6	1.4	0.9	0.3	0.5–1.0
Th	17.5	14.0	15.1	15.1	14.6	13.3	14.3	15.1	11.4	21.9	5.1	21.9	15.0	10.3	3.2	4.0–11
U	7.2	6.8	6.8	6.2	6.4	5.7	6.1	5.5	5.7	7.0	2.4	9.0	10.4	4.1	1.9	4.0–25
V	113	111	117	138	114	129	119	126	96.0	175	48.0	177	321	118	28.0	100–400
W	4.1	3.8	2.9	2.5	3.2	3.7	2.7	3.9	1.9	2.8	1.0	5.6	6.6	2.1	1.0	0.0–15
Y	14.6	12.3	13.3	13.1	13.7	11.6	12.7	12.9	6.3	12.4	5.1	21.8	23.5	7.0	8.2	15–40
Zn	35.4	60.7	59.9	64.6	49.2	66.8	64.5	36.2	22.4	50.6	12.3	116	215	65.2	28.0	60–300
Zr	129	131	123	127	118	110	114	112	88.8	137	26.6	198	103	133	36.0	60–190
REE	266	194	232	209	197	189	209	214	144	207	70.0	282	285	138	60.2	83.8–197
LREE	251	180	217	194	183	176	195	201	133	192	64.9	261	256	128	51.6	75.0–178
HREE	15.1	13.5	14.6	15.1	14.4	12.8	13.7	13.3	10.7	14.4	5.1	21.1	28.8	9.3	8.6	8.8–19.4

[db] - dry basis; [1]Ribeiro et al. (2010a); [2]Ribeiro et al. (2010b), 2011; [3]Ketris and Yudovich (2009).
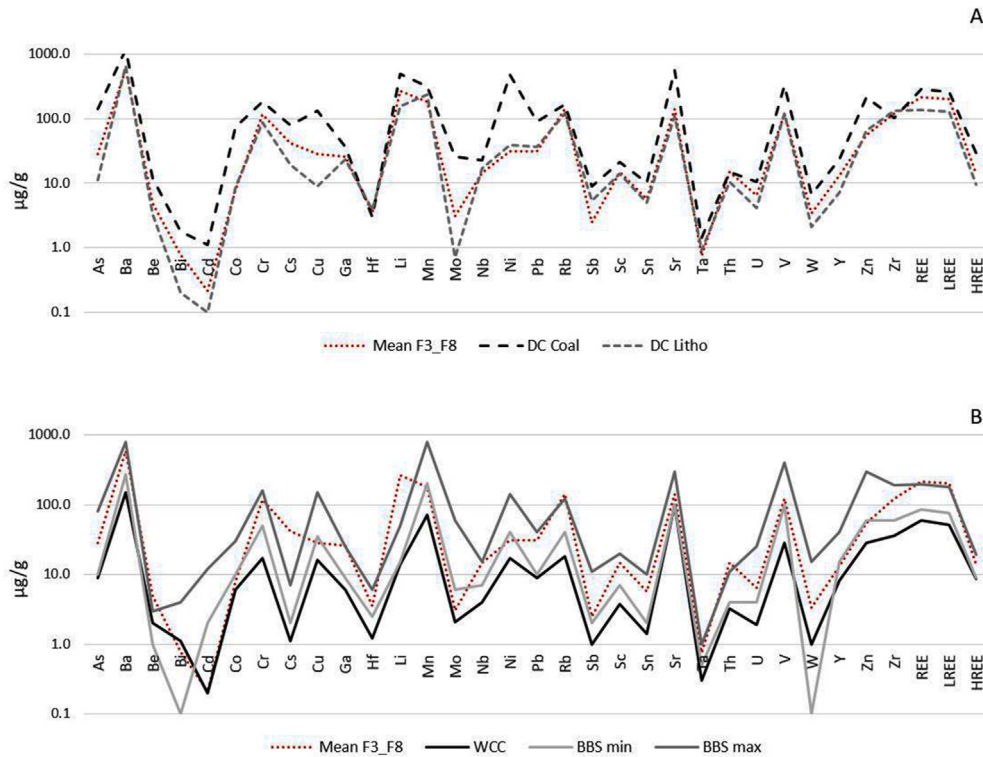
Fig. 3. A) Mean trace elements concentration in the studied samples (n = 8), coal from Douro Coalfield (DC Coal; n = 3; Ribeiro et al., 2011), and bearing lithologies (DC Litho; n = 3; Ribeiro et al., 2011). B) Mean trace elements concentration in the studied samples (n = 8), in world hard coals (WCC; Ketris and Yudovich, 2009), and in background of black shales (BBS; Ketris and Yudovich, 2009).

the REE varies between 189 and 266 mg/kg. The results demonstrate that the composition of studied samples is in accordance with data reported in other studies focused on the surficial waste material collected in SPC waste dump, and in more coal-waste dumps from Douro Coalfield (Ribeiro et al., 2010a; b; 2011).

The major and trace elements concentration in coal mining wastes may have originated mostly from mineral matter comprising the coal-bearing lithologies and partially from coal (varying with coal forming environments and coalification processes) (Saxby, 2000; Querol et al., 2008; Zhao et al., 2008). Therefore, it is expected that the studied samples are composed of the constituents of coal and its main bearing lithologies (carbonaceous shales and lithic arenites). Fig. 3A shows that the chemical composition of the studied samples is within the chemical composition of coal and the main coal-bearing lithologies from Douro Coalfield (Ribeiro et al., 2011). Considering the compositions established for world hard coals (WCC) and for background of black shales (BBS) (Ketris and Yudovich, 2009), the studied coal-waste material has chemical composition within the reference data, as can be seen in Fig. 3B.

3.2. Chemical composition of leachates

Table 2 shows the pH, EC, and chemical composition of leachates obtained from coal-waste samples from the SPC waste dump. The pH varies between 3.8 and 5.4 and the EC varies between 55 μS/cm and 211 μS/cm (Table 2). The acidic range of pH indicates the production of acid drainage in the coal-waste dump, thus promoting ion solubilisation and EC increase. This is evidenced by the EC increase with increasing depth.

The major and some trace elements were identified in the leachates, indicating that they are partially linked with water-soluble and exchangeable compounds. The leached percentages were estimated based on elements' concentration in leachates and their total concentration in bulk samples. The results indicate the leached percentage is lower than 1% in most elements. The elements with leached percentages greater than 1% are the major elements Ca, Mg, Na, and S, and the trace elements Cd, Co, Mn, Ni, and Zn. Fig. 4 shows the leached percentages of these elements plotted relatively against depth of boreholes F3 and F8. As can be observed, Ca, S, and Mn present the greater leached percentages. Fig. 4 also shows the increase of leached percentages from the most superficial to the deepest material, demonstrating the percolation and mobilization of these referred elements inside the coal-waste dump. This is in accordance with the EC increase.

Other studies performed in the SPC waste dump and in other coal-waste dumps from Douro Coalfield demonstrated that the leachable elements with higher extraction amounts (>1%) also comprised Ca, Cd, Co, Mn, Na, Ni, S, and Zn (Ribeiro et al., 2010b; 2011).

Considering the leachates' pH and the sum of selected heavy metals, and according to the Ficklin diagram (Ficklin et al., 1992) illustrated in Fig. 5, leachates are classified as acid high-metal, and only sample F8-1 falls in the field of acid low-metal. Therefore, the leachates percolating inside the SPC waste dump, which may infiltrate in the subjacent and surrounding areas, are acid and have high metal content. The diagram also shows that the metal content of the leachates increases with depth, principally in borehole F8, indicating that the acidic water percolation fosters the increasing of heavy metals dissolution.

3.3. Mode of occurrence of elements

The modes of occurrence of elements affect their behaviour during weathering, leaching, and mobilization and, consequently,

Table 2
pH, electrical conductivity (EC) and concentration of elements in leachates from coal waste material from the SPC waste dump.

Sample Depth		F3-1 (3 m)	F3-2 (6 m)	F3-3 (9 m)	F8-1 (3 m)	F8-2 (6 m)	F8-3 (9 m)	F8-4 (12 m)	F8-5 (15 m)
pH		3.8	4.4	5.4	4.6	4.4	4.6	4.5	4.2
EC	µS/cm	78	65	134	55	88	92	145	211
Al	mg/kg	19.0	27.0	30.0	24.0	20.0	22.0	15.0	22.0
Ba		0.9	0.5	0.8	0.4	0.5	0.5	0.6	0.6
Br		0.7	0.7	0.7	0.9	0.5	0.4	0.5	0.5
Ca		26.0	51.0	154	51.0	79.0	87.0	229	371
Cl		12.0	9.0	7.0	5.0	<2.0	<2.0	<2.0	<2.0
Cu		0.05	0.03	0.04	0.03	0.05	0.04	0.06	0.16
Fe		14.8	15.5	12.2	11.0	15.4	12.7	9.0	10.1
K		70.0	61.0	94.0	53.0	55.0	54.0	64.0	73.0
Mg		26.8	40.9	94.2	51.0	65.3	72.1	96.6	102
Mn		3.8	5.0	8.2	6.2	6.6	9.7	11.3	13.0
Na		30.0	37.0	63.0	38.0	39.0	36.0	43.0	49.0
Ni		0.4	0.4	0.5	0.3	0.4	0.5	0.8	1.0
P		0.3	0.3	0.3	0.5	0.6	0.5	0.2	0.4
S		168	161	373	154	216	221	362	542
Sr		0.7	0.5	0.8	0.4	0.6	0.6	1.0	1.1
Ti		0.4	0.7	1.3	0.7	0.6	0.6	0.6	0.6
V		<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
Zn		0.7	0.6	0.5	0.4	0.5	0.5	0.8	1.1
Ag	µg/kg	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
As		25.0	30.0	21.0	16.0	22.0	23.0	18.0	32.0
Be		16.0	11.0	16.0	7.0	18.0	12.0	29.0	47.0
Bi		<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
Cd		3.3	2.3	6.3	2.4	4.2	5.5	9.1	9.2
Co		141	229	189	120	238	290	350	396
Cs		91.6	124	65.5	87.5	71.6	61.4	61.4	79.6
Ga		6.2	10.0	9.5	7.2	6.8	8.3	4.5	6.4
Ge		0.7	0.8	0.9	0.6	0.8	0.7	0.7	0.6
Hf		0.1	0.4	0.6	0.2	0.2	0.8	0.9	0.4
Hg		<1.0	<1.0	1.0	<1.0	<1.0	2.0	1.0	<1.0
In		<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
Li		1008	637	659	631	1338	576	557	1007
Mo		2.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
Nb		1.8	3.3	4.7	3.3	1.3	2.7	3.5	2.8
Pb		24.0	18.0	17.0	12.0	17.0	18.0	13.0	27.0
Rb		207	256	207	178	173	158	156	214
Sb		2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0
Sc		12.0	19.0	17.0	14.0	15.0	16.0	11.0	14.0
Sn		1.0	2.0	1.0	1.0	1.0	1.0	1.0	1.0
Ta		<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
Th		<2	3.0	2.0	2.0	2.0	3.0	2.0	2.0
Tl		2.1	1.9	1.6	1.0	1.5	1.1	1.1	1.6
U		1.6	2.9	2.3	1.6	2.1	1.7	1.3	2.0
W		<2.0	<2.0	<2.0	<2.0	<2.0	<2.0	<2.0	<2.0
Y		3.0	3.0	3.0	4.0	3.0	2.0	2.0	31.0
Zr		6.0	19.0	18.0	8.0	9.0	20.0	12.0	16.0
REE		79.9	63.4	70.6	42.8	49.6	119	61.1	69.2
LREE		76.0	59.9	62.0	39.5	46.0	111	58.1	59.8
HREE		3.9	3.5	8.6	3.3	3.6	8.1	3.0	9.4

their fate in environment (Querol et al., 1996; Orem and Finkelman, 2003; Finkelman et al., 2018). For identification of elements' mode of occurrence, the Pearson's correlation coefficients were calculated from data sets from chemical compositions of bulk samples and leachates. Generally, elements displaying positive affinity with ash are considered to be associated with mineral matter while elements displaying negative affinity with ash are associated with organic matter in the waste dump (Chuncai et al., 2014; Eskenazy, 2009; Gűrdal, 2008; Spears and Tewalt, 2009). Considering the elements more significantly leached in bulk samples, the Pearson's correlation coefficients indicate that the Mg ($r_{ash-Mg} = 0.63$, $p < 0.05$), Cd ($r_{ash-Cd} = 0.70$, $p < 0.05$), Co ($r_{ash-Co} = 0.88$, $p < 0.05$), Mn ($r_{ash-Mn} = 0.85$, $p < 0.05$), Ni ($r_{ash-Ni} = 0.77$, $p < 0.05$), and Zn ($r_{ash-Zn} = 0.84$, $p < 0.05$) have a significant positive correlation with ash and, therefore, are likely to be associated with mineral matter. The elements Na and Ca do not display any significant affinity,

which may indicate a mixed occurrence. Sulphur displays a negative correlation with ash ($r_{ash-S} = -0.65$, $p < 0.05$). Table 3 shows the Pearson's correlation coefficients of selected elements, including those referred above.

Recently, Finkelman et al. (2018) and Dai et al. (2020) thoroughly discussed modes of occurrence of elements in coals. Considering that the studied coal-waste material includes the constituents of high-rank coal and the rejects from coal bearing rocks, the modes of occurrence described by Finkelman et al. (2018) and Dai et al. (2020) for high-rank coals were considered. Despite the high-rank coals from Douro Coalfield, organic and intimate organic associations may occur at lower extent (Finkelman et al., 2018; Dai et al., 2020). According to these authors, Ca occurs essentially as carbonates (70%) but may also occur in association with organic matter (20%), silicates (5%), and phosphates (5%) (Finkelman et al., 2018). In this study, the correlation of Ca with ash
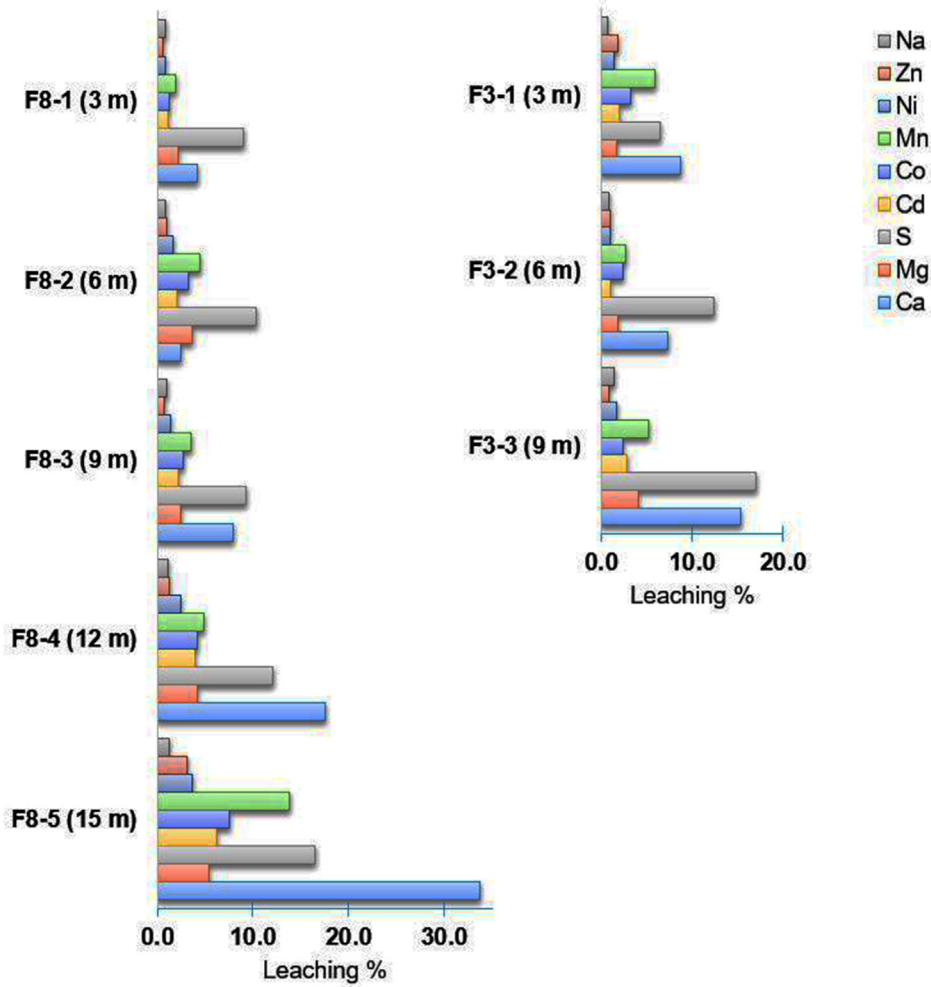
Fig. 4. Percentages of leached selected elements in coal-waste material.
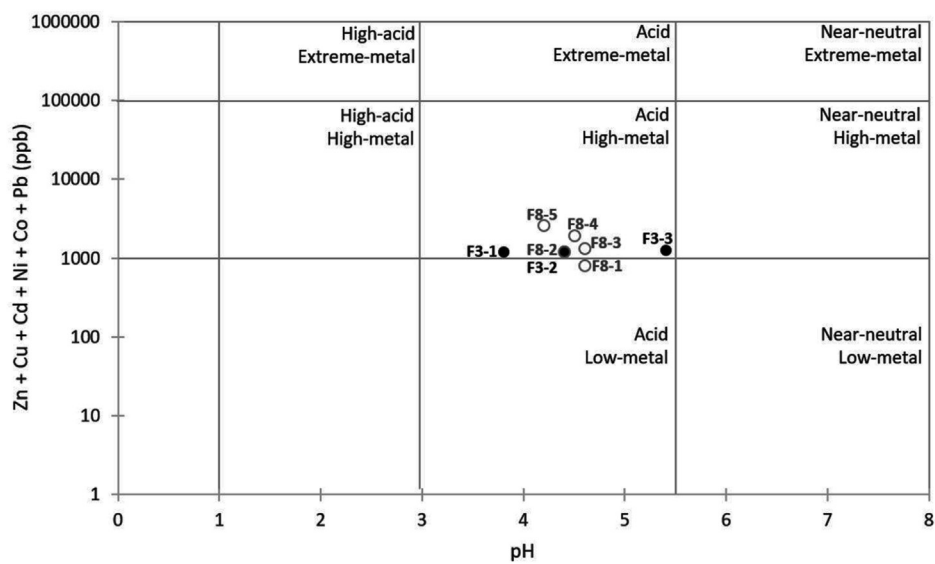

Fig. 5. Ficklin diagram (Ficklin et al., 1992) of concentrations of selected elements in parts per billion (ppb) versus pH of the leachates.

Table 3
Pearson's correlation coefficients between the ash yield and selected major and trace elements determined based on samples of coal waste material chemical composition.

	Ash	Ca	Fe	Mg	Na	P	S	As	Cd	Co	Cu	Mn	Mo	Ni	Pb	Th	Zn
Ash																	
Ca	0.30																
Fe	0.53	0.08															
Mg	**0.63**	-0.15	**0.77**														
Na	-0.03	0.49	-0.56	-0.58													
P	0.20	**0.97**	-0.02	-0.30	0.57												
S	**-0.65**	-0.05	0.03	-0.26	-0.24	-0.11											
As	-0.71	-0.14	-0.39	-0.46	-0.18	-0.13	0.74										
Cd	**0.70**	0.02	**0.61**	**0.81**	-0.29	-0.10	-0.53	-0.83									
Co	**0.88**	0.11	**0.73**	**0.89**	-0.35	0.00	-0.57	-0.70	**0.88**								
Cu	0.31	-0.08	-0.41	-0.05	-0.03	-0.15	-0.35	0.08	0.00	0.09							
Mn	**0.85**	0.08	**0.84**	**0.82**	-0.30	-0.02	-0.39	-0.61	**0.70**	**0.90**	-0.11						
Mo	-0.59	-0.13	-0.35	-0.34	-0.39	-0.09	0.45	0.84	-0.58	-0.50	0.25	-0.60					
Ni	**0.77**	-0.25	**0.68**	**0.91**	-0.54	-0.34	-0.53	-0.56	**0.78**	**0.93**	0.16	**0.86**	-0.37				
Pb	-0.93	-0.43	-0.58	-0.66	-0.05	-0.31	0.57	0.81	-0.83	-0.88	-0.09	-0.81	0.71	-0.67			
Th	-0.69	-0.33	-0.60	-0.77	0.45	-0.14	0.22	0.34	-0.72	-0.81	-0.27	-0.61	0.10	-0.66	0.74		
Zn	**0.84**	0.05	**0.72**	**0.87**	-0.24	-0.09	-0.47	-0.78	**0.92**	**0.94**	0.01	**0.88**	-0.70	**0.85**	-0.91	-0.72	

is positive but weak ($r = 0.30$, $p < 0.05$) and is significantly positive with P ($r = 0.97$, $p < 0.05$), meaning that Ca in the studied samples may have inorganic association, eventually including carbonates and phosphates. The occurrence of Mg is principally related with mineral matter, including silicates and carbonates (Finkelman et al., 2018). Considering the positive correlation of Mg with ash in the studied samples, it is deduced that the occurrence of Mg in mineral matter is principally in clays. Sodium in coals is mostly associated with silicates, principally clays, in high-rank coals, but organic association and Na in pore water or water-soluble salts were also identified (Finkelman et al., 2018). Considering the absence of a significant positive correlation with ash, Na is thought to be inorganically bound and also present in pore water and water-soluble salts (which is consistent with the presence of Na in water-leachable fraction of the studied samples). For Cd, Co, Ni, and Zn the associations with sulphides, silicates, and organic matter were described (Finkelman et al., 2018). For the positive correlation of these elements with ash, Mg and Fe indicates their preferential occurrence in silicates. The negative correlation of these elements with S denotes the low relevance of association with sulphides. Manganese is preferentially bonded to carbonates (principally calcite and siderite) and clays (Finkelman et al., 2018). The strong positive correlation of Mn with ash, Mg ($r = 0.82$, $p < 0.05$), and also with Cd, Co, Ni, and Zn ($r > 0.70$, $p < 0.05$) suggests its association with clays. The presence of these elements in the leachates is principally attributed to their occurrence as water-soluble ions, and in clays and sulphides affected by natural weathering conditions, which promotes their decomposition and occurrence as exchangeable ions. The presence of silicates (principally clays), and minor proportions of carbonates and sulphides, in coal-waste material from Douro Coalfield (Ribeiro et al., 2010b; 2015) corroborates the elements modes of occurrence described above.

In addition to the most significant water-leachable elements, the analysis of other environmentally sensitive elements evidences a significant negative correlation between ash and As ($r = -0.71$, $p < 0.05$), Mo ($r = -0.59$, $p < 0.05$), and Pb ($r = -0.93$, $p < 0.05$) (Table 3). This suggests that these elements are preferentially linked with organic matter in the waste dump. However, As also shows a strong correlation with S ($r = 0.74$, $p < 0.05$), and Mo and Pb present a moderate but positive correlation with S (Table 3), indicating that these elements can be partially associated with sulphides occurring in coal. The association of these elements with organic matter as well as with sulphides is recognized in the literature (Finkelman et al., 2018 and references therein).

The Pearson's correlation coefficients based on the leachates chemical composition evidence strong positive association ($r > 0.7$, $p < 0.05$) amongst the elements with higher leached percentages (>1%), except Ca and Na that present weaker positive correlations, principally with those that are trace elements. This supports their significant occurrence as water-leachable components.

4. Conclusions

The chemical composition of coal-waste material collected at 3–15 m depth in the SPC waste dump and of their leachates resulting from single-batch water-leaching tests were determined. The simulation of the natural percolation of water in the waste dump specifies the elements more easily mobilized and released to subjacent and surrounding environment, thus posing risk to environment.

The chemical composition of samples is in good agreement with values reported in previous studies of coal-waste materials from Douro Coalfield dumps. When considering the values reported for world hard coals (WCC) and the background of black shales (BBS), the chemical composition of the studied samples ranges within the reference data.

The elements with higher water-leachable percentages (Ca, Cd, Co, Mg, Mn, Na, Ni, S, and Zn) are associated with water-soluble and exchangeable fractions and, therefore, are the most easily leached and mobilized into the environment. The presence of these elements in the leachates is principally attributed to their occurrence as water-soluble ions, and in clays and sulphides affected by natural weathering conditions, which promotes their breakdown and occurrence as exchangeable ions. The organic matter can be easily oxidized under natural weathering conditions and, therefore, the elements associated with the organic fraction can also be potentially released into the environment.

Considering the pH and the sum of selected heavy metals in the leachates, the Ficklin diagram demonstrates that the leachates are classified as acid high-metal. The EC and the leached percentages tend to increase from the more superficial to the deeper samples which evidence the growing percolation and mobilization of these elements inside the waste dump. The percolation of acidic water also promotes the increased dissolution of heavy metals, enhancing the concentration of ions in solution. Natural weathering and leaching in the SPC waste dump are the principal paths for trace elements to enter in the environment through percolation and mobilization, posing risk to the soils, waters, and ecosystems in the surrounding areas.

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.

Acknowledgments

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