



# Assessment of mobile mercury concentration in soils of an abandoned coalfield waste pile in Douro region: the Fojo waste pile (Portugal) study case

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## Abstract

**Purpose** Pejão Mining Complex locates in Castelo de Paiva municipality and, until its closure in 1994, was one of the most important coal mines in the Douro Coalfield. This work aims to study the presence, quantify, and evaluate the dissemination of mercury (Hg), a potentially toxic element (PTE) of major public health concern by the World Health Organization (WHO), from a waste pile affected by coal fires.

**Materials and methods** Samples from areas affected and unaffected by the combustion and from surrounding soil were collected from Fojo waste pile region. First, the Hg pseudo-total concentration was estimated for all collected samples by soil microwave-assisted digestion with *aqua regia* (USEPA 3051A). Then, a sequential extraction procedure (SEP), the USEPA 3200, was applied for Hg fractionation and speciation aiming to evaluate Hg mobility and bioavailability to surrounding ecosystems.

**Results and discussion** The results obtained showed a Hg enrichment in soil samples when compared to Portuguese and international reference values for soils. Relatively to the Hg availability and mobility, although it predominates in the semi-mobile fraction, the waste pile materials exposed to combustion showed a concerning increase of Hg levels in the mobile fraction that contains the more labile Hg species, being a major source of environmental contamination by Hg.

**Conclusions** This study allowed to conclude that combustion of mining residues increased Hg mobility, toxicity, and bioavailability, increasing the contamination potential of the coal waste pile. The methodology applied in this work can be replicated in other abandoned mines to monitor, control, and/or mitigate the Hg environmental impact in the surrounding soils and waters.

**Keywords** Mining · Soil contamination · Mercury (Hg) · Fractioning · Mobility · Sequential extraction procedure (SEP) · Combustion of mining residues · Self-burning coal waste

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## 1 Introduction

The mining activity is considered one of the major anthropogenic sources of environmental contamination. The exploitation of mineral resources drastically changes the layout of the soil, altering its properties, the ecosystem and produces huge amounts of waste that are deposited in the surrounding areas of active or deactivated mines in the form of heaps and tailings (Demková et al. 2017; Farjana et al. 2019; Worlanyo and Jiangfeng 2021). The lack of proper monitoring and treatment of the heaps and tailings and their weathering make those residues a source of heavy metals to the environment that can be easily mobilized by acid mine drainage (AMD) (Farjana et al. 2019; Worlanyo and

Jiangfeng 2021; Alvarenga et al. 2021) and, therefore, contaminate the surrounding soil and aquifers.

Heavy metals naturally occur in earth's crust and, although some of those metals are essential for some plants and animals to maintain their biological processes, they are considered potentially toxic elements (PTEs) to organisms at high concentration levels. On the other hand, other non-essential metals and metalloids, such as As, Sb, Hg, and Pb, are highly toxic even at low concentrations (Musilova et al. 2016; Sarwar et al. 2017; Worlanyo and Jiangfeng 2021).

Mercury (Hg) is highly toxic, can persist in the environment for long periods (bioaccumulation) (Li et al. 2021; Jin et al. 2023), being listed as one of the major public health concerns by the World Health Organization (WHO) (WHO 2020; Li et al. 2021). It naturally occurs in metal-rich geologic deposits and coal and its emission to the environment from anthropogenic sources mainly comes from fossil-fuel combustion and mining activity, such as extraction of gold and silver through amalgamation processes (Li et al. 2021).

The Fojo waste pile is one of the many residue deposits that resulted from mining activities in the Pejão Mining Complex, located in the Castelo de Paiva Municipality, being distributed along approximately 9 km from Germunde to the Fojo Paradaça area. The Pejão Mining Complex, closed since 1994, was one of the most relevant extractive industries in Northern Portugal. These mines exploited anthracite A (ISO 5667-3:2018) from the Douro Carboniferous Basin (DCB) latter used for power generation. DCB hosts the most relevant continental carboniferous deposits in Portugal, aged Upper Pennsylvanian (Lower Stephanian C) (Lemos de Sousa and Wagner 1983; Correia et al. 2018). This coal-bearing sequence was deposited in a limnic basin controlled by variations in tectonic activity. The sedimentary sequence includes a basal breccia, followed by fossiliferous shales, siltstones, and sandstones, along with interlayered conglomerates and coal seams (Lemos de Sousa and Wagner 1983; Medeiros et al. 1980). DCB length is approximately 53 km, following a NW–SE alignment, extended from São Pedro de Fins until Janarde, with a thickness that can range from 30 to 250 m (Lemos de Sousa and Wagner 1983; Pinto De Jesus 2003, 2019).

Coal fires in Fojo waste pile occurred between the years of 2017 and 2019, after ignition caused by forest fires, and obliged a technical intervention in 2019 by a Portuguese company responsible for environmental monitoring and rehabilitation of degraded mining areas (EDM—Empresa de Desenvolvimento Mineiro). The coal fires ceased after the wastes remobilization and cooling with water mixed with a cooling agent (see Fig. 1).

Previous studies conducted on self-burning coal waste piles from the DCB highlighted environmental concerns (Ribeiro et al. 2010, 2011, 2013, 2015, 2022; Stracher et al. 2015; Mansilha et al. 2021; Marques et al. 2021; Teodoro et al. 2021; Ribeiro and Flores



**Fig. 1** Photographs of Fojo waste pile, in the year of 2019, showing the intervention on the waste pile to stop the combustion process (left) and the coal mining residues affected by the combustion (right)

2021; Santos et al. 2023) related to high concentration levels of PTEs (As, Pb, Cd, Mn, etc.) in mining residues, some of them significantly higher than reference values defined by the Portuguese Environmental Agency (APA) (APA 2019). However, no information about Hg levels (Li et al. 2021; He et al. 2023) in mine waste piles from this region was reported so far. Thus, this work aims to assess the contamination and dissemination of Hg from untreated mining residues of Pejão Mining Complex, providing information about the risks to surrounding soils, aquifers, and potentially to human health. The approach consisted of first submitting soil subsamples to microwave-assisted digestion with *aqua regia* to obtain the “pseudo-total content” of Hg (USEPA 3051A procedure) (US EPA 2007). However, although the PTEs “total concentration” provides a fair indication of soil contamination in risk assessment studies, the information obtained by total concentration analysis is insufficient for precise risk assessment since PTEs toxicity, bio-availability, and environmental mobility are strongly dependents on its chemical form (Quintanilla-Villanueva et al. 2020; Mourinha et al. 2022; Abdul Rashid et al. 2023). Thus, sequential extraction procedures (SEPs) (Du Laing 2010; Reis et al. 2016; Costa Ferreira et al. 2019; Du et al. 2020; Srithongkul et al. 2020; Mourinha et al. 2022; Wang et al. 2022) can be applied for metal fractioning and speciation according to species mobility by successively applying extraction solutions with increasing reactivity to the same soil sample in a way that the obtained fractions contain species ranging from higher to lower mobility.

In this work, to study Hg mobility and bioavailability, a SEP provided by the U. S. Environmental Protection Agency (EPA), the USEPA 3200 procedure (EPA 2014), was applied to fractionate Hg in mine soil samples into (i) mobile, (ii) semi-mobile, and (iii) non-mobile, where the mobile fraction contains the most concerning labile mercury species.

## 2 Materials and methods

### 2.1 Chemicals and material

The chemicals used in this work were: sodium borohydride (99%, Sigma-Aldrich, Merck), sodium hydroxide ( $\geq 98\%$ , analytical

grade, Sigma-Aldrich, Merck), ethanol (EtOH,  $\geq 99.8\%$ , HPLC grade, Fisher Chemical, Thermo Fisher Scientific), hydrochloric acid (37% w/v, laboratory grade, Fisher Chemical, Thermo Fisher Scientific), and nitric acid (69% w/v, ACS grade, Fisher Chemical, Thermo Fisher Scientific). All reagents and solvents were used without further purification.

All aqueous solutions used in this work were prepared with water purified with a Milli-Q purification system (resistivity  $\geq 18 \text{ M}\Omega\cdot\text{cm}$ ).

## 2.2 Soil sampling and samples pre-treatment

The mining residues (overburden and rejected materials) from the Fojo mine are essentially composed by fragments of carbonaceous shales rich in carbon and lithic arenites. A total of 25 soil surface samples (0–20 cm) were taken from the waste pile and its surrounding region. The spatial distribution of collected samples is shown in Fig. 2 and englobes:

- 10 samples from the waste pile affected by combustion (burnt waste, BW). These sample residues include fine- to coarse-grained reddish-colored material rich in iron oxides and ash (see Fig. 1);

- 5 samples from pile unaffected by the coal fires (unburnt waste, UW). The samples were composed by coarse-grained dark lithic fragments;

- 5 soil samples from the downstream region (downhill soil, DS) to evaluate Hg leaching from the waste pile;
- 5 soil samples from the woods upstream to the waste pile (uphill soil, US) to serve as local background samples.

Each superficial sample was collected using a stainless-steel shovel and consisted of approximately 1.5 kg of soil, stored in a polyethylene bag. The geographic coordinates of the sampling locations were identified using a global positioning system (GPS). Soil samples were dried at room temperature to minimize volatiles loss and sieved at 2 mm to remove gravel and organic residues.

The collected samples were dried for several days at room temperature to minimize losses of volatile Hg. Then, samples were sieved at 2 mm and homogenized. Subsampling was performed using the coning and quartering method (Horwitz 1990; Campos-M and Campos-C 2017). Samples were stored in a refrigerator (4 °C) until use.

## 2.3 Mercury analysis in soil

Cold vapor atomic absorption spectroscopy (CV-AAS) was used for determination of Hg in soil extracts. The measurements were performed using a Thermo Scientific iCE 3000 Series double-beam Atomic Absorption Spectrometer combined with the VP100 accessory, a continuous flow vapor generation (hydride) system. For the cold vapor generation, solutions of 10% (w/v) hydrochloric acid and 1%

**Fig. 2** Sampling sites distribution in Fojo waste pile—Pejão mine



**Table 1** Operating conditions of the CV-AAS system

AAS and VP100 operating conditions	
Slit width	0.5 nm
Burner height	15 mm
Hollow lamp wavelength (Hg)	257.3 nm
Lamp current/voltage	75%/ 6 V
Signal measurement	Transient height
Signal type	Background correction
Total measurement time	100 s
Sample aspiration time	25 s
Carrier gas flow	100 mL min <sup>-1</sup>
Pump speed	40 rpm
Sample uptake rate	7.5 mL min <sup>-1</sup>
Reducing agent uptake rate	1.6 mL min <sup>-1</sup>
Acid uptake rate	0.7 mL min <sup>-1</sup>

(w/v) sodium borohydride, stabilized in 0.5% (w/v) sodium hydroxide, were used. The reductant solution was freshly prepared prior to the measurements. The operational conditions of the CV-AAS system are depicted in Table 1.

For Hg quantification, a calibration curve ranging from 2.00 to 20.0 µg L<sup>-1</sup> was built. The standard solutions were prepared by dilution of a stock solution (C = 1004 ± 7 µg L<sup>-1</sup>, AAS standard solution, SpecPure, Hg 1000 g/mL, Hg in 5% HNO<sub>3</sub>, Alfa Aesar), using an intermediate solution of 2.00 mg L<sup>-1</sup>, and making up the volume with 10% w/v HCl. The typical graphic profile and a representative calibration curve obtained for Hg analysis by CV-AAS are shown in Fig. S1 and Fig. S2, respectively, along with information on the sensitivity of the method, linearity, limit of detection (LOD), limit of quantification (LOQ) (see Table S1, SI), and precision of the analytical result.

## 2.4 Pseudo-total concentration of Hg in soil

The Hg pseudo-total concentration in samples was determined by soil microwave-assisted digestion with *aqua regia* (HCl/HNO<sub>3</sub>, molar ratio 3:1) according to

experimental conditions detailed in USEPA 3051 method (US EPA 2007). Briefly, about 0.3000 g of homogenized soil sub-samples was weighted to digestion vessels followed by addition of HCl (V = 6.0 mL) and HNO<sub>3</sub> (V = 2.0 mL). Then, the samples were submitted to microwave dissolution at 175 °C for 10 min using a microwave system (Analytikjena TOPwave). After cooling of the samples, the final solutions were filtered through a 0.45-µm nylon membrane syringe filter, transferred into 25 mL (or 50 mL) volumetric flasks, and the volume made up with ultrapure water prior to analysis by CV-AAS.

For validation of the digestion procedure for mercury analysis, a certified reference material (CRM), RTC CRM005: Trace Metals—Sewage Amended Soil (Sigma-Aldrich, Merck), was submitted to digestion (5 replications). The obtained Hg recovery range varied from 86 to 118% with a mean value of 97% ± 11% (see Table S3, SI). Thus, the procedure applied for digestion was considered efficient for Hg analysis in soils.

## 2.5 Mercury fractioning (SEP USEPA 3200)

In this work, the USEPA 3200 (EPA 2014) procedure was applied for the sequential extraction of Hg species in three fractions: mobile Hg, semi-mobile Hg, and non-mobile Hg. Briefly, the mobile fraction contains organic and inorganic Hg<sup>2+</sup> species mainly bioavailable for soil-to-plant exchange. The semi-mobile fraction mainly contains elemental Hg and possibly amalgams, while the non-mobile fraction contains sulfides and calomels. The extraction solutions and experimental conditions employed are summarized in Table 2.

## 2.6 Geoaccumulation index

The geoaccumulation index (I<sub>geo</sub>) is commonly used to classify soil pollution (Ackah 2019; Zhao et al. 2021; John et al. 2022). The I<sub>geo</sub> is calculated by the following equation:

$$I_{\text{geo}} = \log_2(C_i/1.5B) \quad (1)$$

**Table 2** Summary of EPA 3200 sequential extraction methodology

Step	Fraction	Reagent	Experimental conditions	Individual Hg species
1	Mobile	HCl 2% + EtOH 10%	Ultrasound-assisted extraction for 7 min at 60 °C (3 times)	CH <sub>3</sub> HgCl; CH <sub>3</sub> CH <sub>2</sub> HgCl; HgCl <sub>2</sub> ; Hg(OH) <sub>2</sub> ; Hg(NO <sub>3</sub> ) <sub>2</sub> ; HgSO <sub>4</sub> ; HgO; Hg <sup>2+</sup> complex
2	Semi-mobile	1:2 HNO <sub>3</sub>	Extraction for 20 min on a water bath at 95 °C (2 times)	Hg <sup>0</sup> ; Hg <sup>0</sup> – Metal (amalgam); Hg <sup>2+</sup> complex; Hg <sub>2</sub> Cl <sub>2</sub> (minor)
3	Non-mobile	1:6:7 HCl:HNO <sub>3</sub> : H <sub>2</sub> O	Extraction for 20 min on a water bath at 95 °C (2 times)	Hg <sub>2</sub> Cl <sub>2</sub> (major); HgS; HgSe
4	Residual	<i>Aqua regia</i>	USEPA 3051A	Strongly bound minerals

where  $C_i$  represents the measured concentration of the contaminant (in  $\text{mg kg}^{-1}$ ),  $B$  represents its background average concentration, and 1.5 is the correction factor for soil heterogeneity. Based on the calculated value, samples are then classified according to  $I_{\text{geo}}$  classification chart (see Table S2, SI).

### 3 Results and discussion

The determination of Hg concentration levels in DCB mining waste piles is of great interest for assessing its impact in the health of surrounding soils, aquifers, and ecosystems. In particular, this work aims to provide an accurate insight on the environmental effects induced by the coal fires on this mine region and investigate any correlation with Hg mobility. Therefore, the first stage of this study focused on the characterization of “pseudo-total” concentrations of Hg in soil samples. Then, a sequential extraction procedure (SEP) was applied to gather information about Hg mobility and bioavailability in the waste pile residues (affected and non-affected by combustion) and in the surrounding soils.

#### 3.1 Mercury pseudo-total concentration in mine soil

The Hg content for the 25 soil samples collected from the Fojo waste pile region was estimated and the results are represented in Fig. 3A (see Table S4, SI). As can be seen, the Hg pseudo-total values (i.e. the *aqua regia* soluble content) were all above the background values proposed by the FOREGS project for European top soils (of  $0.061 \text{ mg kg}^{-1}$ ) (Salminen 2013), averaging  $1.0 \pm 0.1 \text{ mg kg}^{-1}$  and ranging from  $0.1 \pm 0.1$  to  $1.8 \pm 0.1 \text{ mg kg}^{-1}$ .

All samples, excluding DS1, returned Hg pseudo-total values above the APA reference value (of  $0.25 \text{ mg kg}^{-1}$ ) (APA 2019), considering coarse soils and agricultural use, suggesting a natural enrichment of Hg in the soil of the region. Even samples located uphill the waste pile, without influence from the mining residues, presented Hg values above the national background average concentration of Hg in topsoil for Portugal (of  $0.048 \text{ mg kg}^{-1}$ ), reported in the FOREGS Geochemical Atlas (Salminen 2013). This natural enrichment can be explained by the occurrence of abnormal enrichment of Hg associated with cinnabar present in coals from Douro Carboniferous Basin, as previously described (Moura et al. 2018; Costa et al. 2022), also identified by SEM–EDS in the coal residues of the Fojo waste pile.

Furthermore, the mean values of the samples from regions affected (BW1-10,  $1.2 \text{ mg kg}^{-1}$ ) and unaffected (UW1-5,  $1.2 \text{ mg kg}^{-1}$ ) by combustion are about 120% higher than the mean value of the reference region (US1-5,  $0.6 \text{ mg kg}^{-1}$ ), revealing a concerning anthropogenic

enrichment of Hg in these regions with high potential environmental risks for surrounding ecosystems. Moreover, the mean pseudo-total values for the downstream soil samples (DS1-5,  $1.0 \text{ mg kg}^{-1}$ ) are about 25% higher than the mean value of local background samples (US1-5), possibly indicating the spread of the contamination (due to erosion and/or leaching by runoff effects) from the waste pile to the nearby region. Samples DS4 and DS2 show higher concentration levels probably due to terrain irregularities in the water flow patterns. The statistical comparison of the average mercury concentration values can be found in Table S5 (SI).

For better visualization of the Hg spatial distribution over the mine region, an inverse distance weighted (IDW) map for the Fojo region is shown in Fig. 3B, where the blue areas possess lower levels of Hg and the red areas very high degree of Hg contamination.

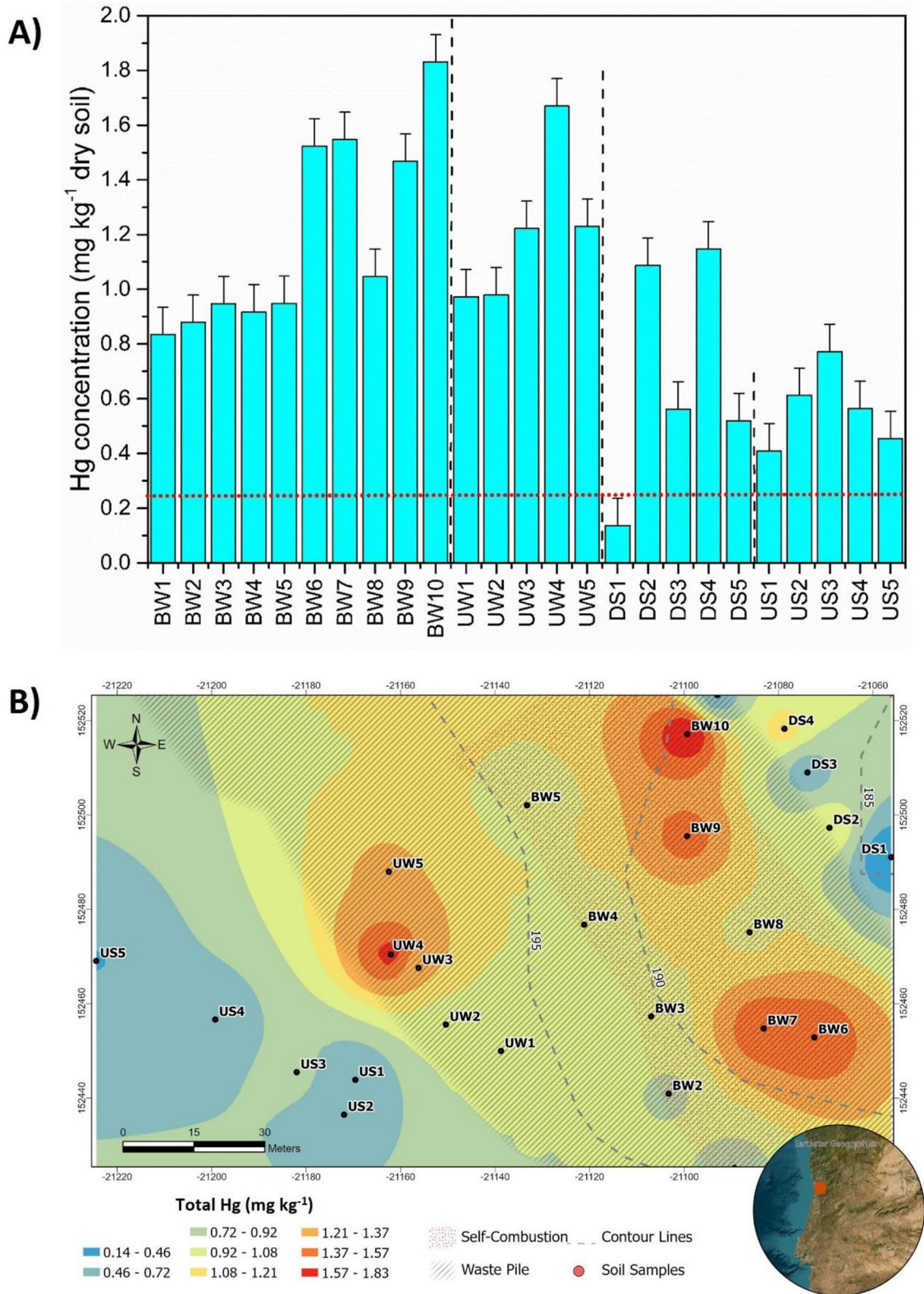
The mean concentration of Hg in the local background, based on the samples collected uphill from the waste pile, was used for the geoaccumulation index ( $I_{\text{geo}}$ ) calculation. Based on the  $I_{\text{geo}}$  classification chart (Table S2, SI) and considering average  $I_{\text{geo}}$  values (see Table S6, SI), the samples of the downstream region (SJ) were classified as “unpolluted” and the waste piles, both affected and unaffected by combustion (BW1-10 and UW1-5), were classified as “unpolluted to moderately polluted,” confirming the waste piles regions as main source for potential contamination of surrounding areas.

Considering that most pseudo-total concentration values for Hg exceeded the APA’s national reference values proposed for agriculture soils, further studies applying a sequential extraction procedure (SEP) were conducted to investigate the mobility of Hg in the mine soil.

#### 3.2 Mercury fractioning and speciation in mine soil

Mercury can be retained in soils by adsorption onto organic matter and mineral surfaces (Fe, Mn, Al oxides, and silicates) affecting its environmental mobility in soil (O’Connor et al. 2019). Furthermore, its toxicity depends on its speciation (see Table 2). The species that belong to the “semi-mobile” category are less toxic than extractable species from the “mobile” fraction. For example,  $\text{Hg}^{2+}$  complexes, elemental Hg and mercury chloride are not readily available for plants and for organisms uptake (Jing et al. 2007; Zhu et al. 2018). However, these inorganic species of soluble Hg can serve as substrate for Hg methylation (Li et al. 2022). Alkyl species, such as methylmercury, are more mobile than inorganic Hg species, being more toxic and easily bioaccumulated. By opposition, the “non-mobile” species, such as Hg sulfides, are chemically stable for long periods and less toxic.

In this work, the SEP USEPA 3200 (EPA 2014) was selected and applied to mining waste pile materials to provide insight on the mobility and availability of Hg, particularly in the areas of major environment concern (BW and



**Fig. 3** **A** Hg pseudo-total concentrations obtained for the Fojo coal waste pile region samples: burnt waste (BW), unburnt waste (UW), uphill soil (US), and downhill soil (DS). The red line in the graphic

represents the APA's reference value for Hg. **B** Spatial distribution of Hg modeled by IDW using the ArcGIS Pro software

UW). The estimated concentration for Hg in the mobile, semi-mobile, and non-mobile phases is graphically represented in Fig. 4 (see Table S4, SI).

A relevant aspect in mercury fractioning studies is the fair correlation between the pseudo-total concentration of mercury and the sum of the Hg fractions (mobile + semi-mobile + non-mobile). In this work, despite the fact that each sample was thoroughly homogenized prior to analysis, sometimes a discrepancy between the total Hg and the mercury extracted by the SEP method was observed. Potential reasons for such discrepancies include (Sánchez et al. 2005; Liu et al. 2006; Issaro et al. 2009; Reis et al. 2010) (i) incomplete extraction, since not all forms of mercury in the soil may be fully extracted in the SEP process; (ii) losses during the extraction and analysis since some mercury species are volatile at room temperature or higher; and (iii) sample heterogeneity, if the sample used for extraction does not represent the overall soil composition. Analytical errors such as calibration errors, matrix effects, or interference from other elements are also a possible source of this error. However, in this work, the stringent analytical quality control measures in place make this possibility unlikely.

After application of the 3-stage Hg SEP, the results revealed that the dominant fraction is the “semi-mobile” one, throughout the Fojo region, with an average mercury concentration value of  $0.50 \text{ mg kg}^{-1}$ , ranging from  $0.05$  to  $1.04 \text{ mg kg}^{-1}$ . The Hg levels found in the “semi-mobile” fraction are greater than the APA’s reference value (of  $0.25 \text{ mg kg}^{-1}$ ), except for the samples from local background (B1-5). Even though this fraction mainly contains species of mercury that are not readily mobilized, they can be easily converted into more labile species (Reis et al. 2010, 2016) and constitute a threat to the environment.

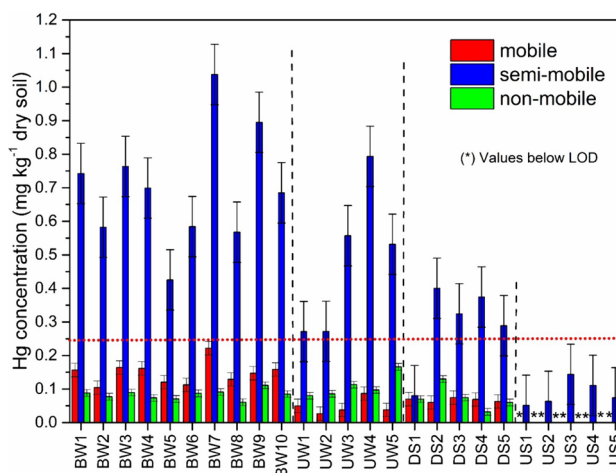
Interestingly, the Hg fractioning profiles in samples affected by coal fires (BW1-10) contrasted with samples unaffected by combustion (UW1-5). For the waste pile samples that had experienced the effects of coal fires, the second most dominant fraction (16% of the sum of the fractions; see Fig. S3, SI) was the “mobile” one, with a Hg average concentration of  $0.15 \pm 0.03 \text{ mg kg}^{-1}$ , ranging from  $0.10 \pm 0.02$  to  $0.22 \pm 0.02 \text{ mg kg}^{-1}$ . For the unburnt samples, the second most dominant fraction (17% of the sum of the fractions; see Fig. S3, SI) was the “non-mobile,” with a Hg average concentration of  $0.11 \pm 0.03 \text{ mg kg}^{-1}$  (ranging from  $0.08 \pm 0.01$  to  $0.17 \pm 0.01 \text{ mg kg}^{-1}$ ), while the “mobile” phase was the less representative (8% of the total sum; average concentration of  $0.05 \pm 0.02 \text{ mg kg}^{-1}$ ). Despite the natural waste heterogeneity, the results showed significant statistical differences (see Table S5, SI) in Hg content in the mobile fractions within samples that had been affected or not by coal fires, strongly suggesting that heat from coal fires is responsible for the increase of Hg labile species from 8% (unburnt waste materials, UW) to 16% (burnt waste materials, BW).

So, in terms of hazardous perception, higher Hg leaching rates are expected in waste pile areas that have experienced combustion, resulting in a greater dispersion potential to the underlying aquifers and surrounding soils, which means with higher toxicity and available Hg.

These results are in close agreement with the literature. Mashyanov et al. (2017) showed that the diverse Hg species (organic matrix-bound Hg, adsorbed elemental Hg, silicate and pyrite-bound Hg, HgS, etc.) existing in coal have different thermal stabilities and releasing behaviors when subjected to heating. Luo et al. (2013) reported the release of pyrite-bound Hg in coal at a temperature range of  $350\text{--}400 \text{ }^\circ\text{C}$ , after destruction of the  $\text{FeS}_2$  lattice.

Overall, several processes can contribute to increase the concentration of mobile Hg species in mine soil samples affected by coal fires, namely: (i) the combustion process generates partial consumption of carbon present in the wastes tending to concentrate the inorganic fractions; (ii) the combustion of fossil organic matter can liberate Hg species originally bound to the organic matrix, as well as adsorbed species; and (iii) liberation of Hg pyrite-bound species from the lattice.

As stated before, Hg species in mobile fraction are highly toxic and bioavailable. Thus, the results obtained suggest that strict monitoring may be advisable for the Fojo mine region, particularly in the waste pile affected by combustion (BW) to control and minimize the Hg environmental impact in surrounding soils and aquifers.



**Fig. 4** Hg concentration in each extracted fraction for the samples from the burnt waste (BW), unburnt waste (UW), uphill soil (US), and downhill soil (DS) from the Fojo coal waste pile region. The red line in the graphic represents the APA’s reference value for Hg

## 4 Conclusions

The study conducted in the Fojo waste pile, included in the Pejão Mining Complex, revealed a soil enrichment in Hg when compared to European background soils, with all samples exceeding the Portuguese Hg reference values threshold proposed as limits for contaminated soils for agriculture.

To fully assess Hg mobility and bioavailability in mine soil, a sequential extraction procedure (SEP), the USEPA 3200, was successfully applied to all soil samples from the waste pile and surrounding areas. The results obtained allowed to conclude that the Hg dominant fraction in the mine soil was the semi-mobile. Nonetheless, an increase of Hg levels in the mobile fraction, containing the more labile Hg species, was observed for the soil samples affected by coal fires, suggesting that combustion of mining residues increases Hg mobility, toxicity, and bioavailability, increasing the contamination potential of the coal waste pile. Thus, the present study should be replicated in abandoned mines with a similar problem in order to monitor and control the Hg environmental impact in the surrounding soils and waters. Moreover, to mitigate the potential toxicity of Hg to humans and ecosystems, several physical, chemical, and biological soil remediation approaches (Eckley et al. 2020; Wang et al. 2020) can be implemented, including thermal desorption, electrokinetic removal, use of emerging materials and nanomaterials (such as CNTs, graphene, nanocomposites, MOFs, COFs, LDHs, clay minerals, manganese oxides), and innovative technologies based on biochar immobilization or involving organisms (phytoremediation, algae-based mercury removal, microbial reduction, constructed wetlands, among others).

**Supplementary Information** The online version contains supplementary material available at <https://doi.org/10.1007/s11368-024-03786-x>.

**Author contribution** All authors contributed to the study conception and design. Marcus Monteiro: writing—original draft, material preparation, data collection and analysis. Patrícia Santos: writing—review and editing, data analysis, conceptualization. Jorge E. Marques: sample collection, material preparation. Deolinda Flores: writing—review and editing, funding acquisition, conceptualization, supervision. Carlos M. Pereira: funding acquisition, conceptualization, supervision. José A. Ribeiro: writing—review and editing, methodology, data analysis, conceptualization, supervision. Manuel Azenha: writing—review and editing, methodology, data analysis, conceptualization, supervision.

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## Declarations

**Ethics approval** Not applicable.

**Consent to participate** Not applicable.

**Consent for publication** Not applicable.

**Competing interests** The authors declare no competing interests.

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