



# Comparison of mercury distribution and mobility in soils affected by anthropogenic pollution around chloralkali plants and ancient mining sites

Rodolfo Fernández-Martínez <sup>a</sup>, Jose M<sup>a</sup>. Esbrí <sup>b</sup>, Pablo Higuera <sup>b</sup>, Isabel Rucandio <sup>a,\*</sup>

<sup>a</sup> Unidad de Espectroscopía, División de Química, Dpto. Tecnología, CIEMAT, Madrid, Spain

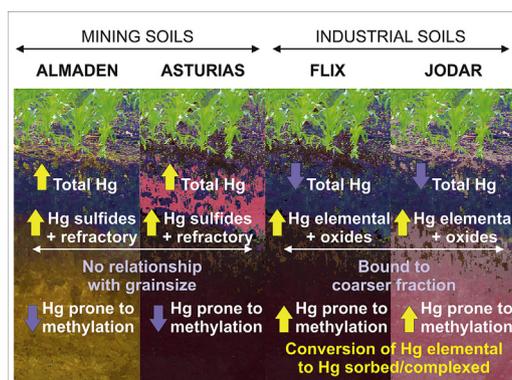
<sup>b</sup> Universidad de Castilla-La Mancha, Instituto de Geología Aplicada, EIMI, Almadén, Spain



## HIGHLIGHTS

- 4 Spanish areas have been studied for characterization of Hg-pollution availability.
- Higher total Hg concentration and in soils related with mines than industries
- Hg bound to sulfide clearly predominate in mining soils.
- Hg bound to crystalline oxides prevails in coarser grain sizes of industrial soils.
- Higher Hg concentration available to methylation in mining soils

## GRAPHICAL ABSTRACT



## ARTICLE INFO

### Article history:

Received 17 December 2018

Received in revised form 6 March 2019

Accepted 22 March 2019

Available online 28 March 2019

### Keywords:

Mercury  
Sequential extraction  
Mine  
Chloralkali  
Spain  
Mobility

## ABSTRACT

A comparative study of total mercury, elemental mercury and mercury fractionation has been performed on particle-size fractions of soils affected by anthropogenic sources of different origins, namely two former chloralkali plants (CAPs) and two historical cinnabar mine sites in Spain. A specifically developed sequential extraction procedure was applied in order to evaluate mercury fractionation, including Labile mercury (F1), mercury bound to humic and fulvic acids (F2), elemental mercury and mercury bound to crystalline iron oxides (F3), and mercury bound to sulfide and refractory species (F4). Markedly higher total mercury concentration were found in ancient mining soils (AMS), with concentration values ranging from 18.6 to 1509  $\mu\text{g}\cdot\text{g}^{-1}$ , whereas soils from CAPs exhibited lower total Hg concentrations (1.7–61.6  $\mu\text{g}\cdot\text{g}^{-1}$ ). Hg(0) was not detected in AMS samples and this indicates the absence of this species in the studied areas. In contrast, very low Hg(0) concentration were found in CAP soils as a consequence of the intense interaction of gaseous Hg deposited along with soil matrix compounds. Sequential extraction analyses revealed different fractionation patterns for both kinds of studied soils: AMS exhibited a clear predominance of Hg bound to sulfide in all particle-size subsamples whereas soils from CAPs mainly contained elemental Hg and Hg bound to crystalline iron oxides in the coarser subsamples. Conversely, Hg bound to sulfide was the major fraction in the finest soils. In summary, the results of the present study indicate a high level of Hg immobilization in CAP soils because of the interaction with soil phases and the

\* Corresponding author at: Avda. Complutense, 40, 28040 Madrid, Spain.  
E-mail address: [Isabel.rucandio@ciemat.es](mailto:Isabel.rucandio@ciemat.es) (I. Rucandio).

prevalence of highly refractory cinnabar in AMS samples. Finally, it is necessary to highlight that, in some cases, compounds with higher reactivity can lead to a lower toxification risk if differences in concentrations are sufficiently marked, as detected in CAPs with respect to AMS.

© 2019 Elsevier B.V. All rights reserved.

## 1. Introduction

Hg pollution in soils from anthropogenic activities is an environmental concern due to the potential risks to biota and human health caused some Hg compounds or species. In particular, chloralkali plants and cinnabar (HgS, virtually the only ore mineral of this element) mining operations are responsible for the release of Hg into the nearby environment despite the fact that processing activities were completed a long time ago. The chloralkali industry based on Hg cell technology has historically been a significant source of atmospheric Hg emissions and direct inputs into the surrounding environment (Ebinghaus et al., 1999; Hintelmann and Wilken, 1995). The main Hg contamination streams from chloralkali plants (CAPs) are aerial emissions, wastewater emissions and solid waste (Garçon et al., 2005). On the other hand, ancient mining soils (AMS) from old Hg mines usually contain high concentrations of total Hg (Martínez-Coronado et al., 2011; Ordóñez et al., 2013; Tersic et al., 2011). Hg mining and metallurgical operations are based on the extraction of cinnabar from natural deposits and the roasting of ore. The long period required for mining and processing of the Hg can leave a legacy of contaminated mine wastes and unprocessed materials surrounding the abandoned mines and retorting plants. These constitute a long term source of Hg that can be mobilized by weathering and by microbiological and physico-chemical processes into more readily available chemical forms that can be dispersed in watersheds or through atmospheric emissions, thus creating environmental hazards (Gray et al., 2013; Li et al., 2013).

The impact of Hg pollution in soils cannot be properly assessed by measurements of total Hg concentrations alone. The mobility, availability and toxicity of Hg depends on the presence in the soil of different Hg species and, in turn, on the interactions between these and the mineral constituents of soils. Organic Hg compounds, such as methylHg, and soluble inorganic Hg species pose a very high potential risk even in small quantities, since they are readily available to plants and can eventually enter the food chain (Bishop et al., 1998; Mohamed et al., 2003) and/or be mobilized to water masses (Beckers and Rinklebe, 2017). Other inorganic Hg species, such as cinnabar, are less prone to mobilization. In addition, the sorption of Hg in soils has a marked dependence on particle size (Bengtsson and Picado, 2008; Fukue et al., 2006; Sahuquillo et al., 2003; Schluter, 1997). Hg can be complexed through charge-transfer and electrostatic forces by anions such as sulfates, as well as by negatively charged surfaces of Fe, Al and Mn oxyhydroxides or organic carbon groups (Brown et al., 1999; Coston et al., 1995; Wen et al., 1998; Yin et al., 1996). The concentrations of Hg and other heavy metals in soils and sediments generally tend to increase with decreasing grain size and this is due to the propensity of metals to bind with finer particles (Boszke et al., 2004). Finer particles are mainly composed of weather-resistant, net negatively charged minerals of Fe and Al, including mainly oxyhydroxides (Coston et al., 1995). In sandy soils with very low contents of organic matter, quartz and feldspar minerals can retain cationic Hg species, which are found predominantly in medium to coarse particle sizes (Barber et al., 1992; Biester et al., 2002).

Sequential extraction procedures (SEPs) have been widely used to determine Hg concentrations associated with relevant solid phases in solid environmental samples (Beatty et al., 2012; Bloom et al., 2003; Fernández-Martínez and Rucandio, 2013; Han et al., 2003). In the SEP process the sample is treated with specific reagents with successively stronger dissolving power in order to simulate the release of Hg into solution under different environmental conditions. In spite of its

operationally defined nature, SEPs constitute a common and feasible approach to characterize the environmental reactivity of Hg in soil and sediments as well as to evaluate its availability to plants.

The work described here concerns an investigation into the differences between the impact of Hg in particle size fractions of soils affected by anthropogenic sources of different origins, specifically, two former CAPs and two old Hg mining sites. For this purpose, total Hg concentrations were determined and an SEP process, which was specifically developed for the fractionation of Hg, was applied to the studied soils. For comparative purposes the Hg(0) was determined by means of a selective desorption technique.

## 2. Experimental

### 2.1. Site descriptions and sampling points

Almadén is the center of the so-called Almadén Hg mining district, which was the largest Hg mine in the world from Roman times to the beginning of the 21st century and is the source of one third of the Hg ever produced (Hernández et al., 1999; Higuera et al., 1999) (Fig. 1). Mining production was centered in Almadén town, with mines of minor importance disseminated in the Almadén syncline (El Entredicho, Nueva Concepción, Vieja Concepción and Las Cuevas; Hernández et al., 1999; Higuera et al., 1999). These ore deposits belong to two different typologies: stratabound deposits and stockwork deposits, with the former typology being the most important in terms of Hg production. Hg was present almost exclusively in the form of cinnabar, with minor proportions of elemental Hg. Interestingly, the deposit was almost completely monoelemental, with extremely low concentration of other metallic elements frequently associated with Hg, such as Sb, As, Ag, etc. As a result of the transformations caused by metallurgical activity, e.g., weathering or reactions in the soil, other Hg compounds are evident in Almadén soils. These include schuetteita ( $\text{Hg}_3\text{O}_2(\text{SO}_4)$ ), metacinnabar (a cubic polymorph of cinnabar), and Hg chloride (calomel) (Esbri et al., 2010). Three samples were taken in the Almadén mining district: from NE-26 in the surroundings of Almadén town, a site related with atmospheric deposition and/or ancient metallurgical works; EDAR-01 close to a small urban wastewater treatment plant and some 500 m East of Almadenejos metallurgical precinct, one of the most polluted sites in the world (Campos et al., 2018; Martínez-Coronado et al., 2011); and NC-01 near a closed shaft of the Nueva Concepción mine, where metallic Hg was a very common Hg component in the ore.

The Asturias Hg mining district comprised >18 mines disseminated in an area of some 3600 km<sup>2</sup> and these were particularly exploited in the 20th century (Fig. 1). Cinnabar and associated minerals appear in these mines as irregular veins, granular aggregates or impregnations in Precambrian to Carboniferous rocks (commonly limestones or siliceous breccias in sandstones). The main difference regarding the Almadén Hg mining district is its polymetallic character, with high proportions of arsenic, and a complex mineral paragenesis including orpiment ( $\text{As}_2\text{S}_3$ ), realgar ( $\text{As}_4\text{S}_4$ ), melnikovite (a variety of pyrite,  $\text{FeS}_2$ ), chalcocopyrite ( $\text{CuFeS}_2$ ), arsenopyrite ( $\text{FeAsS}$ ), stibnite ( $\text{Sb}_2\text{S}_3$ ) and galena ( $\text{PbS}$ ) (Loredo et al., 1999). This area also supported intensive metallurgical activity, with lower calcination temperatures in their rotary furnaces (over 853 °C) than the other mining districts (Luque and Gutiérrez, 2006), producing high proportions of metacinnabar in polluted soils (Esbri et al., 2010). Other differences include the absence of schuetteita and the presence of corderoite ( $\text{Hg}_3\text{S}_2\text{Cl}_2$ ) or HgO. The most

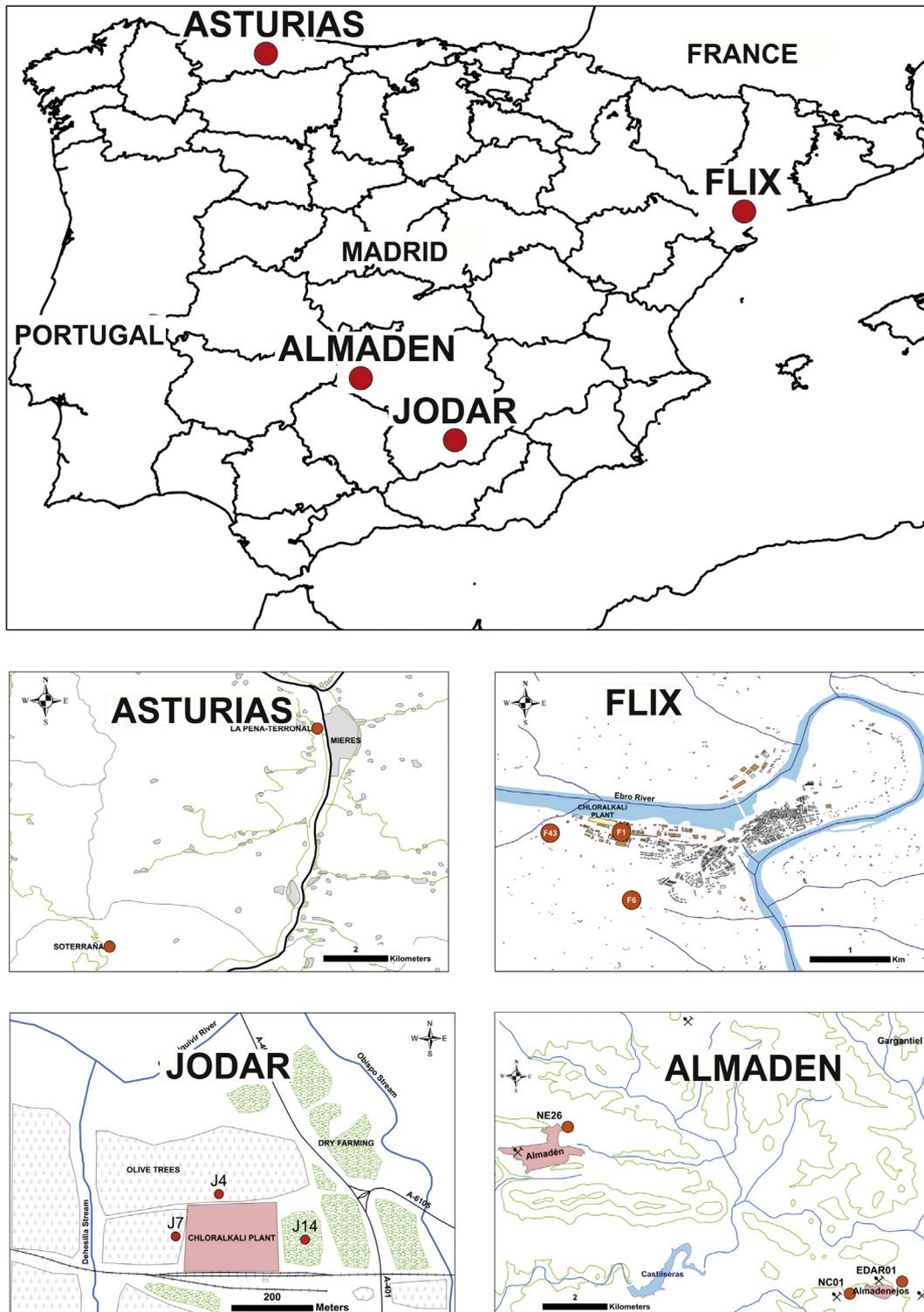


Fig. 1. Location of sampling sites.

important mines in this district are the La Peña-El Terronal and Soterraña mines. Hg in soils from these areas occurs as a mixture of mining and metallurgy wastes (Higueras et al., 2015; Ordonez et al., 2014; Rumayor et al., 2017). Samples SOT1 and SOT2 correspond to soils taken in La Soterraña mine, with Hg appearing as cinnabar or metallic Hg and with minor proportions of pararealgar, orpiment, pyrite, marcasite and arsenopyrite. La Soterraña was an underground mine that was active from Roman times until the 1970s and it had its own metallurgical plant with rotary furnaces. Sample TRR1 was taken in

the surroundings of the La Peña-Terronal mine, where minor proportions of native Hg and higher proportions of arsenic minerals like realgar or As-rich pyrite have been described (Rumayor et al., 2017; Loredo et al., 2003).

The Flix site (Tarragona province, NE Spain) is an area characterized by intense industrial activity since the latter part of the 19th Century (Fig. 1). This site includes a Hg-cell-based technology chloralkali plant that is located very close to the town on the banks of Ebro river and is close to a dam, which is irregularly filled with contaminated wastes

(Palanques et al., 2014). The industrial facility has a long history of chlorinated solvent production from the end of the 19th century and this led to a legacy of pollution mainly in Ebro sediments, but also in surrounding soils, produced by dry and wet deposition of metallic Hg emitted by the Na-Cl production process (Esbrí et al., 2015). On the other hand and considering that mercury used in this type of industries is metallic mercury, it is not expected to find Hg in the forms of sulfides or sulfates in the soils from Flix area. Remediation works in polluted sediments included the removal of sediments and transportation to a waste security deposit some 15 km to the North of Flix (2015). These works may have produced some disturbances to this simple scenario, including the dispersion of dust (particulate matter) consisting of polluted sediments that can reach soils through dry deposition. Sample F1 represents the soil close to the chloralkali facility, with a higher total Hg concentration and higher probability of atmospheric Hg deposition. Samples F6 and F43 represent a gradation in total Hg concentration and these were taken at increasing distances from the industrial site. All of these samples were collected during the initial process of remediation, so the effects of this process are not expected to be evident in our study.

Jódar is a small locality of Jaén province, Southeast of Madrid, and it represents in this study an abandoned industrial site (Fig. 1). The studied area is located on the banks of the Guadalquivir River, which is approximately the same distance from the towns of Jódar and Úbeda. The chloralkali facility was active for only 14 years and activity was ceased due to suspicions about health effects of Hg pollution in local workers (Higuera et al., 2016). The site soil usage comprised mainly agricultural areas dedicated to the cultivation of olive trees. Once again, similarities with the Flix case study include the expected absence of sulfides and sulfates in soils, and the known – but not documented – spillage of polluted sediments into the Guadalquivir River. In this case, the absence of a dam led to the dilution of this problem. Samples J4, J7 and J14 were taken around the decommissioned facility, at the north (J4), east (J14) and west (J7) of the abandoned plant, from an olive grove (J4 and J7) and from dry land cultivation soils (J14).

## 2.2. Reagents, standards and apparatus

All standards and reagents were of analytical grade and most were purchased from Merck (Darmstadt, Germany). Ultrapure water (resistivity  $\geq 18.2 \text{ M}\Omega \cdot \text{cm}$ ) was obtained from a Milli-Q Element A10 system (Millipore, Bedford, Ma, USA). A Hg stock standard solution of  $1000 \text{ mg L}^{-1}$  in  $2 \text{ M HNO}_3$  (Scharlau, Spain) was used to prepare the Hg standard solutions. Ar and  $\text{O}_2$  gases of purity higher than 99.999%, used in CV-AFS and DMA-80 instruments, were supplied by AlphaGaz. All glassware and bottles were cleaned by soaking in  $0.5 \text{ M HNO}_3$  for 2 days followed by rinsing three times with deionized water.

The equipment employed for the extractions consisted of a vortex mixer (LabNet Inc.) with a variable speed, a bench-top centrifuge (Eppendorf 5804), a rotary shaker (Bunsen ARR-8) and a thermostat-controlled drying oven (Proeti S.A.) with a maximum adjustable temperature of  $200 \text{ }^\circ\text{C}$ .

## 2.3. Sample collection and preparation

Soil samples were taken from the topsoil layer (0–20 cm) using an Eijkkamp stainless steel drill, discarding the soil surface covered with vegetation and cleaning the drill with deionized water and a metallic brush between each sample. All samples were stored in polyethylene bags prior to laboratory analysis. Soil samples were dried at room temperature for 30 days. After this period, sample preparation included disaggregation, mixing, homogenization and splitting, with four aliquots separated: for analysis, granulometry determinations, pedological parameters and an untreated sample for preservation. The aliquot for total Hg determinations was ground (50 g) in an automatic agate mortar for 2 min. The aliquot for grain size determinations (400 g) was subjected to dry sieving using a sieve shaker for 5 min, with pauses of

10 s every minute to achieve greater efficiency in the selection of the finest grains. Seven distinct particle size fractions were separated:  $<0.06$ ,  $0.06\text{--}0.125$ ,  $0.125\text{--}0.25$ ,  $0.25\text{--}0.5$ ,  $0.5\text{--}1$ ,  $1\text{--}2$  and  $2\text{--}4 \text{ mm}$ . Among them,  $<0.06$ ,  $0.5\text{--}0.25$  and  $2\text{--}1 \text{ mm}$  were selected to evaluate the influence of grain size on Hg distribution in the studied soils. Each grain size fraction was weighed and stored in plastic bags prior to analysis.

## 2.4. Analytical methods

Total Hg (THg) concentrations were obtained by Atomic Absorption Spectrometry with Zeeman Effect using a Lumex RA-915+ system coupled to a PYRO-915 pyrolyser. In this technique Hg contained in the solid sample was atomized using a two-stage heating chamber. The quantification of Hg atoms was carried out in an external analytical chamber. The lamp energy was checked every hour or 20 samples. Quality control included analysis of CRMs NIST 2710a and NIST 2711, with percentage recoveries of 98–109%.

An overview of the sequential scheme for the fractionation of Hg used in this research is given in Table 1. This is an SEP specifically developed to evaluate Hg fractionation in solid environmental samples according to the unique physical and chemical properties of the numerous Hg species (Fernández-Martínez and Rucandio, 2013). Extractions were conducted in centrifuge tubes with 0.5g of dried soil. Continuous agitation was maintained for an appropriate time with a rotary shaker. Samples were centrifuged at 4000 rpm for 10 min after each extraction step. The supernatants were removed using a Pasteur pipette and transferred to a vial. All samples were washed with 5 mL of ultrapure water between the different extractions. Washed solutions were combined with their corresponding extracts, filtered through  $0.45 \mu\text{m}$  cellulose paper, and diluted with water to a final volume of 50 mL.

The determination of Hg in fractions from the SEP was carried out by Cold Vapor Atomic Fluorescence Spectrometry (CV-AFS) using a PS Analytical Millenium Merlin instrument. The EPA 245.7 method (EPA, 2005) was followed in general terms but adapted for each solution. This method is based on the oxidation of all Hg forms to the Hg(II) oxidation state using a bromine monochloride solution (BrCl). Fractions F1 and F3, which were nitric acid solutions, did not require prior oxidation with the BrCl solution and nor did F4. According to the recommendations of Babi et al. (2002), in the case of fraction F4 an alkaline solution of  $\text{SnCl}_2$  was used instead of acid due to the need to break the highly stable bonds between Hg and iodide ions.

Elemental Hg (Hg(0)) samples were evaluated by means of a pyrolysis technique by following procedures reported in the literature (Navarro et al., 2006; Sladek and Gustin, 2003). Sample aliquots (1 g) were placed in porcelain crucibles and were initially heated at  $80 \text{ }^\circ\text{C}$  to achieve thermal desorption of Hg(0) according to the recommendations of Sladek and Gustin (2003). A portion of the sample was then taken for Hg determination, while Hg(0) was calculated from the difference between total Hg concentrations before and after the heating process. Determination of Hg(0) in AMS samples was performed in a Lumex RA-915M device coupled to a PYRO-915 unit to overcome problems with high Hg concentrations in samples. This technique involves thermal desorption of Hg compounds using a heat ramp configuration described by Rumayor et al. (2016). The rate of temperature increase was  $38 \text{ }^\circ\text{C min}^{-1}$ .

**Table 1**  
Sequential extraction scheme for Hg fractionation.

Fraction	Extractant solution	Duration/temperature	Target phase
F1	20 mL 0.2 M $\text{HNO}_3$	2 h agitation $50 \text{ }^\circ\text{C}$	Labile Hg species
F2	10 mL 0.1 M $\text{Na}_4\text{P}_2\text{O}_7$	16 h agitation rt	Humic and fulvic complexes
F3	20 mL 7.2 M $\text{HNO}_3$	21 h agitation rt	Elemental Hg and bound to crystalline oxides
F4	10 mL 0.03 M KI in 5.1 M HCl	45 min agitation $70 \text{ }^\circ\text{C}$	Hg sulfide and refractory species

rt: room temperature.

The pH was measured immediately after sample collection using a Pt–Ag/AgCl CRISON selective electrode on sample/water suspensions at a 1:2.5 ratio (w/v) (McLean, 1982). A LECO CS-244 elemental analyzer was used for the total carbon (TC) determination in the soil samples by means of combustion in an induction furnace in the presence of oxygen gas; the amount of carbon dioxide released during this combustion was measured by an infrared detection method. Total inorganic carbon (TIC) was determined using a Shimadzu-VCHS instrument equipped with a solid sample combustion unit. Total Organic Carbon (TOC) was determined as the difference between TC and TIC.

Accuracy and precision of the analytical procedures for total element concentration by CV-AFS and LUMEX were verified using the certified reference material (CRM) San Joaquin Soil NIST 2709a. The results were consistent with the certified values with errors of <5%. Element concentrations in procedure blanks and in all reagents were always below the detection limit. In addition, the suitability of the sequential extraction method was assessed by its application to CRM NIST 2710 Montana soil (with elevated trace element concentrations), whose certified Hg concentration is  $32.6 \pm 1.8 \text{ mg kg}^{-1}$ . The sum of Hg concentrations extracted in every fraction was  $30.6 \pm 2.5 \text{ mg kg}^{-1}$ , which is in good agreement with the certified value at the 95% confidence level (*t*-test).

The statistical relationship between some selected variables in the studied samples was determined by bivariate correlation using the Pearson coefficient in a two-tailed test ( $P < 0.05$  and  $P < 0.01$ ).

### 3. Results and discussion

#### 3.1. Total Hg and Hg(0)

Total Hg concentrations in grain-size subsamples from AMS were notably higher than those obtained for CAP soils, which indicates that

mining activities release higher amounts of Hg to soils (Table 2 and Fig. 2). Mining and metallurgical activities involve, as surface activities, transport of ore, stockpiling, roasting, emissions and losses that lead to widespread Hg impact in soils from these areas (Higueras et al., 2006). Meanwhile, activity in CAPs is restricted to an indoor facility and this only leads to Hg(0) emissions to the atmosphere and eventually wastewater and solid waste dispersion (Biester et al., 2002).

Very high THg concentrations were observed in all AMS subsamples, both from Almadén and Asturias ( $18\text{--}4500 \text{ } \mu\text{g}\cdot\text{g}^{-1}$ ); these concentrations are comparable to (but lower than) those previously reported in soils and mine tailings from La Peña-El Terronal mine site in Asturias ( $45\text{--}27,000 \text{ } \mu\text{g}\cdot\text{g}^{-1}$ ) (Fernández-Martínez et al., 2005) and they are also in the same order of magnitude as those corresponding to soils from the Idrija cinnabar mine (Slovenia) ( $9\text{--}370 \text{ } \mu\text{g}\cdot\text{g}^{-1}$ ) (Kocman et al., 2004). The highest concentration corresponded to NC01 subsamples, which were taken from a location close to an old shaft of the Nueva Concepcion mine and probably contain polluted wastes from underground works.

Regarding Hg(0), quantifiable concentrations were not found in AMS, whereas very low levels were observed in certain subsamples of CAP soils. Although these results could be considered contradictory, since Hg(0) is the primary source of Hg in CAP soils (Esbri et al., 2015), it has been established that Hg deposition occurs preferentially as Hg(II), i.e., Hg is previously oxidized by atmospheric oxidants like  $\text{Br}^-$  or  $\text{OH}^-$  or directly emitted by the CAP as Hg(II) (Elgazali et al., 2018). The other possibility is direct dry deposition of Hg(0), which is readily oxidized to Hg(II) by biotic and abiotic reactions and subsequently sorbed onto soils via organic and inorganic cation-exchange, iron oxides or complexed by organic matter (Soares et al., 2015). In addition, other routes that can be considered are (i) the abiotic conversion of Hg(0) to Hg(II), which is promoted by the presence of thiol compounds (R–SH) due to the formation of highly stable R–S–Hg(II) complexes (Yamamoto, 1995), and (ii) biotic oxidation

**Table 2**

Main parameters measured in the studied soils. Abbreviations: CAP: chloralkali plants; AMS: ancient mining soils; TOC: total organic carbon; Hg(0) (%) is referred to THg.

Source	Area	Sample	Grain-size (mm)	THg ( $\mu\text{g g}^{-1}$ )	Hg(0) ( $\mu\text{g g}^{-1}$ )	Hg(0) (%)	TOC (%)	S (%)	pH	
CAP	Jódar	J4A	2–1	1.71	<0.01	<0.6	1.7	<0.1	8.7	
			0.5–0.25	1.86	<0.01	<0.5	1.4	<0.1	8.5	
			< 0.06	2.21	0.35	15.9	1.9	<0.1	8.4	
		J7A	2–1	2.35	0.01	0.4	3.1	<0.1	8.6	
			0.5–0.25	2.68	0.19	6.9	3.0	<0.1	8.2	
			< 0.06	2.79	0.22	8.0	1.6	<0.1	7.8	
		J14A	2–1	2.35	0.01	0.6	1.7	<0.1	8.4	
			0.5–0.25	2.29	0.17	7.2	1.5	<0.1	8.3	
			< 0.06	3.01	0.44	14.6	1.4	<0.1	8.0	
		Flix	F1A	2–1	5.4	<0.01	<0.2	1.7	<0.1	7.7
				0.5–0.25	16.4	0.75	4.6	1.4	0.98	7.6
				< 0.06	21.1	0.31	1.5	1.9	0.65	7.9
	F6A		2–1	0.4	<0.01	<2.5	3.1	0.11	7.9	
			0.5–0.25	0.6	0.01	1.7	3.0	0.10	8.0	
			< 0.06	2.1	0.1	4.8	1.6	<0.1	8.1	
	F43	2–1	20.7	<0.01	<0.05	1.7	0.53	7.9		
		0.5–0.25	18.5	1.8	9.7	1.5	0.38	7.9		
		< 0.06	61.6	<0.01	<0.02	1.4	0.61	7.8		
	AMS	Asturias	SOT1	2–1	445	<0.01	<0.1	1.0	<0.1	7.8
				0.5–0.25	1097	<0.01	<0.1	2.6	0.10	7.5
				< 0.06	1782	<0.01	<0.1	2.6	0.15	6.9
SOT2			2–1	18.6	<0.01	<0.1	1.2	<0.1	7.8	
			0.5–0.25	41.5	<0.01	<0.1	1.8	<0.1	7.0	
			< 0.06	202	<0.01	<0.1	1.9	<0.1	6.8	
TRR1		2–1	91.4	<0.01	<0.1	1.9	0.47	7.4		
		0.5–0.25	302	<0.01	<0.1	20.1	0.44	6.1		
		< 0.06	471	<0.01	<0.1	14.8	0.37	6.2		
Almadén		EDAR1	2–1	154	<0.01	<0.1	1.0	<0.1	6.8	
			0.5–0.25	169	<0.01	<0.1	1.4	0.12	7.1	
			< 0.06	222	<0.01	<0.1	1.5	0.52	6.5	
		NE26	2–1	154	<0.01	<0.1	1.5	<0.1	7.2	
			0.5–0.25	134	<0.01	<0.1	1.5	<0.1	7.2	
			< 0.06	368	<0.01	<0.1	2.7	<0.1	6.7	
NC1	2–1	1393	<0.01	<0.1	1.9	0.10	6.9			
	0.5–0.25	2633	<0.01	<0.1	3.5	0.15	6.9			
		< 0.06	4509	<0.01	<0.1	3.7	0.17	7.0		

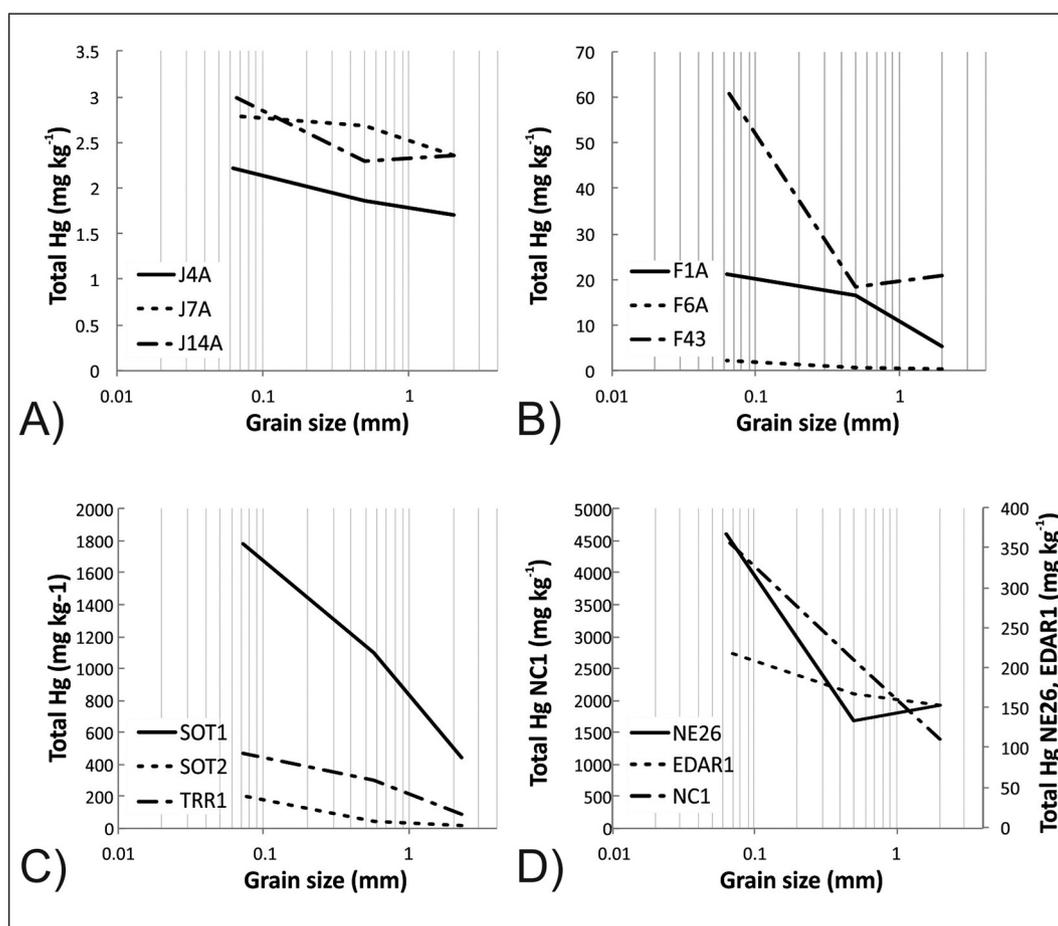


Fig. 2. Distribution of total Hg concentrations in terms of grain size. Soils from: A) Jódar; B) Flix; C) Asturias and D) Almadén.

that can be caused by both aerobic and anaerobic bacteria through enzymatic paths (Colombo et al., 2014; Smith et al., 1998).

Among the studied CAP soils, samples from the Flix area generally exhibited higher THg concentrations, possibly due to the longer time over which the CAP was operated in this area. Although Jódar samples presented the lowest Hg concentration, these largely exceeded the baseline levels for agricultural soils ( $0.05\text{--}0.3\ \mu\text{g}\cdot\text{g}^{-1}$ ) (Alloway, 2004), which indicates an enrichment in Hg due to anthropogenic activities. In the case of the Flix soils, significantly higher concentrations of Hg were observed in the finest-grain subsamples ( $<0.06\ \text{mm}$ ) than in the medium and coarse subsamples ( $0.5\text{--}0.25\ \text{mm}$  and  $2\text{--}1\ \text{mm}$ ). This finding indicates a trend for the element to be accumulated in finer fractions, as generally occurs with Hg and other heavy metals in soils and sediments (Bengtsson and Picado, 2008; Boszke et al., 2004; Fernández-Martínez et al., 2014; Xu et al., 2014). In contrast, a significant influence of grain size does not seem to occur in Jódar soils, since variations in the Hg concentrations were relatively low. It has been hypothesized that in eroded soils that lack of vegetation, as in the soils dedicated to olive cultivation (Gómez et al., 2014), coarser material is likely to contain higher concentrations of soil-bound Hg (Burke et al., 2010). Regarding Hg(0), the Jódar samples exhibited significant concentrations and these were accumulated in the finest subsamples, representing 8–16% of total Hg concentration, whereas lower percentages were obtained for Flix samples. These figures are higher than others reported for three European chloralkali plants (Biester et al., 2002), where the proportion of Hg(0) was negligible, and the authors explain these results by the low proportion (4.4–8%) of Hg(0) previewed by dry deposition models developed by United States Environmental Protection Agency (USEPA).

The absence of Hg(0) in AMS is in contrast to situations in other historic cinnabar sites such as Idrija (Slovenia), where the presence of volatile Hg(0) has been reported (Kocman et al., 2004). However, Idrija may be a different case to AMS (from Asturias and Almadén) because of the marked differences in the presence of elemental Hg in ore bodies: The occurrence of Hg(0) in ore bodies reaches levels of 30% (Kobal and Dizdarevic, 1997) in Idrija. Besides, Carr (1998) reported high levels of native Hg in Idrija ore bodies, with levels of 50% reached in mineralized clastites, while Bavec et al. (2014) described how native Hg spills were frequent both in the mine and in solid wastes, with the latter due to inefficient roasting technologies. However, the AMS analyzed in this work belongs to mining districts with lower proportions of Hg(0) in their mineralization: the Almadén site only has significant Hg(0) levels in the Las Cuevas deposit (Rytuba, 2003), which was not considered in this study, and the Asturias site only has a low proportion of Hg(0) in ore bodies (Ordonez et al., 2013). When considering these differences in Hg sources, some discrepancies can be found in the Idrija Hg speciation data, with minor proportions of Hg(0) found in tailings – as detected by thermal desorption techniques (Biester et al., 1999).

### 3.2. Hg fractionation

#### 3.2.1. CAPs soils

**3.2.1.1. Labile Hg species.** The labile Hg fraction (F1, Table 1) proved to extract the most soluble Hg compounds, including water soluble, exchangeable, inorganic free and low molecular-weight organic Hg species, which represent the most readily available Hg fractions (Fernández-Martínez and Rucandio, 2013). As a consequence, a low

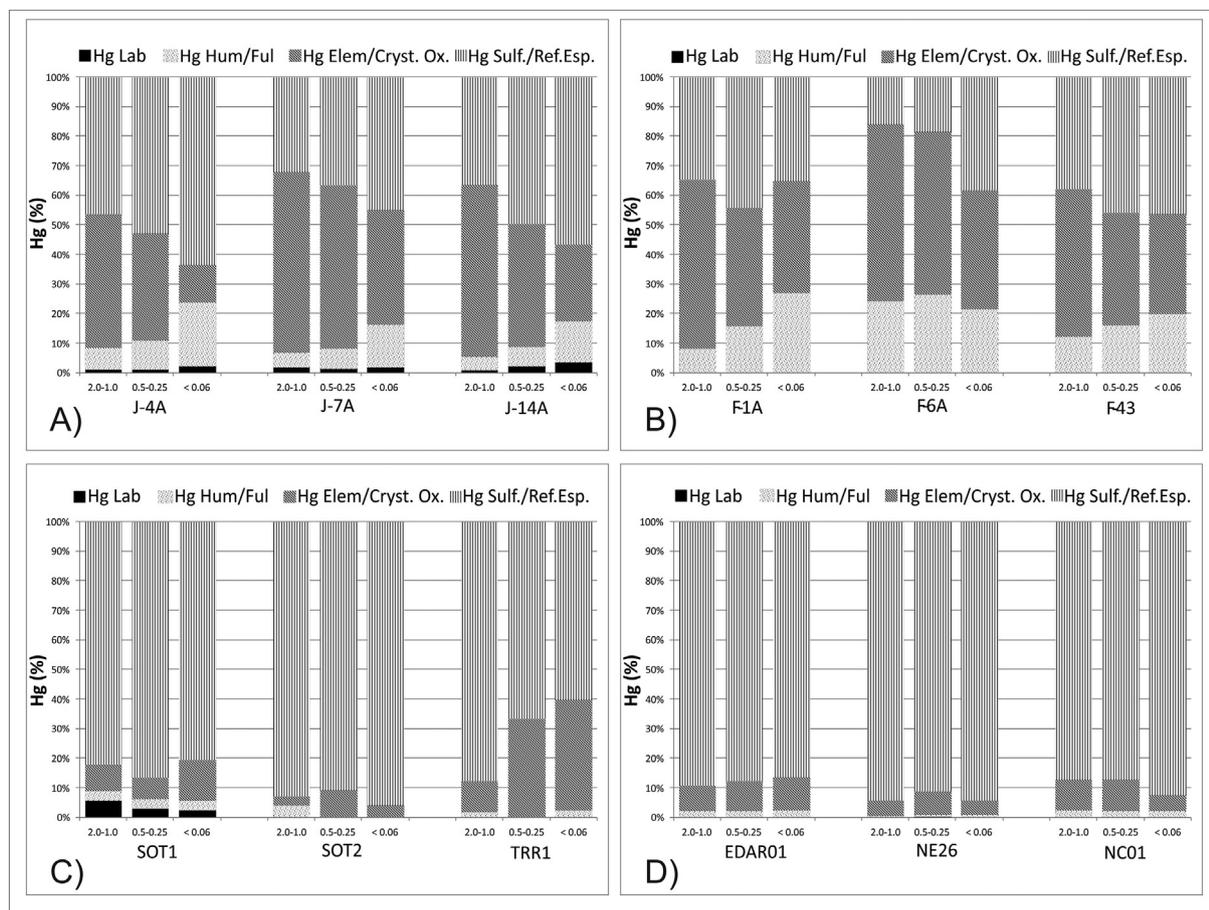


Fig. 3. Proportions of Hg fractions in the studied sites: A) Jódar; B) Flix; C) Asturias and D) Almadén.

mobility of Hg was found in CAP soils since the Hg concentrations in the labile fraction were undetectable in Flix samples (Fig. 3b) and almost negligible in Jódar samples (Fig. 3a), i.e., they accounted for only 0.02–0.10  $\mu\text{g}\cdot\text{g}^{-1}$ , which corresponds to only 1.2–3.6% of THg. These percentages were comparable to those observed in soils impacted by CAPs: a mean value of 1.3% was reported for soils from North-Western Portugal (Reis et al., 2010); <2% of mobile fractions were reported in a facility in Tuzla, Bosnia-Herzegovina (Huremovic et al., 2017); and, more recently, labile Hg concentration below 0.7% were registered for soils close to Lake Xolotlan (Nicaragua) (Fernández-Martínez et al., 2016). Although it has been established that a proportion of the Hg emitted by CAPs is deposited as readily available Hg(II) (Biester et al., 2002; USEPA, 1997), these species can be lixiviated or bound by humic acids and sulfides (Biester et al., 2002; Skyllberg et al., 2006). Another explanation for these low labile fraction concentration could come from the sampling technique, which only corresponds to surficial soil (top 15 cm, with the upper 2 cm discarded). In any case, low proportions of labile fractions in samples with high total Hg concentration could constitute an environmental concern due to their potential bioavailability and subsequent risk of entering the trophic chain. It is noteworthy that the major proportion of the labile fractions were found in the Jódar facility, which is located in a region with a drier climate – a condition less favorable to soil washing than in the Flix area.

**3.2.1.2. Humic and fulvic complexes.** The humic and fulvic complexes fraction (F2, Table 1) tends to extract selectively the Hg that is bound to humic and fulvic acids present in soils, as well as associated metals, through an alkaline treatment (Bagheri et al., 2007). The complexation of Hg by humic and fulvic acids plays an important role in controlling

Hg speciation and its availability to ecosystems (Biester et al., 2002; Zhang et al., 2009). A very similar contribution was observed for F2 in both CAP sites, as this fraction accounted for 4.5–21.3% of THg in Jódar samples (Fig. 3a) and 8.3–26.7% of THg in Flix samples (Fig. 3b). In addition, particle-size appeared to have a marked influence since the highest concentration corresponded broadly to the finest particle-size subsamples (<0.06 mm), with the exception of sample F-6A, in which the F2 concentration remained almost constant for the three particle-size subsamples. In contrast, F2 concentration do not seem to have a dependence on TOC. This was confirmed by the poor and negative correlation between F2 and TOC ( $r = -0.356$  for Flix samples and  $r = -0.322$  for Jódar samples at  $P < 0.05$ ).

**3.2.1.3. Elemental Hg and bound to crystalline oxides.** Elemental Hg and Hg bound to crystalline oxides (F3) were extracted under the conditions detailed in Table 1. The results indicate that both CAP areas showed very significant recoveries of F3, with values of 13–61% for the Jódar area (Fig. 3a) and 34–60% for the Flix area (Fig. 3b). According to the applied SEP, Hg extracted in F3 is related to elemental Hg and Hg associated with crystalline Fe oxides; hence, a priori it can be considered that this is not easy to mobilise. However, considering that Hg(0) can be (i) emitted from soils through volatilization and uptake by plants via aerial deposition on leaves (Higuera et al., 2012; Naharro et al., 2018) and (ii) be converted to more reactive Hg(II) and even methylated by bacteria (Colombo et al., 2013; Fernández-Martínez and Rucandio, 2005; García-Sánchez et al., 2009; Gray et al., 2004; Hu et al., 2013), its presence in soils may be of environmental concern. Given that anthropogenic inputs from CAPs occur predominantly in the form of Hg(0) and Hg(II), this fraction is usually dominant in soils affected by CAPs emissions (Frentiu et al., 2013; Reis et al., 2010). The observed percentages

are in the same range as those reported recently for soils from CAPS areas in Southern Siberia (Russia) (Gordeeva et al., 2017). No significant correlation was found between Hg(0) concentration and Hg concentration in F3 fraction. This means that the main contribution in this fraction may correspond to Hg associated to crystalline iron oxides. Regarding particle-size distribution, F3 was predominant for the coarsest subsamples, whereas it was the second in importance for the finest subsamples. The enrichment of Hg extracted in the F3 fraction in the coarsest subsamples is more pronounced for Jódar samples, since it represented not only higher percentages but also higher absolute Hg concentrations than those of the finest subsamples. The same trend has been observed in other studies on soils affected by CAPs. Hg(0) and Hg associated with crystalline Fe oxides correspond to Hg bound to the mineral lattice and, as a consequence, Hg in these environments is more strongly associated with coarse-grain particles (Huremovic et al., 2017).

**3.2.1.4. Hg sulfide and refractory species.** The measurement of Hg sulfide and refractory species extracted in the fourth extraction (F4, Table 1) may be interpreted as an estimation of the Hg present as cinnabar or other sulfide Hg forms, which represent the least mobilizable species. This fraction represented 32–63% of THg in Jódar samples (Fig. 3a) and 16–46% of THg in Flix samples (Fig. 3b). Among the studied soils related to CAPs, our results were slightly lower than those reported by Bernaus et al. (2006) in the Netherlands, who found this fraction to be major (36–91% of THg) and higher than that obtained by Reis et al. (2010) in soils from Portugal (3–35% of THg). In contrast to the F3 fraction, higher F4 concentrations were found in the finest subsamples, as in other studied soils (Huremovic et al., 2017). The relatively high proportion of F4 may be explained by the stabilization of Hg sorbed onto soil by complexation with naturally present sulfide-containing ligands – the formation of such complexes is favored over complexation with organic matter or Fe and Mn oxides (Feyte et al., 2010; Fuhrmann et al., 2002). This process seems to be dominant in the CAPs investigated in this work, i.e., two locations with high proven Hg(0) and/or Hg(II) emissions (Esbri et al., 2015; Higuera et al., 2016).

### 3.2.2. Soils from cinnabar mining and metallurgy districts

**3.2.2.1. Labile Hg species.** The labile Hg fraction (F1) generally shows negligible concentrations of most AMS from both studied areas (Fig. 3c, d). As a consequence, the mobility of Hg in these soils can be considered very low, which is consistent with the results of other studies carried out on soils from the Almadén and Asturias mining districts (Fernández-Martínez et al., 2014; Millan et al., 2011) and other ancient cinnabar mines (Kocman et al., 2004). The exception was the sample SOT1, from Asturias (Fig. 3c), where F1 represented around 2.7–5.9% of total Hg, which corresponds to concentrations of 18.9–49.7  $\mu\text{g}\cdot\text{g}^{-1}$ ; given the high mobility and availability of this fraction, the relatively high concentrations obtained for this sample imply an environmental risk, since it could release large quantities of Hg by runoff mine water. A high F1 concentration may indicate the presence of reactive species such as  $\text{HgCl}_2$ ,  $\text{HgO}$  or  $\text{HgSO}_4$  as well as Hg bound to carbonates (Millan et al., 2011; Rimondi et al., 2014; Voros et al., 2018; Yin et al., 2016). It has been established that the presence of highly reactive secondary mineral phases is characteristic of sites affected by metallurgical activities due to inefficient cinnabar conversion (Gray et al., 2004). This effect is particularly important in La Soterraña because it represents the major Hg metallurgical centre in the Asturias region and it received raw material and concentrates from other Hg mines (Brañalamosa and Maramuñiz) to be treated in its retorts or tub furnaces (Ordoñez et al., 2013). This high proportion of labile fraction in La Soterraña produced the maximum Hg concentration in waters downstream from mining centers in Asturias (1–14  $\mu\text{g}\cdot\text{L}^{-1}$ ) (Ordoñez et al., 2013).

**3.2.2.2. Humic and fulvic complexes.** The humic and fulvic complexes fraction (F2, Table 1) showed low Hg recoveries for both mining areas,

namely 0.2–6.3% in samples from Asturias (Fig. 3c) and 0.6–2.4% in samples from Almadén (Fig. 3d). In spite of the strong affinity of Hg for humic substances (Shi et al., 2005), the low concentration of Hg associated with organic matter are typical of mining sites. Our results are comparable to those previously reported for soils from Almadén (2.6–5.9% of total Hg) or Idrija soils (0.3–7% of total Hg) (Fernández-Martínez and Rucandio, 2014; Kocman et al., 2004), although other data suggest that the proportions of this fraction can be higher (Campos et al., 2018; Higuera et al., 2003). However, in recent studies developed on soils from La Soterraña and El Terronal mining sites, large proportions of Hg associated to organic matter were found (Rumayor et al., 2017). This has been attributed to the presence of Hg bound to organo-mineral matter from vegetation and organometallic species formed during roasting process (Rumayor et al., 2017). This contradictory behavior may be explained because of the electivity of  $\text{Na}_4\text{P}_2\text{O}_7$  solution for humic and fulvic complexes, excluding Hg associated organic phases with higher stability. As expected, F2 is enriched in the finest subsamples for SOT1 and TRR1 from Asturias (Fernández-Martínez et al., 2014). However the opposite trend was observed for sample SOT2 and this behavior has also been observed in other studies (Kocman et al., 2004). In the case of Almadén samples, a significant influence of particle size was not observed. Once again, a negative correlation between TOC and F2 percentages was found ( $r = -0.577$  for Asturias samples and a poor positive correlation ( $r = 0.125$ ) for Almadén samples). The significant negative correlation is not consistent with the current established view on the positive effects of TOC and Hg accumulation (Covelli et al., 2012; Wu et al., 2013). Similar behavior was observed in sediments from a mangrove area in Brazil ( $r = -0.750$ ) (Machado et al., 2016). A possible explanation for the lack of positive correlation may be the presence of non-humified organic matter, which is less efficient in complexing Hg(II) species (Biester et al., 2002; Voros et al., 2018).

**3.2.2.3. Elemental Hg and Hg bound to crystalline oxides.** Elemental Hg and Hg bound to crystalline oxides (F3) were below 15% for Almadén (Fig. 3d) and La Soterraña (Asturias) soil samples (Fig. 3c), whereas the values ranged from 10.4% to 37.4% for La Peña-El Terronal (also in Asturias) subsamples. Regardless of the other studied areas, the sample from La Peña-El Terronal mine site showed a clear tendency for Hg F3 accumulation in the finest subsample. The high F3 concentration found in La Peña-El Terronal subsamples are not surprising, since high percentages in this fraction have been reported previously in the same area, where highly contaminated calcine wastes occur (Fernández-Martínez et al., 2014; Fernández-Martínez et al., 2006). Hg recovery in F3 is due to the extraction of metallic Hg, which condensed during the ore roasting process and was sorbed onto crystalline Fe oxides (Gray et al., 2004). In addition, in the case of La Peña-El Terronal soil, where relatively low calcination temperatures were used in rotary furnaces (over 853 °C) (Luque and Gutiérrez, 2006), another contribution to this fraction may be the presence of other secondary phases, such as calomel or finely ground organo-sulfur, which can be extracted by highly concentrated  $\text{HNO}_3$  solutions (Esbri et al., 2010; Rimondi et al., 2014).

**3.2.2.4. Hg sulfide and refractory species.** The measurement of Hg sulfide and refractory species, as one might expect, gave high levels for most of the AMS samples, with values in the range 86–94% of total Hg for Almadén soils (Fig. 3d) and 60–95% of total Hg for Asturias soils (Fig. 3c). The predominance of sulfide Hg phases in soils from La Soterraña confirms the findings by Rumayor et al. (2017) using thermodesorption analysis, and it can be attributed to the presence of mine wastes containing  $\text{HgS}$  and  $\text{Hg-FeS}_2$ . This means that Hg in the AMS occurs mainly as sulfide phases, such as cinnabar and metacinnabar. According to the literature, the predominance of such sulfide phases is expected in soils from cinnabar districts. Esbri et al. (2010) reported proportions for the sum of cinnabar and metacinnabar concentration in the range of 46–62% for soils from Almadén and

50–100% for soils from Asturias. A significant influence of particle-size on the F4 percentage was not observed for Almadén and La Soterraña samples, since only small differences were found. With the exception of sample TRR1, a clear distribution pattern among subsamples could not be established. This contradictory behavior regarding the accumulation of sulfide Hg phases on particle-size fractions is not unprecedented. Several studies on soils affected by mining or industrial activities led to opposite conclusions about the distribution of cinnabar in terms of particle-size fractions (Baptista-Salazar et al., 2017; Huremovic et al., 2017). It seems that particle-size distribution of sulfide phases is governed by the form in which the cinnabar is present and the physicochemical characteristics of soils, which are largely site-specific (Fernández-Martínez et al., 2005; Lusilao-Makiese et al., 2013).

### 3.3. Comparison between CAPs and AMS

The distribution patterns of Hg species for CAPs soils and AMS highlight the different origins of the pollution for both types of site, with some factors like climatic conditions or time-lapse since the last emission period acting as secondary factors in the incorporation of Hg into the soil geochemistry. In general, extracted Hg concentrations obtained by the SEP correlate positively with total Hg concentration. Regarding specific fractionation, fraction F3 (elemental Hg and Hg bound to crystalline oxides) typically appears more abundant in CAP soils, which is in agreement with the source of pollution, since anthropogenic Hg in CAP sites is mainly derived from Hg(0) deposition and subsequent oxidation to Hg(II) or direct Hg(II) deposition. In contrast, AMS exhibited very high F4 (Hg sulfides and refractory species) concentrations, which is consistent with the origin of the massive input of Hg to the sites in these areas from cinnabar ores – a highly insoluble Hg compound that remains almost unaltered, despite being exposed to weathering. Unlike the typical behavior in natural soils (Malehase et al., 2016), Hg associated with soil organic matter, represented by the concentration of Hg Hum/Ful fraction (F2), is not a major phase in any of the studied soils. Although higher proportions were found in CAP soils, the highest concentrations in this fraction corresponded to AMS. In this case, other factors like composition of organic matter or climatic conditions have to be taken in consideration to explain these low Hg concentration in fraction F2 in AMS, and again the predominance of cinnabar in the ore and soils can lead to a decrease in the proportion of available Hg to be complexed by organic matter. In spite of not being considered as a readily available Hg fraction, Hg associated with humic acids has been identified as the Hg fraction with enhanced reactivity with respect to microbial methylation (Liu et al., 2006; Moreau et al., 2015).

In all of the studied soils, total Hg appears at higher concentrations in the finest fractions. In CAPs, compounds related with F3 reach higher concentrations in coarser fractions, while the other fractions appear to be more concentrated in finer fractions. This trend was not observed for AMS, or at least not so clearly, with some samples showing higher proportions of F3 in finer fractions (SOT1, TRR1, EDAR1), while in others the Hg fractions did not show any trend beyond the predominance of cinnabar and the almost total absence of labile compounds. These differences in trends as a function of grain-size in CAP and AMS samples could be a consequence of the more complex incorporation of Hg in the soil geochemistry in AMS environments. This could be due to the complexity of Hg sources (Hg fractionation in ore bodies, mining operations and metallurgical activity) in AMS locations when compared to the simplicity of Hg sources in CAP locations (Hg(0) and Hg(II) diffuse emissions, with a low role of solid wastes in Hg dispersion process). It is important to consider the total absence of particulate Hg in atmospheric Hg emissions in CAP locations, and the total predominance of gaseous Hg (Hg(0) and Hg(II)) in deposition processes to explain the clear trends in granulometric fractions.

In terms of risk assessment, it is necessary to consider three important findings:

- The high total Hg concentrations in AMS, which make minor fractions, such as the Hg fraction linked to humic/fulvic compounds (F2), more worrisome in terms of total Hg available to be methylated when compared with major fractions in CAPs soils, which have lower total Hg concentrations.
- The proportions of low lability fractions (F1) in CAP soils and their almost total absence in AMS, combined with the high proportions of the refractory fraction (F4), produce an effective immobilization of Hg in the soil matrix regardless of soil composition or the nature of the source.
- The low elemental Hg concentrations in both CAPs and their absence in AMS provide evidence that gaseous Hg deposited in soils by dry or wet deposition interacts with the soil matrix (humic and fulvic acids, crystalline Fe oxides, organo-sulfur compounds). In this way almost all Hg(0) is converted into Hg sorbed/complexed to other soil compounds, although the specific details differ, probably as a consequence of local soil characteristics such as composition and reactivity.

## 4. Conclusions

Differences in Hg fractionation in soils were investigated as a function of source (mining or industrial) and grain size in order to gain a better understanding of the soil immobilization capacity for Hg. The main findings are as follows:

- Higher amounts of total Hg entering soils were found in mining soils from a complex Hg source including mining operations, metallurgical activity and Hg fractionation in ore bodies. CAP soils contained lower levels of total Hg, which comes from a single source of gaseous Hg (Hg(0) and Hg(II)).
- Fractionation of Hg shows a predominance of Hg sulfide and refractory species in mining soils and elemental Hg and Hg bound to crystalline oxides in CAPs.
- Grain size proved to be an important factor for Hg fractionation in CAP environments, with elemental Hg and Hg bound to crystalline oxides more abundant in coarser fractions whereas the other fractions were more abundant in the finest fractions.
- Although CAP sites show higher Hg percentages in fractions that are more prone to methylation, greater concentrations of Hg in these fractions in AMS could represent a major risk as they could enter the human trophic chain.
- Low Hg(0) concentrations in CAP soils and its absence from AMS provide evidence that gaseous Hg deposited in soils interacts strongly with the soil matrix, thus converting almost all Hg(0) into Hg sorbed/complexed to other soil compounds.

## Acknowledgements

This study was funded by the Spanish Ministry of Economy and Competitiveness, projects CTM2012-33918 and CGL2015-67644-R.

## Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.scitotenv.2019.03.348>.

## References

- Alloway B. Bioavailability of elements in soil. In: O. Selinus BA, J. A. Centeno, R. B., Finkelman RF, U. Lindh, P. Smedley, editors. *Essentials of Medical Geology*. Elsevier, Amsterdam, 2004, pp. 347–372.
- Bavec, S., Biester, H., Gosar, M., 2014. Urban sediment contamination in a former Hg mining district, Idrija, Slovenia. *Environ. Geochem. Health* 36, 427–439.
- Babi, D., Schaedlich, F.H., Schneeberger, D.R., 2002. Correction techniques for iodine and bromine interferences in continuous flow aqueous mercury analysis. *Anal. Bioanal. Chem.* 374, 1022–1027.
- Bagheri, A., Ioppolo, A., Negre, M., Gennari, M., 2007. A method for isolating soil organic matter after the extraction of humic and fulvic acids. *Org. Geochem.* 38, 140–150.

- Baptista-Salazar, C., Richard, J.H., Horf, M., Rejc, M., Gosar, M., Biester, H., 2017. Grain-size dependence of mercury speciation in river suspended matter, sediments and soils in a mercury mining area at varying hydrological conditions. *Appl. Geochem.* 81, 132–142.
- Barber, L.B., Thurman, E.M., Runnells, D.D., 1992. Geochemical heterogeneity in a sand and gravel aquifer - effect of sediment mineralogy and particle-size on the sorption of chlorobenzenes. *J. Contam. Hydrol.* 9, 35–54.
- Beatty, W.L., Schroeder, K., Beatty, C.L.K., 2012. Mineralogical associations of mercury in FGD products. *Energy Fuel* 26, 3399–3406.
- Beckers, F., Rinklebe, J., 2017. Cycling of mercury in the environment: sources, fate, and human health implications: a review. *Crit. Rev. Environ. Sci. Technol.* 47, 693–794.
- Bengtsson, G., Picado, F., 2008. Mercury sorption to sediments: dependence on grain size, dissolved organic carbon, and suspended bacteria. *Chemosphere* 73, 526–531.
- Bernaus, A., Gaona, X., van Ree, D., Valiente, M., 2006. Determination of mercury in polluted soils surrounding a chlor-alkali plant - direct speciation by X-ray absorption spectroscopy techniques and preliminary geochemical characterisation of the area. *Anal. Chim. Acta* 565, 73–80.
- Biester, H., Gosar, M., Muller, G., 1999. Mercury speciation in tailings of the Idríja mercury mine. *J. Geochem. Explor.* 65, 195–204.
- Biester, H., Muller, G., Scholer, H.F., 2002. Binding and mobility of mercury in soils contaminated by emissions from chlor-alkali plants. *Sci. Total Environ.* 284, 191–203.
- Bishop, K.H., Lee, Y.H., Munthe, J., Dambrine, E., 1998. Xylem sap as a pathway for total mercury and methylmercury transport from soils to tree canopy in the boreal forest. *Biogeochemistry* 40, 101–113.
- Bloom, N.S., Preus, E., Katon, J., Hiltner, M., 2003. Selective extractions to assess the biogeochemically relevant fractionation of inorganic mercury in sediments and soils. *Anal. Chim. Acta* 479, 233–248.
- Boszke, L., Kowalski, A., Siepak, J., 2004. Grain size partitioning of mercury in sediments of the Middle Odra River (Germany/Poland). *Water Air and Soil Pollution* 159, 125–138.
- Brown, G.E., Henrich, V.E., Casey, W.H., Clark, D.L., Eggleston, C., Felmy, A., et al., 1999. Metal oxide surfaces and their interactions with aqueous solutions and microbial organisms. *Chem. Rev.* 99, 77–174.
- Burke, M.P., Hogue, T.S., Ferreira, M., Mendez, C.B., Navarro, B., Lopez, S., et al., 2010. The effect of wildfire on soil mercury concentrations in Southern California watersheds. *Water Air and Soil Pollution* 212, 369–385.
- Campos, J.A., Esbri, J.M., Madrid, M.M., Naharro, R., Peco, J., García-Noguero, E.M., et al., 2018. Does mercury presence in soils promote their microbial activity? The Almadenejos case (Almaden mercury mining district, Spain). *Chemosphere* 201, 799–806.
- Carr, J., 1998. Mineralized rocks and ore residues in the Idríja region. In: Miklavc, V. (Ed.), *Proceedings of the meeting of researchers entitled: Idríja as a natural and anthropogenic laboratory, Mercury as a major pollutant*, pp. 10–15.
- Colombo, M.J., Ha, J.Y., Reinfelder, J.R., Barkay, T., Yee, N., 2013. Anaerobic oxidation of Hg(0) and methylmercury formation by *Desulfovibrio desulfuricans* ND132. *Geochim. Cosmochim. Acta* 112, 166–177.
- Colombo, M.J., Ha, J., Reinfelder, J.R., Barkay, T., Yee, N., 2014. Oxidation of Hg(0) to Hg(II) by diverse anaerobic bacteria. *Chem. Geol.* 363, 334–340.
- Coston, J.A., Fuller, C.C., Davis, J.A., 1995. Pb<sup>2+</sup> and Zn<sup>2+</sup> adsorption by a natural aluminum-bearing and iron-bearing surface coating on an aquifer sand. *Geochim. Cosmochim. Acta* 59, 3535–3547.
- Covelli, S., Protopsalti, I., Acquavita, A., Sperle, M., Bonardi, M., Emili, A., 2012. Spatial variation, speciation and sedimentary records of mercury in the Guanabara Bay (Rio de Janeiro, Brazil). *Cont. Shelf Res.* 35, 29–42.
- Ebinghaus, R., Tripathi, R.M., Wallischlager, D., Lindberg, S.E., 1999. Natural and anthropogenic mercury sources and their impact on the air-surface exchange of mercury on regional and global scales. In: Ebinghaus, R., Turner, R.R., Lacerda, L.D., Vasiliev, O., Salomons, W. (Eds.), *Mercury Contaminated Sites*. Springer Verlag, Heidelberg, pp. 1–51.
- Elgazali, A.A.S., Gajdosechova, Z., Abbas, Z., Lombi, E., Scheckel, K.G., Donner, E., et al., 2018. Reactive gaseous mercury is generated from chloralkali factories resulting in extreme concentrations of mercury in hair of workers. *Sci. Rep.* 8.
- EPA. Method 245.7. Mercury in Water by Cold Vapor Atomic Fluorescence Spectrometry. Environmental Protection Agency (EPA), Washington DC (USA), 2005.
- Esbri, J.M., Bernaus, A., Avila, M., Kocman, D., García-Noguero, E.M., Guerrero, B., et al., 2010. XANES speciation of mercury in three mining districts - Almaden, Asturias (Spain), Idria (Slovenia). *J. Synchrotron Radiat.* 17, 179–186.
- Esbri, J.M., Lopez-Berdonces, M.A., Fernandez-Calderon, S., Higuera, P., Diez, S., 2015. Atmospheric mercury pollution around a chlor-alkali plant in Flix (NE Spain): an integrated analysis. *Environ. Sci. Pollut. Res.* 22, 4842–4850.
- Fernández-Martínez, R., Rucandio, M.I., 2005. Determination of methylmercury in soils by a simple extraction process and direct mercury analysis. In: Trindade, R.B.E., Melamed, R., Sobral, L.G.S., Barbosa, J.P. (Eds.), XIII International Conference on Heavy Metals in the Environment (ICHMET). Brazil, Rio de Janeiro, pp. 65–66.
- Fernández-Martínez, R., Rucandio, I., 2013. Assessment of a sequential extraction method to evaluate mercury mobility and geochemistry in solid environmental samples. *Ecotoxicol. Environ. Saf.* <https://doi.org/10.1016/j.ecoenv.2013.07.013>.
- Fernández-Martínez, R., Rucandio, I., 2014. Total mercury, organic mercury and mercury fractionation in soil profiles from the Almadén mercury mine area. *Environmental Science: Processes & Impacts* 16, 333–340.
- Fernández-Martínez, R., Loredó, J., Ordóñez, A., Rucandio, M.I., 2005. Distribution and mobility of mercury in soils from an old mining area in Mieres, Asturias (Spain). *Sci. Total Environ.* 346, 200–212.
- Fernández-Martínez, R., Loredó, J., Ordóñez, A., Rucandio, M.I., 2006. Physicochemical characterization and mercury speciation of particle-size soil fractions from an abandoned mining area in Mieres, Asturias (Spain). *Environ. Pollut.* 142, 217–226.
- Fernández-Martínez, R., Loredó, J., Ordóñez, A., Rucandio, I., 2014. Mercury availability by operationally-defined fractionation in granulometric distributions of soils and mine wastes from an abandoned cinnabar mine. *Environmental Science: Processes & Impacts* 16, 1069–1075.
- Fernández-Martínez, R., Gomez-Mancebo, B., Pena, E.J., Galan, P., Matsuyama, A., Garcia, F., et al., 2016. Monitoring of mercury and other metals mobility by sequential fractionation in soils nearby an abandoned chlor-alkali plant in Managua (Nicaragua). *Environmental Earth Sciences* 75.
- Feyte, S., Tessier, A., Gobeil, C., Cossa, D., 2010. In situ adsorption of mercury, methylmercury and other elements by iron oxyhydroxides and organic matter in lake sediments. *Appl. Geochem.* 25, 984–995.
- Frentiu, T., Pintican, B.P., Butaciu, S., Mihaltan, A.I., Ponta, M., Frentiu, M., 2013. Determination, speciation and distribution of mercury in soil in the surroundings of a former chlor-alkali plant: assessment of sequential extraction procedure and analytical technique. *Chemistry Central Journal* 7.
- Fuhrmann, M., Melamed, D., Kalb, P.D., Adams, J.W., Milian, L.W., 2002. Sulfur polymer solidification/stabilization of elemental mercury waste. *Waste Manag.* 22, 327–333.
- Fukue, M., Yanai, M., Sato, Y., Fujikawa, T., Furukawa, Y., Tani, S., 2006. Background values for evaluation of heavy metal contamination in sediments. *J. Hazard. Mater.* 136, 111–119.
- García-Sánchez, A., Murcigo, A., Alvarez-Ayuso, E., Santa-Regina, I., Rodríguez-González, M.A., 2009. Mercury in soils and plants in an abandoned cinnabar mining area (SW Spain). *J. Hazard. Mater.* 168, 1319–1324.
- Garron, C., Gagne, F., Ernst, W., Julien, G., Bernier, M., Caldwell, C. Mercury contamination of marine sediments and blue mussels (*Mytilus edulis*) in the vicinity of a mercury cell chlor-alkali plant in Dalhousie, New Brunswick, Canada. *Water Quality Research Journal of Canada* 2005; 40: 1–15.
- Gómez, J.A., Infante-Amate, J., González de Molina, M., Vanwalleghem, T., Taguas, E.V., Lorite, I., 2014. Olive cultivation, its impact on soil erosion and its progression into yield impacts in Southern Spain in the past as a key to a future of increasing climate uncertainty. *Agriculture* 4, 170–198.
- Gordeva, O.N., Belogolova, G.A., Pastukhov, M.V., 2017. Mercury speciation and mobility in soils of industrial areas in the Baikal region, Southern Siberia, Russia. *Environmental Earth Sciences* 76, 10.
- Gray, J.E., Hines, M.E., Higuera, P.L., Adatto, I., Lasorsa, B.K., 2004. Mercury speciation and microbial transformations in mine wastes, stream sediments, and surface waters at the Almaden Mining District, Spain. *Environmental Science & Technology* 38, 4285–4292.
- Gray, J.E., Pribil, M.J., Higuera, P.L., 2013. Mercury isotope fractionation during ore retorting in the Almaden mining district, Spain. *Chem. Geol.* 357, 150–157.
- Han, Y., Kingston, H.M., Boylan, H.M., Rahman, G.M.M., Shah, S., Richter, R.C., et al., 2003. Speciation of mercury in soil and sediment by selective solvent and acid extraction. *Anal. Bioanal. Chem.* 375, 428–436.
- Hernandez, A., Jebrak, M., Higuera, P., Oyarzun, R., Morata, D., Munha, J., 1999. The Almaden mercury mining district, Spain. *Mineral. Deposita* 34, 539–548.
- Higuera, P., Oyarzun, R., Lunar, R., Sierra, J., Parras, J., 1999. The Las Cuevas deposit, Almaden district (Spain): an unusual case of deep-seated advanced argillic alteration related to mercury mineralization. *Mineral. Deposita* 34, 211–214.
- Higuera, P., Oyarzun, R., Biester, H., Lillo, J., Lorenzo, S., 2003. A first insight into mercury distribution and speciation in soils from the Almaden mining district, Spain. *J. Geochem. Explor.* 80, 95–104.
- Higuera, P., Oyarzun, R., Lillo, J., Sanchez-Hernandez, J.C., Molina, J.A., Esbri, J.M., et al., 2006. The Almaden district (Spain): anatomy of one of the world's largest Hg-contaminated sites. *Sci. Total Environ.* 356, 112–124.
- Higuera, P., Amorós, J.A., Esbri, J.M., García-Navarro, F.J., 2012. Time and space variations in mercury and other trace element contents in olive tree leaves from the Almaden Hg-mining district. *J. Geochem. Explor.* 123, 143–151.
- Higuera, P., Fernández-Martínez, R., Esbri, J.M., Rucandio, I., Loredó, J., Ordóñez, A., et al., 2015. Mercury soil pollution in Spain: A review. In: Barceló, D., Kostianoy, A.G. (Eds.), *Handbook of Environmental Chemistry*. 32. Springer, pp. 135–158.
- Higuera, P.L., Amorós, J.A., Esbri, J.M., Perez-de-los-Reyes, C., Lopez-Berdonces, M.A., García-Navarro, F.J., 2016. Mercury transfer from soil to olive trees. A comparison of three different contaminated sites. *Environ. Sci. Pollut. Res.* 23, 6055–6061.
- Hintelmann, H., Wilken, R.D., 1995. Levels of Total and methylmercury compounds in sediments of the polluted Elbe River - influence of seasonally and spatially varying environmental-factors. *Sci. Total Environ.* 166, 1–10.
- Hu, H.Y., Lin, H., Zheng, W., Tomanicek, S.J., Johs, A., Feng, X.B., et al., 2013. Oxidation and methylation of dissolved elemental mercury by anaerobic bacteria. *Nat. Geosci.* 6, 751–754.
- Huremovic, J., Horvat, M., Kotnik, J., Kocman, D., Zizek, S., Guevara, S.R., et al., 2017. Characterization of mercury contamination surrounding a chloralkali production facility in Tuzla, Bosnia and Herzegovina. *Anal. Lett.* 50, 1049–1064.
- Kobal, A., Dizdarevic, T., 1997. The health safety programme for workers exposed to elemental mercury at the mercury mine in Idríja. *Water Air and Soil Pollution* 97, 169–184.
- Kocman, D., Horvat, M., Kotnik, J., 2004. Mercury fractionation in contaminated soils from the Idríja mercury mine region. *J. Environ. Monit.* 6, 696–703.
- Loredó, J., Ordóñez, A., Baldo, C., García-Iglesias, C., 2003. Arsenic mobilization from waste piles of the El Terronal mine, Asturias, Spain. *Geochim. Explor. Environ. Anal.* 3, 229–237.
- Li, P., Feng, X.B., Qiu, G.L., Zhang, J.F., Meng, B., Wang, J.X., 2013. Mercury speciation and mobility in mine wastes from mercury mines in China. *Environ. Sci. Pollut. Res.* 20, 8374–8381.
- Liu, G.L., Cabrera, J., Allen, M., Cai, Y., 2006. Mercury characterization in a soil sample collected nearby the DOE Oak Ridge Reservation utilizing sequential extraction and thermal desorption method. *Sci. Total Environ.* 369, 384–392.

- Loredo, J., Ordóñez, A., Gallego, J.R., Baldo, C., García-Iglesias, J., 1999. Geochemical characterisation of mercury mining spoil heaps in the area of Mieres (Asturias, northern Spain). *J. Geochem. Explor.* 67, 377–390.
- Luque, C., Gutiérrez, M., 2006. *La Minería del Mercurio en Asturias: Rasgos Históricos*: Editors.
- Lusilao-Makiese, J.G., Cukrowska, E.M., Tessier, E., Amouroux, D., Weiersbye, I., 2013. The impact of post gold mining on mercury pollution in the west Rand region, Gauteng, South Africa. *J. Geochem. Explor.* 134, 111–119.
- Machado, W., Sanders, C.J., Santos, I.R., Sanders, L.M., Silva, E.V., Luiz-Silva, W., 2016. Mercury dilution by autochthonous organic matter in a fertilized mangrove wetland. *Environ. Pollut.* 213, 30–35.
- Malehase, T., Daso, A.P., Okonkwo, J.O., 2016. Determination of mercury and its fractionation products in samples from legacy use of mercury amalgam in gold processing in Randfontein, South Africa. *Emerging Contaminants* 2, 157–165.
- Martínez-Coronado, A., Oyarzun, R., Esbrí, J.M., Llanos, W., Higuera, P., 2011. Sampling high to extremely high Hg concentrations at the Cerco de Almadenejos, Almaden mining district (Spain): the old metallurgical precinct (1794 to 1861 AD) and surrounding areas. *J. Geochem. Explor.* 109, 70–77.
- McLean, E.O., 1982. Soil pH and lime requirement. In: Page, A.L., Miller, R.H., Keeney, D.R. (Eds.), *Methods of Soil Analysis. Part 2 - Chemical and Microbiological Properties*. (2nd Ed.). American Society of Agronomy, Inc., Madison, WI (USA), pp. 199–224.
- Millan, R., Schmid, T., Sierra, M.J., Carrasco-Gil, S., Villadoniga, M., Rico, C., et al., 2011. Spatial variation of biological and pedological properties in an area affected by a metallurgical mercury plant: Almadenejos (Spain). *Appl. Geochem.* 26, 174–181.
- Mohamed, A.E., Rashed, M.N., Mofty, A., 2003. Assessment of essential and toxic elements in some kinds of vegetables. *Ecotoxicol. Environ. Saf.* 55, 251–260.
- Moreau, J.W., Gionfriddo, C.M., Krabbenhoft, D.P., Ogorek, J.M., DeWild, J.F., Aiken, G.R., et al., 2015. The effect of natural organic matter on mercury methylation by *Desulfobulbus propionicus* 1p3. *Front. Microbiol.* 6.
- Naharro, R., Esbrí, J.M., Amorós, J.Á., García-Navarro, F.J., Higuera, P., 2018. Assessment of mercury uptake routes at the soil-plant-atmosphere interface. *Geochem.: Explor., Environ., Anal. geochem* 2018-019.
- Navarro, A., Biester, H., Mendoza, J.L., Cardellach, E., 2006. Mercury speciation and mobilization in contaminated soils of the Valle del Azogue Hg mine (SE, Spain). *Environ. Geol.* 49, 1089–1101.
- Ordóñez, A., Alvarez, R., Loredo, J., 2013. Asturian mercury mining district (Spain) and the environment: a review. *Environ. Sci. Pollut. Res.* 20, 7490–7508.
- Ordóñez, A., Alvarez, R., Loredo, J., 2014. Soil pollution related to the mercury mining legacy at Asturias (Northern Spain). *International Journal of Mining Reclamation and Environment* 28, 389–396.
- Palanques, A., Grimalt, J., Belzunces, M., Estrada, F., Puig, P., Guillen, J., 2014. Massive accumulation of highly polluted sedimentary deposits by river damming. *Sci. Total Environ.* 497, 369–381.
- Reis, A.T., Rodrigues, S.M., Davidson, C.M., Pereira, E., Duarte, A.C., 2010. Extractability and mobility of mercury from agricultural soils surrounding industrial and mining contaminated areas. *Chemosphere* 81, 1369–1377.
- Rimondi, V., Bardelli, F., Benvenuti, M., Costagliola, P., Gray, J.E., Lattanzi, P., 2014. Mercury speciation in the Mt. Amiata mining district (Italy): interplay between urban activities and mercury contamination. *Chem. Geol.* 380, 110–118.
- Rumayor, M., Lopez-Anton, M.A., Diaz-Somoano, M., Maroto-Valer, M.M., Richard, J.H., Biester, H., et al., 2016. A comparison of devices using thermal desorption for mercury speciation in solids. *Talanta* 150, 272–277.
- Rumayor, M., Gallego, J.R., Rodríguez-Valdes, E., Diaz-Somoano, M., 2017. An assessment of the environmental fate of mercury species in highly polluted brownfields by means of thermal desorption. *J. Hazard. Mater.* 325, 1–7.
- Rytuba, J.J., 2003. Mercury from mineral deposits and potential environmental impact. *Environ. Geol.* 43, 326–338.
- Sahuquillo, A., Rauret, G., Bianchi, M., Rehnert, A., Muntau, H., 2003. Mercury determination in solid phases from application of the modified BCR-sequential extraction procedure: a valuable tool for assessing its mobility in sediments. *Anal. Bioanal. Chem.* 375, 578–583.
- Schluter, K., 1997. Sorption of inorganic mercury and monomethyl mercury in an iron-humus podzol soil of southern Norway studied by batch experiments. *Environ. Geol.* 30, 266–279.
- Shi, J.B., Liang, L.N., Jiang, G.B., Jin, X.L., 2005. The speciation and bioavailability of mercury in sediments of Haihe River, China. *Environ. Int.* 31, 357–365.
- Skyllberg, U., Bloom, P.R., Qian, J., Lin, C.M., Bleam, W.F., 2006. Complexation of mercury (II) in soil organic matter: EXAFS evidence for linear two-coordination with reduced sulfur groups. *Environmental Science & Technology* 40, 4174–4180.
- Sladek, C., Gustin, M.S., 2003. Evaluation of sequential and selective extraction methods for determination of mercury speciation and mobility in mine waste. *Appl. Geochem.* 18, 567–576.
- Smith, T., Pitts, K., McGarvey, J.A., Summers, A.O., 1998. Bacterial oxidation of mercury metal vapor, Hg(0). *Appl. Environ. Microbiol.* 64, 1328–1332.
- Soares, L.C., Egreja, F.B., Linhares, L.A., Windmoller, C.C., Yoshida, M.I., 2015. Accumulation and oxidation of elemental mercury in tropical soils. *Chemosphere* 134, 181–191.
- Tersic, T., Gosar, M., Biester, H., 2011. Distribution and speciation of mercury in soil in the area of an ancient mercury ore roasting site, Frbežene trate (Idrija area, Slovenia). *J. Geochem. Explor.* 110, 136–145.
- USEPA. Mercury Study Report to Congress. Volume III: Fate and Transport of Mercury in the Environment Office of Air Quality Planning and Standards. U.S. Environmental Protection Agency (USEPA), Washington, D.C., 1997, pp. 376.
- Voros, D., Diaz-Somoano, M., Gerslova, E., Sykorova, I., Suarez-Ruiz, I., 2018. Mercury contamination of stream sediments in the North Bohemian Coal District (Czech Republic): mercury speciation and the role of organic matter. *Chemosphere* 211, 664–673.
- Wen, X.H., Du, Q., Tang, H.X., 1998. Surface complexation model for the heavy metal adsorption on natural sediment. *Environmental Science & Technology* 32, 870–875.
- Wu, F.C., Xu, L.B., Liao, H.Q., Guo, F., Zhao, X.L., Giesy, J.P., 2013. Relationship between mercury and organic carbon in sediment cores from lakes Qinghai and Chenghai, China. *J. Soils Sediments* 13, 1084–1092.
- Xu, J., Kleja, D.B., Biester, H., Lagerkvist, A., Kumpieni, J., 2014. Influence of particle size distribution, organic carbon, pH and chlorides on washing of mercury contaminated soil. *Chemosphere* 109, 99–105.
- Yamamoto, M., 1995. Possible mechanism of elemental mercury oxidation in the presence of SH compounds in aqueous-solution. *Chemosphere* 31, 2791–2798.
- Yin, Y.J., Allen, H.E., Li, Y.M., Huang, C.P., Sanders, P.F., 1996. Adsorption of mercury(II) by soil: effects of pH, chloride, and organic matter. *J. Environ. Qual.* 25, 837–844.
- Yin, R.S., Gu, C.H., Feng, X.B., Zheng, L.R., Hu, N.N., 2016. Transportation and transformation of mercury in a calcine profile in the Wanshan Mercury Mine, SW China. *Environ. Pollut.* 219, 976–981.
- Zhang, J., Dai, J.L., Wang, R.Q., Li, F.S., Wang, W.X., 2009. Adsorption and desorption of divalent mercury (Hg<sup>2+</sup>) on humic acids and fulvic acids extracted from typical soils in China. *Colloids and Surfaces a-Physicochemical and Engineering Aspects* 335, 194–201.