

1     **Thermo-desorption: a valid tool for mercury speciation in soils and**  
2 **sediments?**

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19     **Abstract**

20     Mercury (Hg) speciation by thermo-desorption is considered an alternative to  
21 laborious sequential chemical procedures; hence its popularity has increased in the  
22 last years. In this work, steps were taken to improve the information obtained by Hg  
23 speciation through thermo-desorption, specifically to improve peak resolution and  
24 increase the number of species that can be identified. The thermo-desorption  
25 behaviour of Hg bound to iron oxides was characterized, as well as a new Hg-humic  
26 acids synthetic standard material. In contrast to previous studies, the peak  
27 corresponding to the Hg fraction associated with humic acids was clearly separated  
28 from the mineral fraction, and identified in some natural samples. With increasing  
29 temperature, Hg species are released in the following order: HgCl<sub>2</sub>=Hg associated  
30 with Fe<sub>2</sub>O<sub>3</sub> < Hg associated with humic acids < HgS < HgO, with an overlap of HgCl<sub>2</sub>  
31 and Hg associated with iron oxides.

32     An evaluation of the effects of sample pre-treatment and storage on Hg speciation  
33 was also performed. It was found that sieving to < 2 mm improved the sample

1 homogeneity. The importance of fast sample analysis was highlighted, given that  
2 after 10 days of storage at room temperature, volatile Hg<sup>0</sup> could no longer be  
3 identified in the sample. The suitability of thermo-desorption for mercury speciation in  
4 soils and sediments is discussed.

5

6 **Keywords:** Mercury; speciation; thermo-desorption; soil; sediment

7

## 8 **1 Introduction**

9

10 Soil and sediment mercury (Hg) contamination is a significant environmental  
11 problem, in which interest has increased in the past decades due to the growing  
12 awareness of the need for risk assessment and remediation of contaminated sites  
13 (Ure and Davidson, 2002). Understanding mercury speciation is key for risk  
14 assessment of mercury contaminated areas (Bollen et al., 2008) because, even  
15 though Hg is an highly toxic element, its bioavailability, solubility, toxicological, and  
16 ecological effects are largely influenced by speciation and the way the different  
17 species interact with soil or sediment constituents (Biester et al., 2002a; Clarkson,  
18 2002). These interactions are complex and many chemical, physical and biological  
19 processes are involved. These processes are, in turn, dependent on soil and  
20 sediment characteristics, especially pH, organic matter, chloride and sulfide content  
21 (Biester et al., 2002b; Miretzky et al., 2005). The combination of these factors has, in  
22 part, hindered the development of a harmonised protocol for Hg speciation, despite  
23 the fact that this subject has been given considerable attention by several research  
24 teams, as is evident in the review provided by Issaro *et al.* (2009). There are three  
25 main approaches to Hg speciation in soil and sediment: 1) sequential chemical  
26 extraction (Fernández-Martínez and Rucandio, 2013; Issaro et al., 2009); 2) X-ray  
27 absorption spectroscopy (mainly XAFS and EXAFS) (Kim et al., 2000; Kim et al.,  
28 2004); and 3) thermo-desorption (Biester and Scholz, 1997; Reis et al., 2012).  
29 Sequential extraction procedures have several known limitations (Bacon and  
30 Davidson, 2008), including non-specific removal of Hg species, as they distribute Hg  
31 content into operationally defined fractions, instead of isolating specific chemical  
32 species. Direct measurement of Hg species by XAFS is possible, but requires total  
33 Hg concentration above 100 mg kg<sup>-1</sup>, restricting its applicability to contaminated

1 sites. In the last decades, thermo-desorption has increasingly been used for Hg  
2 speciation in solid matrices (Biester and Scholz, 1997; Bollen et al., 2008; Higuera  
3 et al., 2003; Hojdová et al., 2008; Hojdová et al., 2009; Piani et al., 2005; Rallo et al.,  
4 2010; Rumayor et al., 2013). This technique allows different Hg-binding forms to be  
5 distinguished in soils and sediments based on the thermal release of Hg species.  
6 Through comparison with standards, Hg species can be identified. Although it is a  
7 promising technique for Hg speciation due to its simplicity, there are still some  
8 inherent problems that prevent achieving its full potential, such as overlapping peaks  
9 (Biester and Scholz, 1997; Reis et al., 2012).

10 In previous work, described in Reis *et al.* (2012), an alternative method for Hg  
11 speciation in soils and sediments using a direct mercury analyser for Hg was  
12 presented and its advantages over existing thermo-desorption methods mentioned.  
13 The limitations of the approach were discussed as well, namely the difficulty of  
14 distinguishing between HgCl<sub>2</sub> and Hg associated with organic matter, due to peak  
15 overlap, and also the fact that only a limited range of standard materials were  
16 analysed and characterised. Because Hg behaviour in soil and sediment is complex,  
17 and many constituents may act as Hg sorbents, further method development has  
18 been undertaken to try to expand the information that can be obtained. Two new  
19 standard materials were considered: Hg associated with iron (III) oxide (Fe<sub>2</sub>O<sub>3</sub>) and  
20 Hg bound to humic acids. The study of Hg-iron oxides complexes in soil and  
21 sediment is important due to the role of iron oxides in controlling Hg mobility in these  
22 matrices. Humic acids have been considered previously. In the previous work the  
23 humic acid-Hg complex was obtained by extraction from a soil sample (Reis et al.,  
24 2012) whereas, in this work, a synthetic humic acid sodium salt was used. Thus all  
25 standards were of synthetic origin, and their composition known and well-  
26 characterised.

27 The applicability of the method was tested by analysing soil and sediment  
28 samples with different characteristics and Hg origins (natural vs. anthropogenic), and  
29 a large range of total Hg content. Additionally the influence of sample pretreatment  
30 and time between sampling and analysis were also assessed because it has been  
31 reported that common pretreatment procedures such as air-drying, homogenisation,  
32 sieving, or storage in plastic bags can be sources of error, particularly in the case of  
33 volatile Hg<sup>0</sup> that can easily be lost (Rasemann et al., 1995).

34

## 1 **2 Materials and methods**

2

### 3 **2.1 Sampling**

4 Samples were collected at Hg-contaminated sites with known different physico-  
5 chemical characteristics and Hg sources.

6 Soil samples were collected in Estarreja, North-East Portugal (designated sample  
7 Estarreja and another soil sample from this area was used to study the effect of  
8 pretreatment and storage), from agricultural fields within a radius of < 1 km from a  
9 chemical industrial complex. For many years this complex was home to a large  
10 chlor-alkali plant which formerly produced chlorine and caustic soda using the Hg  
11 cell process, where Hg was utilized as a cathode in the electrolysis of a saturated  
12 brine solution (Ullrich et al., 2007). As other studies show Hg-cell chlor-alkali plants  
13 have been identified as major sources of Hg to the environment (Reis et al., 2009;  
14 Ullrich et al., 2007). Until 1975 the liquid effluents from this plant were transported for  
15 several kilometres through the agricultural fields surrounding the industrial complex,  
16 in man-made effluent streams, and directly discharged in Ria de Aveiro, a nearby  
17 coastal lagoon, without any previous treatment.

18 Another set of soil samples was collected in the Caveira sulfide mine area, South-  
19 East Portugal (samples Caveira 1 and Caveira 2), which is located in the Iberian  
20 Pyrite Belt (IPB), a well-known mining district of worldwide significance, due to its  
21 unusual concentration of large and medium sized mineral deposits, including ores of  
22 copper, iron, lead, sulfur and zinc. Antimony, arsenic, cadmium, cobalt, gold,  
23 mercury, selenium and silver can also be found in soils from the IPB (Barriga, 1990).  
24 Past mining activities include pyrite ( $\text{FeS}_2$ ) and copper (Cu) extraction (Barriga,  
25 1990), resulting in the production of large tailing volumes (estimated to be larger than  
26 2 Mt) (Cardoso Fonseca and Ferreira da Silva, 2000). Rainwater circulates and  
27 percolates easily over and through these tailing materials causing significant erosion  
28 and transport of tailings debris to areas nearby and downstream. Recent analysis  
29 revealed that soils surrounding the mine have a high mercury content (Rodrigues et  
30 al., 2010).

31 The Almadén mining district (Central Spain) was responsible for one-third of the  
32 total world Hg production and is considered one of the most Hg-contaminated places  
33 on Earth, due to its numerous Hg ore deposits, which have in common a simple

1 mineralogy that includes dominant cinnabar (HgS) and minor pyrite (FeS<sub>2</sub>) (Higuera  
2 et al., 2006). Asturias (Northern Spain) was also a site of abundant mining activities  
3 due to the large number of Hg deposits, in the form of cinnabar, metacinnabar and  
4 occasionally native mercury. The abandoned solid waste and industrial installations  
5 are still present in agricultural and pastoral fields (Ordóñez et al., 2013). Although  
6 these mines are now closed, soil metal contamination and acid mine drainage still  
7 pose severe environmental problems at the sites. One sample from each site was  
8 analysed (designated samples Almadén and Asturias).

9 Surface soil samples (0-15 cm) were collected and transported to the laboratory in  
10 plastic bags. After they were air-dried (room temperature less than 20 °C), and  
11 aggregates crushed, soils were sieved to < 2 mm using nylon sieves.

12 Additionally, three replicate cores of estuarine sediment were collected at the  
13 Laranjo basin, the most Hg-contaminated area of Ria de Aveiro (Ramalhosa et al.,  
14 2006), using a core drill of 7 cm diameter and 50 cm depth. The sediment cores  
15 were then sliced into 1 cm layers for vertical profile characterization, the three  
16 replicates of each layer depth were combined to create a composite sample, air-  
17 dried (room temperature less than 20 °C), and sieved to < 1 mm using nylon sieve.

18

## 19 **2.2 Samples characterisation**

20 The soil and sediment pH (CaCl<sub>2</sub>) was determined using a WTW pH meter-538,  
21 according to the ISO 10390:1994 method.

22 For the determination of organic carbon content in soils (OrgC), an excess of 4  
23 mol L<sup>-1</sup> hydrochloric acid was added to a crucible containing a weighed quantity of  
24 soil or sediment in order to remove carbonates. The crucibles were left to stand for 4  
25 hours at room temperature and at 16 hours at 60-70 °C, and the carbon content of  
26 the residue was measured on an Elemental Analysis instrument (LECO CNH-2000),  
27 according to ISO 10694:1995. Organic matter in sediments was estimated by loss on  
28 ignition, placing the sediment in a muffle furnace at 550 °C, until constant weight  
29 (approximately 6 hours). The amount of organic matter was estimated by the weight  
30 difference between the dry sediment and the remaining ash (Heiri et al., 2001).

31 Sulfur content (S) was measured on an Elemental Analysis instrument (LECO  
32 CNH-2000).

1 The pseudo-total contents of aluminium (Al), iron (Fe), and manganese (Mn) in  
2 soils and sediments were extracted by aqua regia, as described in ISO 11466:1995,  
3 and analysed by ICP–OES (ICP-OES Jobin Yvon Activa M, Burgener Mira Mist  
4 nebulizer), according to ISO 11885:2007 (2<sup>nd</sup> edition). The operational conditions  
5 used are summarized as follow: RF power: 1200 W; plasma gas flow (argon): 12 L  
6 min<sup>-1</sup>; sample flow rate: 1 mL min<sup>-1</sup>.

7 Analytical working range for Al and Fe was 0.5 – 50 mg L<sup>-1</sup>, and 0.05 – 10 mg L<sup>-1</sup>  
8 for Mn. Quantification limits were 0.5 mg L<sup>-1</sup> and 0.05 mg L<sup>-1</sup>, respectively.

9 Amorphous iron (Fe<sub>ox</sub>) and aluminium oxides (Al<sub>ox</sub>) were determined by the  
10 extraction of 2.5 g of soil with 50 mL of a 0.1 mol L<sup>-1</sup> oxalic acid solution (buffered to  
11 pH 3 by ammonium oxalate) and shaken mechanically in the dark for 2 hours.  
12 Aluminium and iron contents in the filtered extracts were analysed by ICP–OES  
13 (aforementioned operational conditions). Two replicate extractions were performed  
14 for each sample. Two extraction blanks were included in each batch of 20 bottles.

15 The particle size distribution and clay contents of the soil samples were  
16 determined using a Coulter LS230 laser diffraction particle size (particle size  
17 distribution of Asturias sample was not determined). The classification of soils  
18 followed the USDA Texture Classes: sand fraction (0.050-2 mm), silt fraction (0.002-  
19 0.050 mm), and clay fraction (< 0.002 mm). Classification of samples was achieved  
20 by using the *Talwin 42*<sup>®</sup> classification software program. Fine particles (<63 µm) of  
21 the sediments were determined by wet sieving, by weighing 5 g of dried sediments  
22 (in duplicate) and sieving the sediment through a 63 µm sieve under a gentle water  
23 flux (Pereira, 1996). The major advantage of this method is the disaggregation of the  
24 sediments clusters, formed in the drying process of the sediments, which sometimes  
25 it is impossible with the dry sieving. After sieving, the retained fraction (>63 µm) was  
26 dried at 120 °C until constant weight and the fraction <63 µm was estimated by the  
27 weight difference.

28

### 29 **2.3 Total mercury in soil and sediments**

30 Total Hg concentrations were determined by thermal decomposition atomic  
31 absorption spectroscopy (AAS) with gold amalgamation (LECO<sup>®</sup>, model AMA-254)  
32 [1]. Briefly, the system consists of a nickel boat carrying the sample into a quartz  
33 combustion tube in which the solid sample is initially dried (10 s) prior to

1 decomposition in an oxygen atmosphere, which for total Hg determination occurs at  
2 750 °C (150 s). The mercury vapor produced is then trapped on the surface of a gold  
3 amalgamator. After a pre-determined time interval (45 s), the amalgamator is heated  
4 to 900 °C to quantitatively release the Hg, which is transported to a heated cuvette  
5 (120 °C) prior to analysis by AAS using a silicon diode detector, at  $\lambda=253.6$  nm.

#### 6 **2.4 Mercury speciation by thermo-desorption**

7 Mercury speciation analysis was carried out using the solid fraction thermo-  
8 desorption technique presented in previous work (Reis et al., 2012). Basically, this  
9 method involves the thermal release of Hg compounds from the matrix, according to  
10 their desorption temperatures. Briefly describing the procedure, once the solid  
11 sample is placed in the equipment, temperature is increased from 76 °C to 768 °C  
12 and results are depicted as Hg thermo-desorption curves (TDC), which show Hg  
13 release ( $\text{mg kg}^{-1}$ ) plotted against temperature (°C). The Hg species were  
14 characterized by the temperature range at which they were released, from the  
15 temperature at which thermal-release starts, through the peak maximum, to the point  
16 where the curve returns to baseline. Synthetic standard materials were used to  
17 identify Hg species. A detailed description of the development and validation of this  
18 technique can be found in Reis *et al.* (2012).

19 In the part of this work already published (Reis et al., 2012) the thermal release  
20 behaviour of  $\text{HgCl}_2$ , Hg-humic acids (extracted from a soil) and (red-)HgS was  
21 studied. Two new standard materials were now considered: iron (III) oxide ( $\text{Fe}_2\text{O}_3$ )  
22 from Panreac and humic acid sodium salt, from Sigma Aldrich. Both were purchased  
23 in technical grade and no further modifications were made. They were found to have  
24 a total Hg content of 0.045 and 0.26  $\text{mg kg}^{-1}$ , respectively.

25 Each standard or sample was analyzed at least three times, and depending on its  
26 total Hg content, 0.5-40 mg were weighted for each thermo-desorption analysis.

27

#### 28 **2.5 Effect of sample pretreatment and storage**

29 To test the effects that pretreatment and storage may have on Hg speciation, one  
30 soil sample from Estarreja (the sampling location nearest to the laboratory, in order  
31 to reduce to minimum the effects of transport) was collected, using the sampling  
32 procedure described above, and brought to the laboratory where it was immediately  
33 analysed (original sample – day 1). The same sample was then analysed after air-

1 drying for 24 hours and sieving to < 2 mm (day 2). This fraction was re-analysed  
2 after 5 and 10 days. During this time, the sample was stored in a double plastic bag,  
3 at room temperature. This storage procedure was chosen to mimic the typical one  
4 used in soil sampling campaigns.  
5

## 6 **2.6 Quality control and quality assurance**

7 Analytical procedures were conducted using ultra-clean glassware (Derquin 5%,  
8 24 hours; HNO<sub>3</sub> 25%, 24 hours). Care was taken to avoid cross-contamination of the  
9 samples.

10 The accuracy of the LECO AMA-254 was assessed daily by the analysis of  
11 certified reference materials BCR-142R and CRM 021 for soil, and MESS-3 and  
12 PACS-2 for sediment. Recoveries were within the certified confidence interval and  
13 within the range of 82–117%.  
14

## 15 **3 Results and discussion**

16 The thermo-desorption curves (TDC) obtained for standard materials are shown in  
17 Figure 1. A full characterization of the thermo-release behaviour of HgCl<sub>2</sub> and  
18 synthetic red-HgS can be found in previous work concerning the method  
19 development and validation (Reis et al., 2012). In the same work, a standard of Hg  
20 bound to humic acids (HgHA) was considered, with a release peak between 100 and  
21 240 °C that overlapped HgCl<sub>2</sub>. While that humic acid-Hg complex was obtained by  
22 extraction from a soil sample, in the current work synthetic humic acid sodium salt  
23 was used. In this case, Hg thermo-release behaviour occurs between 194 and 424  
24 °C and is characterised by a main peak immediately followed by two smaller peaks  
25 (Figure 2). To explain this three-step release behaviour it is important to consider  
26 Hg<sup>2+</sup>-humic acids interaction. Humic acids offer more than one reactive site to which  
27 Hg<sup>2+</sup> can bind. Mercury will preferentially form covalent bonds with reduced sulfur  
28 atoms in reactive sites, hence the overlapping of the second peak with that of HgS.  
29 However, as only about 2% of these sites actively take part in the binding of  
30 mercury, they easily become saturated and additional mercury ions have to bind to  
31 oxygen- and nitrogen-containing groups, such as phenolic, carboxylic and amine  
32 groups (Gismera et al., 2007). The different bound forms have different stability



1 constants, which lead to the three-step thermo-release of Hg from humic acids. The  
2 comparison of the thermo-desorption curves of soil-extracted and synthetic HgHA  
3 (Figure 2) shows the difference between the temperature releases. Humic acids  
4 were extracted from soil using  $1 \text{ mol L}^{-1}$  HCl, which most likely extracted labile  
5 species as well; therefore, soil-extracted HgHA is released at lower temperature than  
6 synthetic HgHA.

7 Hg associated with iron oxides is mainly released between 100 and 285 °C, while  
8 a second, much smaller peak can be observed at 500-610 °C. This overlaps with  
9  $\text{HgCl}_2$ . Therefore, it will not be possible to distinguish the two compounds in a natural  
10 sample. Still, characterisation of the sample and consideration of its origin may help  
11 to infer the species that are most likely present, as will be exemplified below.

12

### 13 **3.1 Soil samples**

14 Estarreja soil is an acidic silt loam containing 1.7% organic carbon, 0.65% iron  
15 oxide, and 0.11% sulfur (Table 1). Thermal-desorption occurred between 146 and 424  
16 °C (Figure 3 a), although Hg was mainly released in the 146–320 °C temperature  
17 interval, which is consistent with Hg associated with humic acids. This is in  
18 accordance with the physical-chemical characterisation of the sample, as the acidic  
19 pH favours the adsorption to organic matter, and this is in higher abundance than the  
20 other soil components likely to bind Hg.

21 Soil sample Caveira 1 shows one major peak at 125-250 °C (Figure 3 b), which  
22 overlaps  $\text{HgCl}_2$ , Hg bound to iron oxides, and Hg associated with humic acids. This  
23 means that Hg can either be chemically bound to functional groups of organic matter  
24 or physically adsorbed to mineral surfaces, but it is difficult to distinguish the species.  
25 In fact, both processes can happen, as  $\text{Hg(II)}$ -organic complexes may be specifically  
26 adsorbed onto the mineral surfaces of the matrix, forming organo-mineral Hg  
27 complexes. The soil characterisation, presented in Table 1, may help to interpret the  
28 speciation, as the percentage of iron oxides (10.42%) is significantly higher than the  
29 percentage of organic matter (0.51%). As there is no known possible source of  
30 chloride at this location it is likely that Hg is mainly associated with iron oxides. There  
31 is also evidence of the presence of cinnabar in the 400-600 °C interval.

32 Soil sample Caveira 2 shows three clearly distinguishable peaks (Figure 3 c). The  
33 first, released at 120-210 °C is consistent with  $\text{HgCl}_2$  or Hg bound to iron oxides. The

1 second peak suggests the presence of complexes of Hg with organic matter. The  
2 last species that can be identified is possibly cinnabar. Although the TDC does not  
3 completely match that of the HgS standard, it has been reported that Hg in natural  
4 cinnabar is released at higher temperatures when compared to synthetic HgS  
5 (Biester et al., 2000). This is mainly due to the breakdown of the cinnabar lattice, in a  
6 process that causes the sudden release of 'pulses' of Hg; hence, decomposition  
7 occurs in several steps, which explains the succession of "small peaks".

8 The thermo-desorption curves for Spanish mine soils from Asturias and Almadén  
9 are presented in Figure 4 a and b, respectively. In the Asturias soil, the position of  
10 the first peak suggests that Hg is associated not only with organic matter, but also  
11 with iron; cinnabar was also identified in the sample, although in lower concentration.  
12 Soil chemical composition corroborates the results of the thermogram, as Asturias  
13 soil has 9.9% of organic matter and 4.3% of iron, and 0.23% of sulfur, three strong  
14 mercury scavengers.

15 The Hg in Almadén soils seems to be present mainly as cinnabar, as would be  
16 predicted considering the source of this sample is a former cinnabar mine.  
17

### 18 **3.2 Sediment samples**

19 The total mercury vertical profile of the sediment core collected in Ria de Aveiro is  
20 shown inset in Figure 5. The higher concentration between 20 and 30 cm  
21 corresponds to the years of the more pronounced effluent discharges from the chlor-  
22 alkali plant. In order to evaluate differences between top and deeper layers (less and  
23 more contaminated layers), some sections were chosen for speciation analysis. The  
24 mercury speciation results in the sediment vertical profile indicate that, with  
25 exception of section 0-1 cm, thermo-desorption curves have one peak between 140  
26 °C and 280 °C, indicating the occurrence of mercury associated with components  
27 such as iron oxides, chloride ions, or organic matter. Sorption of  $\text{Hg}^{2+}$  on sediments  
28 is a complex process controlled by a number of parameters, such as pH,  
29 temperature, mercury concentration, composition of sediment and aqueous media,  
30 presence of other cations (e.g.  $\text{Fe}^{3+}$ ,  $\text{Al}^{3+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Ca}^{2+}$ ) and anions (such as  $\text{S}^{2-}$ ,  $\text{SO}_4^{2-}$   
31 ) (Pelcová et al., 2010). Vegetated Ria de Aveiro sediments contain about 20-40%  
32 organic matter and have iron oxide contents that range between 0.50 and 2.6%  
33 (Table 1). Due to the high organic matter content, it would be expected that mercury

1 would be solely sorbed to that fraction, but this was not the case. Mercury sorption to  
2 sediments is pH-dependent, and the pH in these sediments is close to neutral,  
3 varying from 6.1 to 6.9 (Table 1), which favours sorption to mineral particles (Gabriel  
4 and Williamson, 2004). Speciation of the superficial layer (0-1 cm) also revealed that  
5 mercury is mainly present as organic complexes.  $\text{HgCl}_2$  was not identified, but it can  
6 be easily lost to the water column ( $\text{HgCl}_2$  solubility in water is 7.4 g/ 100 mL, T=20  
7 °C). Also, mercury sorption to iron oxides is diminished in the presence of chloride  
8 ions (Skylberg, 2010). A second, smaller peak between 400 °C and 490 °C was  
9 detected in all layers and can be attributed to the presence of mercury oxide (Biester  
10 et al., 2000).

11

### 12 **3.3 Effect of sample pretreatment and storage on Hg speciation**

13 The effects of sample pretreatment and storage in Hg speciation were studied by  
14 analysing a soil sample from Estarreja straight from the field (day 1), and then the <  
15 2 mm fraction after air drying for 24 hours (day 2), 96 hours (day 5), and 10 days  
16 (day 10). As the sample was collected in the summer, it air dried in less than 24  
17 hours. Figure 6 shows the thermo-desorption curves for each day after sampling.  
18 Surprisingly, a peak below 100 °C was identified, which should correspond to  $\text{Hg}^0$   
19 (Biester et al., 2000). This peak has not been observed in previous samples from the  
20 same location. All other samples analysed and presented in Reis *et al.* (2012) and in  
21 the current work were stored for longer periods; therefore,  $\text{Hg}^0$  could have been  
22 present in the samples but lost before analysis.

23 As can be seen in Figure 6, the thermo-desorption curve changes significantly  
24 over the 10-day period. The disappearance of the  $\text{Hg}^0$  peak is noticeable and it is  
25 likely that the species is lost during storage, due to its extremely volatile character.

26 The total Hg and  $\text{Hg}^0$  concentrations during the studied period are presented in  
27 Table 2. During the 10-day period, almost 32% of total Hg were lost, which mainly  
28 corresponds to the loss of  $\text{Hg}^0$  (Table 2). This problem concerns not only Hg  
29 speciation, but also total Hg determination in soils; often is not possible to analyse  
30 samples immediately after sampling and these results show that Hg concentration  
31 can be underestimated due to Hg losses during sample storage.

32 Another conclusion that can be drawn from Figure 6 is the higher heterogeneity of  
33 the original sample, as revealed by the higher standard deviations (n=4). After drying

1 and sieving, the heterogeneity is reduced, as lower standard deviations were  
2 achieved (n=4). Among the different species,  $\text{Hg}^0$  has a higher associated standard  
3 deviation. One possible explanation for this high heterogeneity may be in the origin  
4 of  $\text{Hg}^0$ . While Hg in soil is mostly present as  $\text{Hg}^{2+}$  associated with soil constituents  
5 (organic matter, mineral particles), free or weakly bound  $\text{Hg}^{2+}$  can be reduced to  $\text{Hg}^0$   
6 (Robles et al., 2014); being an occasional phenomenon this causes the distribution  
7 of  $\text{Hg}^0$  in the soil to be uneven. Atmospheric deposition can also be considered as a  
8 possible origin, since  $\text{Hg}^0$  emissions are associated with chlor-alkali plants (Biester  
9 et al., 2002b) and the presence of heterogeneously distributed  $\text{Hg}^0$  in the soil  
10 (Biester and Scholz, 1997).

11 It is noteworthy that 10 years after the change of production method from Hg to  
12 membrane-cells in the Estarreja chlor-alkali plant,  $\text{Hg}^0$  can still be found in the  
13 surrounding environment, confirming the persistence of this element in the  
14 environment.

15

#### 16 **4 Conclusion**

17 This study allowed some conclusions to be drawn about Hg speciation in soils and  
18 sediments using thermo-desorption. By using only synthetic standards materials, the  
19 peak corresponding to Hg bound to organic matter was able to be separated from  
20 other matrix constituents, which seemed a promising improvement in Hg speciation  
21 by this technique. However, when natural samples were analysed, it was still  
22 impossible to completely separate all Hg species. This indicates that thermo-  
23 desorption cannot be considered a stand-alone tool in Hg speciation analysis.  
24 Knowledge of the physico-chemical characteristics of the sample and of whether Hg  
25 is of geogenic origin or results from anthropogenic input is useful to complement and  
26 interpret the results. Samples where Hg was of geogenic origin showed higher  
27 standard deviations between replicates. This was mainly due to the release of Hg in  
28 cinnabar, which involves diffusion from inner-sphere sorption sites during the  
29 breakdown of the mineral lattice.

30 This work also proved that samples stored in plastic bags need to be analysed  
31 soon after collection, in order to obtain full information on Hg speciation. Longer  
32 storage periods can result in loss of volatile  $\text{Hg}^0$ . After only 10 days the peak  
33 corresponding to  $\text{Hg}^0$  no longer appeared in thermograms. Sieving to < 2 mm was

1 beneficial, as homogenation of the sample was improved. In future experiments  
2 different storage and pretreatment conditions will be considered, such as the use of  
3 different containers (e.g. amber or glass bottles), and the use of freeze-drying to dry  
4 the soil.

5

6

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11 methods for assessing the origin, mobility and toxicity of mercury from contaminated  
12 solid matrices and preparation of new sediment and soil reference materials  
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Table 1. Soil and sediment samples characterisation.

| PORTUGUESE SOIL SAMPLES |                           |                         |           |        |                      |       |          |          |          |                    |
|-------------------------|---------------------------|-------------------------|-----------|--------|----------------------|-------|----------|----------|----------|--------------------|
| Sample                  | Hg (mg kg <sup>-1</sup> ) | pH (CaCl <sub>2</sub> ) | Org C (%) | Fe (%) | Fe <sub>ox</sub> (%) | S (%) | sand (%) | silt (%) | clay (%) | USDA texture class |
| Estarreja               | 1.2                       | 4.8                     | 1.66      | 1.14   | 0.65                 | 0.11  | 18.62    | 71.00    | 10.38    | silt loam          |
| Caveira 1               | 6.9                       | 3.3                     | 0.51      | 4.2    | 10.42                | <0.05 | 25.26    | 61.28    | 13.46    | silt loam          |
| Caveira 2               | 34.2                      | 2.9                     | 0.93      | 6.56   | 11.23                | 0.42  | 49.87    | 39.77    | 10.36    | loam               |

| SPANISH SOIL SAMPLES |                           |                         |                |        |       |          |          |          |                    |  |
|----------------------|---------------------------|-------------------------|----------------|--------|-------|----------|----------|----------|--------------------|--|
| Sample               | Hg (mg kg <sup>-1</sup> ) | pH (CaCl <sub>2</sub> ) | Org matter (%) | Fe (%) | S (%) | sand (%) | silt (%) | clay (%) | USDA texture class |  |
| Asturias             | 153.6                     | 6.5                     | 9.9            | 4.26   | 0.23  | -        | -        | -        |                    |  |
| Almadén              | 64.8                      | 5.4                     | 1.3            | 2.7    | 0.12  | 43.16    | 30.6     | 26.24    | loam               |  |

| SEDIMENT SAMPLES           |                           |                         |         |        |                      |                       |
|----------------------------|---------------------------|-------------------------|---------|--------|----------------------|-----------------------|
| Sample depth               | Hg (mg kg <sup>-1</sup> ) | pH (CaCl <sub>2</sub> ) | LOI (%) | Fe (%) | Fe <sub>ox</sub> (%) | Fraction <0.63 µm (%) |
| Laranjo <sub>0-1cm</sub>   | 8.8                       | 6.5                     | 41.2    | 3.19   | 1.89                 | 33                    |
| Laranjo <sub>2-3cm</sub>   | 4.3                       | 6.1                     | 30.2    | 4.03   | 2.54                 | 34                    |
| Laranjo <sub>5-6cm</sub>   | 6.3                       | 6.1                     | 22.5    | 3.56   | 2.56                 | 21                    |
| Laranjo <sub>10-11cm</sub> | 5.8                       | 6.2                     | 28.4    | 3.28   | 2.17                 | 26                    |
| Laranjo <sub>14-15cm</sub> | 11.5                      | 6.1                     | 31.2    | 3.39   | 0.57                 | 30                    |
| Laranjo <sub>20-21cm</sub> | 6.9                       | 6.2                     | 31.3    | 3.47   | 0.56                 | 20                    |
| Laranjo <sub>25-26cm</sub> | 50.9                      | 6.4                     | 32.8    | 4.04   | 0.58                 | 32                    |
| Laranjo <sub>30-31cm</sub> | 26.1                      | 6.8                     | 30.7    | 3.94   | 0.52                 | 26                    |
| Laranjo <sub>38-39cm</sub> | 0.7                       | 6.9                     | 26.4    | 3.15   | 0.50                 | 28                    |

Table 2. Evolution of total Hg and Hg<sup>0</sup> concentrations (mean ± standard deviation; n = 4) with pretreatment and 10-day storage period.

|        | Total Hg (mg kg <sup>-1</sup> ) | Hg <sup>0</sup> (mg kg <sup>-1</sup> ) |
|--------|---------------------------------|----------------------------------------|
| Day 1  | 34.2 ± 2.8                      | 9.5 ± 4.9                              |
| Day 2  | 32.6 ± 1.5                      | 6.8 ± 1.3                              |
| Day 5  | 33.1 ± 1.5                      | 8.9 ± 2.0                              |
| Day 10 | 23.4 ± 0.6                      | 0.05 ± 0.01                            |

## FIGURE CAPTION

Figure 1. Thermo-desorption curves (average  $\pm$  standard deviation, n=10) for Hg species in synthetic standards materials: mercury chloride ( $\text{HgCl}_2$ ) and cinnabar ( $\text{HgS}$ ) – left Y axis; Hg bound to humic acids ( $\text{HgHA}$ ) and to iron oxides ( $\text{HgFe}$ ) – right Y axis.

Figure 2. Thermo-desorption curves (average  $\pm$  standard deviation, n=10) for Hg bound to humic acids:  $\text{HgHA}$  extracted from a soil (blue) (Reis et al., 2012) and synthetic (green).

Figure 3. Thermo-desorption curves of Portuguese soils (average  $\pm$  standard deviation, n=3). a) Industrial soil of Estarreja; b) Mine soil of Caveira 1; c) Mine soil of Caveira 2.

Figure 4. Thermo-desorption curves of Spanish mine soils (average  $\pm$  standard deviation, n=3). a) Asturias; b) Almadén.

Figure 5. Thermo desorption curves of Ria de Aveiro sediments vertical profile (average  $\pm$  standard deviation, n=3). Inset: total Hg concentration of the profile.

Figure 6. Thermo-desorption curve (average  $\pm$  standard deviation, n=4) of a soil sample where the effects of sample pretreatment and storage can be observed.

Figure 1

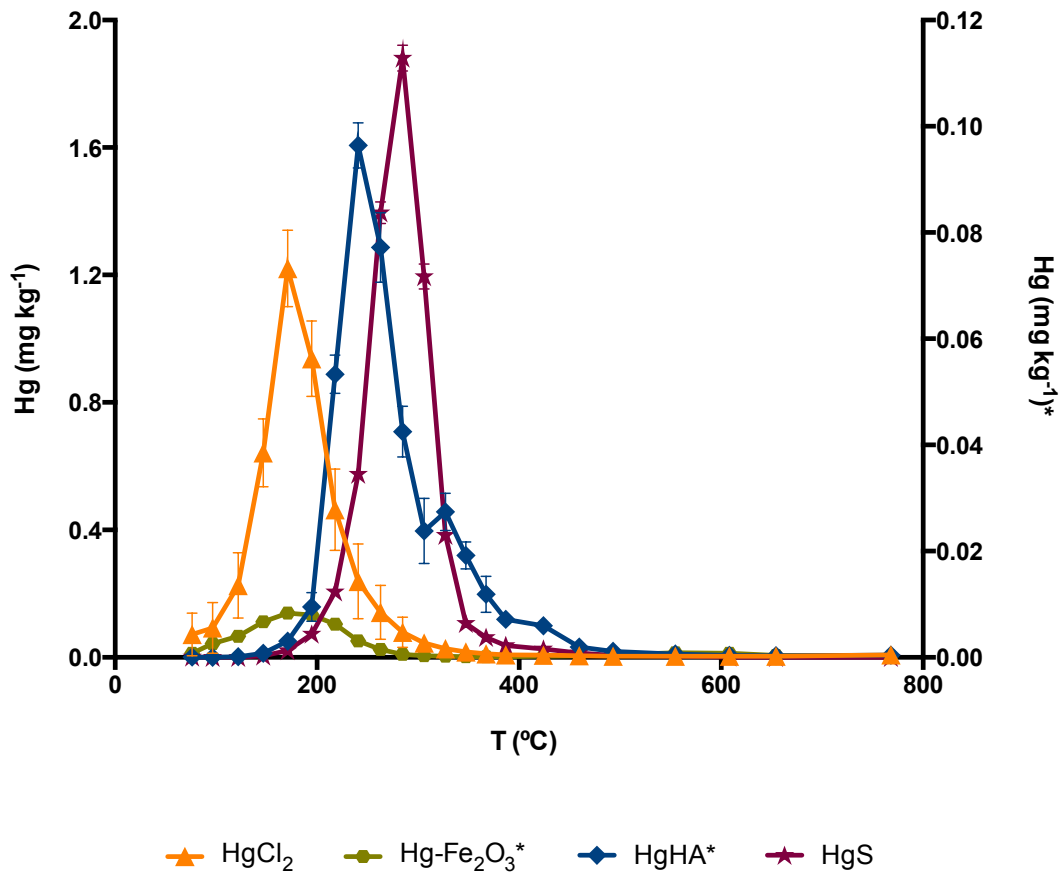


Figure 2

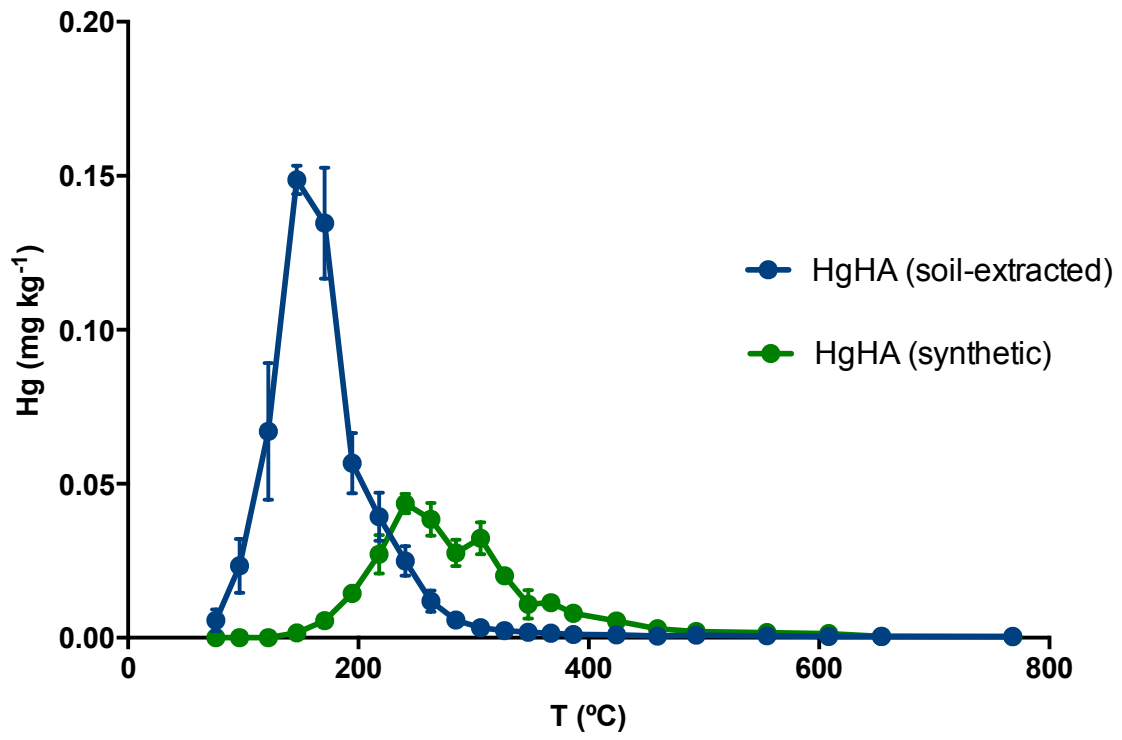


Figure 3

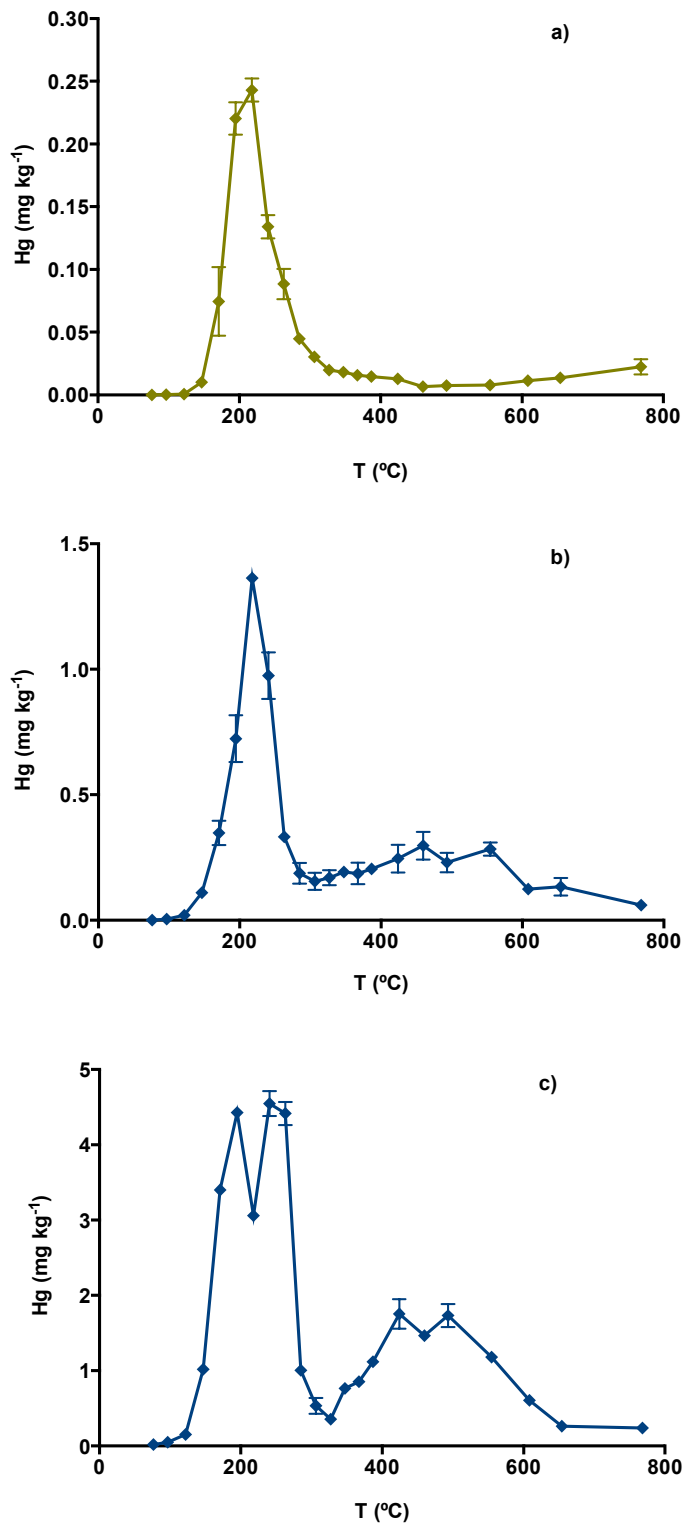


Figure 4

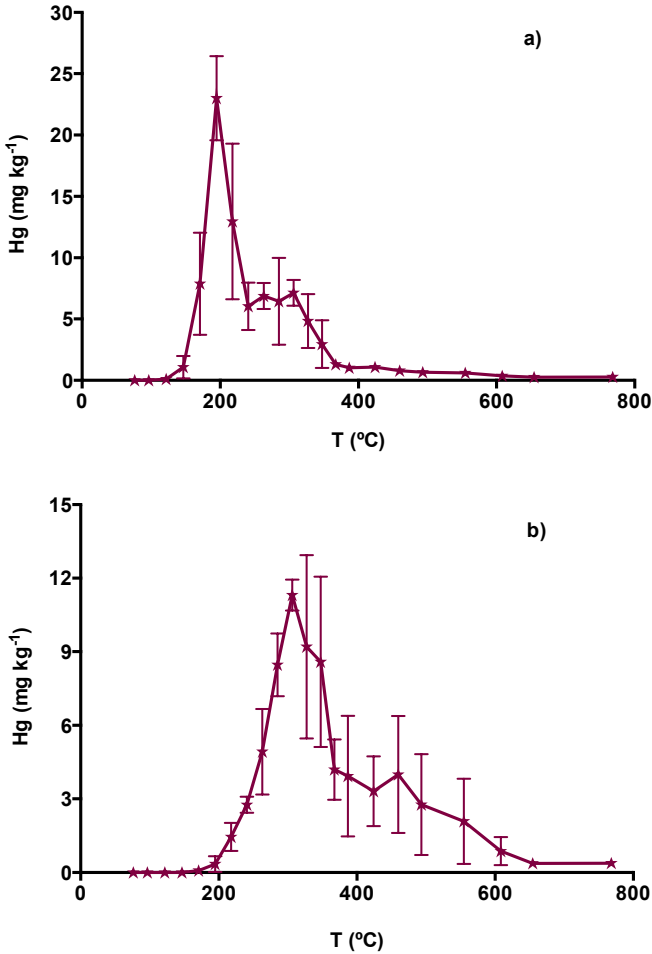


Figure 5

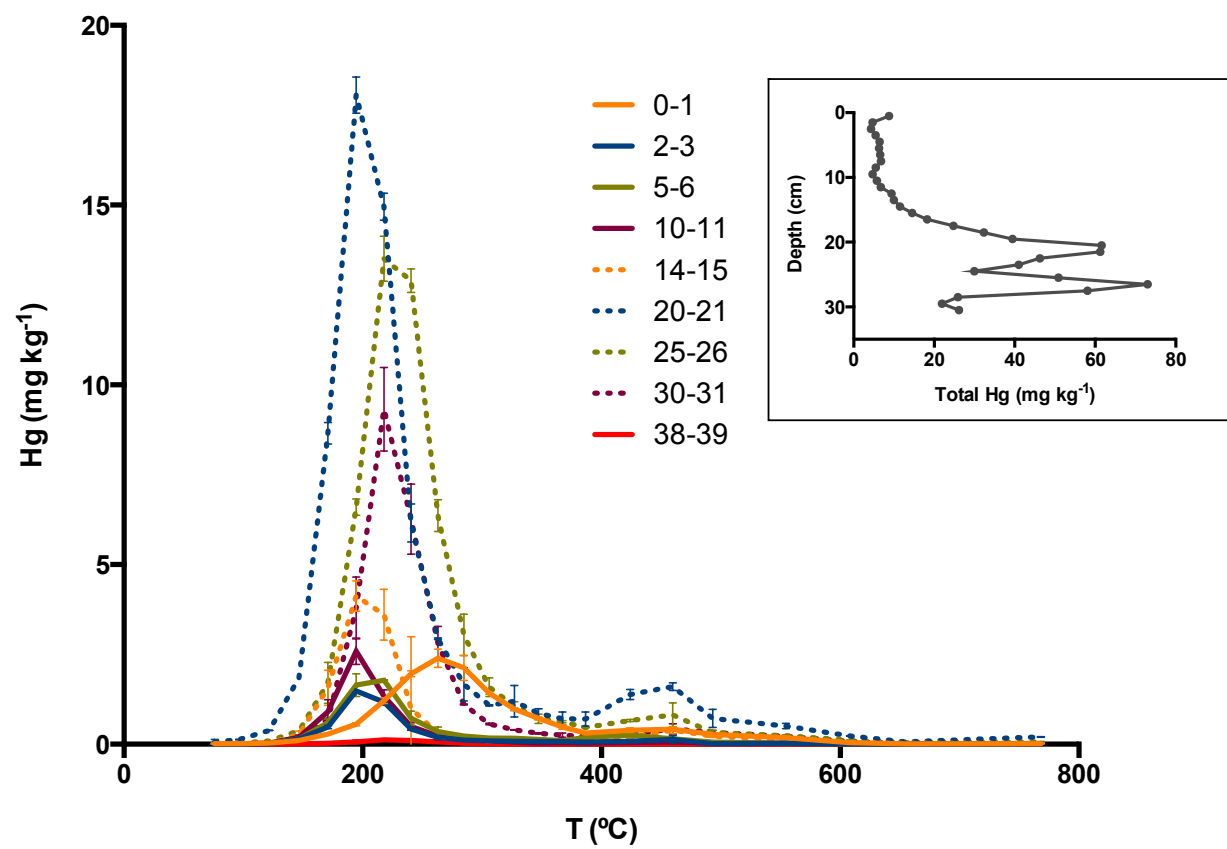




Figure 6

