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Study of mercury fractionation and thermal treatments to detect elemental mercury in soils from a contaminated area in Brazil

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Abstract

The aim of this work is to study the behavior of Hg present in soil from a contaminated area due to old gold mining activities in Brazil. It was performed quantitative analysis using the HGAAS technique, Hg speciation analysis by thermodesorption system coupled to atomic absorption spectrometer and chemical fractionation using the following: deionized water, CH_3COOH 0.1 $mol.L^{-1}$ + HCl 0.001 $mol.L^{-1}$, KOH 1 $mol.L^{-1}$, HNO_3 12 $mol.L^{-1}$, HCl 6 $mol.L^{-1}$ and aqua regia. The physical and chemical characterization of the samples along with chemical fractionation showed that the Hg is not in a mobile form. This indicates that this metal is oxidized and bound mainly to oxy-hydroxides of Fe, Al and Mn. Part of it is also linked to the humic fraction, reaching 30%. A study on the use of the heating treatment as a procedure to determine Hg^0 was also performed and it showed that part of the Hg^{2+} is reduced and volatilized at 180 °C for 48h. It shows that the methodology applied by many authors may be overestimating the quantification of Hg^0. It was also concluded that it is possible to decontaminate the soil from this and probably other contaminated areas avoiding using high temperatures.

Keywords: Sequential extraction, Speciation, Thermodesorption, Brazil.

1. Introduction

Inorganic contaminants, such as Hg warrant highlighting because of its high toxicity and mobility in ecosystems (ISSARO et al., 2009).

Metallic Hg was found buried at a site in the town of Descoberto, Minas Gerais State, Brazil in 2002 during the opening of an access road to a resident's rural property. This Hg originated from gold mining activity that began in the XIX century. The contaminated site has been isolated and constantly monitored since February 2003. The investigation of the surface soil contamination indicated that 1300 m^2 of the site had Hg concentrations greater than the value of 12 mg kg^{-1} that CONAMA, 420/2009 (Conselho Nacional do Meio Ambiente, Brazil) recommends for interventing at a contaminated agricultural site. Durão Junior et al. (2009) revealed concentrations in the site soil ranging from 0.0371 mg kg^{-1} to 161 mg kg^{-1} and found that, although the site was contaminated with Hg^0, a large part of the metal in the soil was oxidized. Although the total mercury (THg) concentration in these contaminated soils has been well

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documented, the mobility of Hg at the site is not well known. The area thus remains isolated, and no remediation plan for the area has been developed.

The mobility and reactivity of Hg in the environment depends on the form in which it is found. Hg may be found in the environment in three states of oxidation: elemental Hg (Hg^0), mercurous ion (Hg^{1+} or Hg_2^{2+}), and mercuric ion (Hg^{2+}). Hg compounds are distributed in the environment as volatile species, such as Hg^0 and dimethylmercury, reactive or water-soluble species, such as $HgCl_2$, and slightly reactive species, such as HgS (VALLE et al., 2006).

Once in the soil, Hg can be transformed in a variety of ways depending on a range of factors (SÁNCHEZ et. al., 2005). The formation of methylmercury, a key step in the biogeochemistry cycle of mercury, is associated with the pH, percentage of organic matter (OM), temperature, redox potential of the medium, presence of microrganisms, concentrations of Clay, Iron, Sulfur and Phosphorous (BISINOTI e JARDIM, 2004).

Sequential extraction methods are used to characterize the different Hg fractions in the soil and thus allow a greater understanding of the mobility of this contaminant in the environment. Sequential extraction consists of the successive addition of solutions with increasing extraction strength (HALL e PELCHAT, 2005; LIU et al., 2006; COUFALÍK et al., 2012; FERNÁNDEZ-MARTÍNEZ e RUCANDIO, 2013). This methodology facilitates the evaluation of the mineralogical phase to which the Hg is bonded and the determination of whether it is bonded to organic compounds, such as humic acids. Although the methodology does not provide an exact identification of the chemical species that are present, it does supply precise data on the biogeochemistry of the metal in sediments and soils (BLOOM et al., 2003). The correct choice of the chemical extractor reagent depends on the Hg compounds to be determined, and an adjustment of the contact time and sample/extractor ratio is very important (OKORO et al., 2012). Many authors have been used the fractionation to get information about the Hg species and/or interactions with solid matrices, as soils (COUFALÍK et al., 2012; FERNÁNDEZ-MARTÍNEZ e RUCANDIO, 2013; OKORO et al., 2012). However, no current consensus on the choice of the reagent or protocol exists to guarantee the specificity of the Hg extraction.

The thermal desorption method coupled with atomic absorption spectrometry (TDAAS) has been used and is considered one of the best methods (WINDMÖLLER et al., 1996; BIESTER e SCHOLZ, 1997; WALLSCHLÄGER et al., 1998; SHUVAEVA et al., 2008) to qualitatively detect the presence of elemental Hg in solid samples (SLADEK e GUSTIN, 2003). These authors use a constant sample heating rate and do not generally quantify the species due to difficulties in producing an analytical calibration curve. The principle of the technique is that thermal desorption occurs at different temperatures for different Hg species, and its greatest potential is the distinguishing of Hg^0 from other species of Hg^{2+} (REIS et al., 2012; 2015).

Many researchers in the literature describe the use of heating as a process to eliminate and determine Hg^0 in solid samples. Lechler et al. (1997) subjected their samples to thermal treatment at 180 °C for 48 h and found that approximately 90% of the total Hg was volatilized. These researchers considered all of the volatilized Hg to be Hg^0. Varejão et al. (2009) also submitted soil samples from a mining site contaminated with Hg to thermal treatment at 180 °C for 48 h and confirmed that approximately 50% of the total Hg was Hg^0.

Pestana et al. (2000) also used the heating conditions of 180 °C for 48 h to determine the Hg^0 in contaminated soils and observed that the percentage of Hg^0 tends to be greater than 50% if the concentration of total Hg is greater than 0.070 mg kg^{-1}. Bouffard and Amyot (2009) concluded that heating the samples at 150 °C for 2 h was "sufficient to induce the total elimination of Hg^0". Although 150 °C is less than the thermal desorption temperature for other species of Hg in sediments, these researchers stated that small quantities of other species might desorb at this temperature.

Sladek and Gustin (2003) considered the ideal thermal treatment conditions for the removal of Hg^0 to be heating at 80 ºC for 8 h, although they showed that $HgCl_2$ volatilizes under these conditions. According to Issaro et al. (2009), many errors can be generated by determining Hg^0 based on the loss of volatile Hg through heating because other compounds, such as $HgCl_2$ and Hg_2Cl_2, may also be volatilized in this process.

The objective of the present study was to evaluate the mobility and environmental availability of Hg-contaminated soils in the rural town of Descoberto in Minas Gerais, Brazil. A sequential extraction method for Hg was used in this study. Soil samples with different metal concentrations were used, and various physical and chemical characterization parameters were determined. A study on the viability of using thermal treatment as a technique for indirectly determining the amount of Hg^0 in contaminated soils was also conducted.

2. Experimental procedure

2.1. Collection of samples

The site contaminated with Hg consists of sloping land next to the watercourse that is known locally as the Rico Stream, which is a tributary of the Gama River belonging to the Paraíba do Sul River basin. The sampling points were chosen based on information from studies that were previously conducted at the site (DURÃO JUNIOR et al., 2009), which have mapped the most contaminated points.

The C4, C5, C6, E3 and E4 samples were collected from soil surface layer (upper 30 cm) of the hot spots using manual steel auger-type sampler. Samples of soil leachate carried by rainwater were also collected from the sedimentation boxes that have been constructed at the lower part of the sloping land (Bx3 and Bx4). Rainwater passes through these boxes and two tanks, which retain the particulate material before the water flows into the stream. One sample was also collected from one of these tanks (T2C1).

All samples were maintained in polyethylene plastic bags at 4 °C. They were dried at room temperature in the laboratory, disaggregated, and sieved to a granulometric fraction of less than 2.0 mm. A GPS (Global Positioning System) was used to record the geographical coordinates of the sampling points, which are shown in Table 1.

2.2. Reagents

All the reagents used were of analytical grade from Merck (Darmstadt, Germany). All the solutions and dilutions were prepared using Milli-Q water (resistivity of 18.2 MΩ cm, Millipore Direct-Q 3, Molsheim, France).

Table 1. Geographical location of the collected samples.

Sample		C4	C5	C6	E3	E4	Bx3	Bx4	T2C1
Location*	S	7632350	7632357	7632365	7632356	7632364	7632362	7632365	7632360
	W	715732	715740	715747	715709	715704	715718	715712	715708

* TM coordinates, fuse 23 K.

The calibration curves were prepared with an appropriate dilution of a standart solution from Merck (Darmstadt, Germany) with a concentration of 1.000 mg L^{-1}. Two certified reference materials (CRM) NIST 2711 – Montana Soil and NIST 1944 – New York/New Jersey Waterway Sediment with nominal values of 6.25 ± 0.19 mg kg^{-1} and 3.4 ± 0.5 mg kg^{-1} for Hg, respectively, were analyzed to evaluate the accuracy of the methods.

2.3. Determination of Al, Fe, Mn and organic matter (OM)

The amounts of Al, Fe and Mn were determined by extraction using 6.0 mol L^{-1} HCl and analysis by Flame Atomic Absorption Spectrometry (FAAS) from Perkin-Elmer (model AAnalyst 200, Shelton, USA). A volume of 40 mL of HCl was added to 1.0 g of the sample in a 50 mL vial. The samples were agitated for 18 h, centrifuged, and the supernatant was analysed.

The percentage of OM was determined using the Walkley-Black method described by Embrapa (1999). This method involves the oxidation of the OM in a potassium dichromate solution and the subsequent titration of the excess dichromate with a solution of ammonium ferrous sulfate. All analyses were conducted in triplicate.

2.4. Total mercury (THg) determination

The THg was determined by extraction at room temperature in aqua regia (3:1; HCl:HNO_3). A volume of 10 mL of aqua regia was added to a 50 mL vial with a maximum of 1.0 g of the sample. The sample was then agitated for 18 h, diluted to 40 mL, and centrifuged for 20 min at 3.000 rpm. The supernatant was analyzed by Hydride Generation (model FIAS 100, Shelton, USA) coupled to an Atomic Absorption Spectrometry (HGAAS) from Perkin-Elmer (model AAnalyst 200, Shelton, USA).

2.5. Chemical fractionation of Hg

The chemical fractionation of Hg via sequential extraction was performed on samples C4, C5, E3, Bx3, Bx4, and T2C1. CRMs to evaluate the accuracy of each extraction step are still not available, so the CRMs NIST 2711 and NIST 1944 were also subjected to the same procedure and compared to the sum of the results of all extraction steps of the samples.

The method used was modified from the method proposed by Bloom et al. (2003), which had been developed specifically to analyse the mobility of Hg in soil and sediment matrices. In this method, fractions one through four (F1 through F4) solubilize water-soluble compounds of Hg, compounds soluble in human stomach acid, Hg bound to humus, and elemental Hg, respectively. A fifth fraction (F5) was included in this study to solubilize inorganic Hg bound to oxyhydroxides of Al, Fe, and Mn because the matrix analyzed is a fully weathered red Ultisol with large quantities of these mineralogical constituents. The F6 fraction was used to extract compounds of Hg with low solubility, which are characterized as residual compounds. All extractions were performed in triplicate.

For F1 extraction, 1.0 g of sample was accurately weighed and 40 mL of deionized water were added to the sample in a 50 mL vial. The extraction was conducted by shaking on an orbital shaker at 30 rpm at room temperature for 18±4 h. The mixture was centrifuged for 20 min at 3000 rpm. The liquid phase was then separated from the solid phase. Then, 40 mL of CH_3COOH 0.1 mol L^{-1} + HCl 0.001 mol L^{-1} solution (F2) were added to the remaining solid residue and the vial was subjected to the same procedure used for the first extraction. The solid residue remaining was washed with deionized water and the next extraction was performed using 30 mL of a 1.0 mol L^{-1} solution of KOH (F3). The residues were used successively for the subsequent extractions following the same procedures. The F4 extraction was performed using 12.0 mol L^{-1} HNO_3, whereas F5 was performed with 6.0 mol L^{-1} HCl, and F6 was performed with a mixture of 6 mL of concentrated HCl and 2 mL of concentrated HNO_3 (3:1; HCl:HNO_3; aqua regia). Then, 1.25 mL of the oxidizing agent BrCl was added to the supernatants obtained in the first two extractions, and 10 mL was added to the third extraction. The solution of 0.2 mol L^{-1} BrCl was prepared immediately before use by mixing equal quantities of a solution of 1% m v^{-1} $KBrO_3$ and 20% v v^{-1} HCl to produce 0.2 mol L^{-1} BrCl. After the sample was slightly agitated, the Hg was determined by HGAAS.

The sum of the values obtained in all of the steps of the sequential extraction was compared with the value obtained in an independent extraction in aqua regia as the percent recovery value.

2.6. Thermal desorption analysis

The Hg speciation was determined using an atomic absorption spectrometer (CG Analytica model GBC 392 AA) coupled to a thermal desorption oven (TDAAS). The technique is based on heating the sample from room temperature to approximately 600 °C at a constant rate (33 °C min^{-1}). The vapors released by the samples were carried by a nitrogen flow (200 mL min^{-1}) to an atomic absorption detector cell. Thermograms, which are records of the absorbance units as a function of the temperature, were then obtained (WINDMÖLLER et al., 1996; WALLSCHLÄGER et al., 1998). The differentiation between Hg^0, Hg^{2+}, and possibly the types of bonding of the mercuric ion present in the samples were determined by comparing the obtained thermal desorption profiles with the standard Hg profiles from previous studies (VALLE et al., 2005). All samples were analysed. A mass of between 1.0 and 2.0 g was used, and the analyses were conducted at least twice.

2.7. Evaluation of thermal treatment for the determination of the Hg^0

Although the method proposed by Bloom et al. (2003) did not use a thermal treatment to quantify Hg^0 as the first step of the sequential extraction, we decided to evaluate whether this type of treatment would be appropriate for the analysis of the Descoberto samples. Two

CRM (NIST 2711 – Montana Soil and NIST 2709 – San Joaquim Soil) and two soil samples from Descoberto (C6 and E4) were used for investigation. It was not possible to use the same samples that had been subjected to sequential extraction because these had been exhausted in the previous tests; however, the two samples were collected from the same area. In each test, approximately 2.0 g of the sample was placed in a ceramic "boat" that was then heated in an oven. Two thermal treatment conditions were used, both used by other authors: 80 °C for 8 h (SLADEK e GUSTIN, 2003) and 180 °C for 48 h (LECHLER et al., 1997; PESTANA et al., 2000; VAREJÃO et al., 2009). The samples treated were submitted to quantitative analysis by HGAAS and speciation (Hg^0 and Hg^{2+}) by TDAAS. An intermediate treatment (180 °C for 3 h) was employed only to observe with more details the thermograms and look for reduced Hg species signal. Before each thermal treatment these samples were analyzed by TDAAS.

The Hg released under these treatments was evaluated using the difference between the THg concentrations before and after the thermal treatments. The analyses were conducted in triplicate.

2.8. Statistical treatment

The Pearson linear correlation coefficient was used to obtain information of the degree of correlation (r) between the variables studied. The statistical analysis was performed using the ORIGIN® (version 8.0) program.

3. Results and discussion

3.1. Characterization and sequential extraction of Hg from the soil samples

Table 2 shows the concentrations of Al, Fe, Mn and OM in the studied samples, and table 3 shows the results of the sequential extraction of Hg as percent recovery values. The aqua regia extraction was considered the total extraction, and the sum of the values obtained in all of the steps of the sequential extraction was considered a recovery percentage. Thus, the values obtained varied between 84.62% and 105.71%, which indicates good recovery.

Table 2. Chemical characterizations of the samples and CRM.

Sample	Mean ± S.D., n = 3			
	Al (%)	Fe (%)	Mn (mg kg^{-1})	OM (%)
C4	1.53 ± 0.02	3.09 ± 0.08	103.12 ± 7.40	1.53 ± 0.03
C5	1.78 ± 0.06	3.42 ± 0.03	225.65 ± 3.78	2.51 ± 0.26
E3	1.18 ± 0.01	3.20 ± 0.07	145.22 ± 1.41	2.15 ± 0.05
Bx3	0.79 ± 0.04	2.15 ± 0.25	101.12 ± 4.22	2.60 ± 0.37
Bx4	1.19 ± 0.06	2.85 ± 0.57	67.96 ± 3.25	3.72 ± 0.12
T2C1	3.17 ± 0.27	10.14 ± 3.15	307.91 ± 26.27	2.32 ± 0.01
NIST 2711	6.42 ± 0.22	2.76 ± 0.14	644 ± 32	3.10 ± 0.43
NIST 1944	4.86 ± 0.15	3.35 ± 0.12	494 ± 29	6.45 ± 0.23

Table 3. Results of the sequential extraction.

	Content of Hg (mg kg^{-1}) mean ± S.D., n = 3								
Sample	F1*	F2*	F3*	F4*	F5*	F6*	Sum of extractions	Total Hg (aqua regia)	Recovery (%)
C4	0.17 ± 0.03	0.22 ± 0.01	0.34 ± 0.05	0.18 ± 0.03	0.22 ± 0.02	< LD	1.13	1.30 ± 0.17	86.92
C5	0.40 ± 0.03	0.50 ± 0.12	0.88 ± 0.09	0.31 ± 0.01	3.62 ± 0.13	< LD	5.71	6.51 ± 0.38	87.71
E3	0.14 ± 0.01	0.13 ± 0.02	0.34 ± 0.05	<LD	0.40 ± 0.03	< LD	1.01	1.16 ± 0.05	86.41
Bx3	0.26 ± 0.06	0.17 ± 0.03	3.13 ± 0.51	3.23 ± 0.46	15.98 ± 0.40	< LD	22.77	21.54 ± 1.46	105.71
Bx4	0.07 ± 0.01	< LD	6.04 ± 0.04	0.34 ± 0.01	9.93 ± 0.84	0.12 ± 0.03	16.50	18.16 ± 0.28	90.86
T2C1	0.08 ± 0.01	0.16 ± 0.01	1.91 ± 0.07	11.80 ± 0.79	50.29 ± 0.40	0.90 ± 0.02	65.14	68.93 ± 1.48	94.50
NIST 2711	0.39 ± 0.01	0.29 ± 0.07	1.42 ± 0.10	1.15 ± 0.25	2.55 ± 0.53	< LD	5.80	6.68 ± 0.21	86.83
NIST 1944	0.18 ± 0.03	0.29 ± 0.02	0.85 ± 0.07	0.21 ± 0.01	1.55 ± 0.15	< LD	3.08	3.64 ± 0.26	84.62

LD = 0.06 mg kg^{-1} considering a sample mass of 1.0 g.

* F1= Hg solubilized in water; F2= Hg solubilized in human stomach acid; F3= Hg bound to humus; F4= elemental Hg; F5= Hg bound to oxyhydroxides of Al, Fe and Mn; F6= residual Hg.

The Hg recoveries of the certified materials NIST 2711 and NIST 1944 with respect to the certified value were 84.62% and 86.83%, respectively. Fig. 1 shows graphics of the percentage of Hg extracted from the studied samples in each extraction step. It can be observed that the fractions of Hg that are soluble in water (F1) and in stomach acid medium (F2) were low in four of the samples (C5, Bx3, Bx4 and T2C1), which indicates low availability of the metal in these samples.

The greatest percentage of Hg bonded to the humic fraction (F3) was found in sample Bx4 (36.3%), which, amongst the samples collected from the contaminated site, also had the greatest amount of OM (3.72%). The appearance of sample Bx4 shows that this soil has very fine granulometry. This soil sample, which was carried to a sedimentation box by rainwater, exhibited high concentrations of Hg (18.16 ± 0.28 mg kg^{-1}). The certified sample NIST 1944 also exhibited a relatively high percentage of Hg in this extraction step (27.1%) and the greatest amount of OM amongst the studied samples. Although the number of samples was not large, the results indicate that the interaction of Hg with OM is important in these samples.

The fifth extraction step (F5) showed greater concentrations of Hg in nearly all of the samples (Fig. 1).

This step principally extracts the metal bonded to the oxyhydroxides of Al, Fe and/or Mn. Boszke et al. (2006; 2008) found that extraction with HCl can also solubilize Hg bonded to humus; however, an earlier step in the protocol used in the present study served this purpose. Hence, the possibility of Hg bonded to organic compounds being quantified during this extraction step (F5) was not considered. The amount of soluble Hg extracted from sample T2C1 in this step was approximately 50.29 mg kg^{-1}. Because the concentration of THg in this sample was 68.93 mg kg^{-1}, the percentage of Hg extracted in this step was close to 77.2%. The analysis of the data in Table 3 and Fig. 1 revealed that a relationship exists between the concentration of THg and the percentage of Hg in F5: a greater concentration of Hg results in a greater percentage of Hg extracted by HCl.

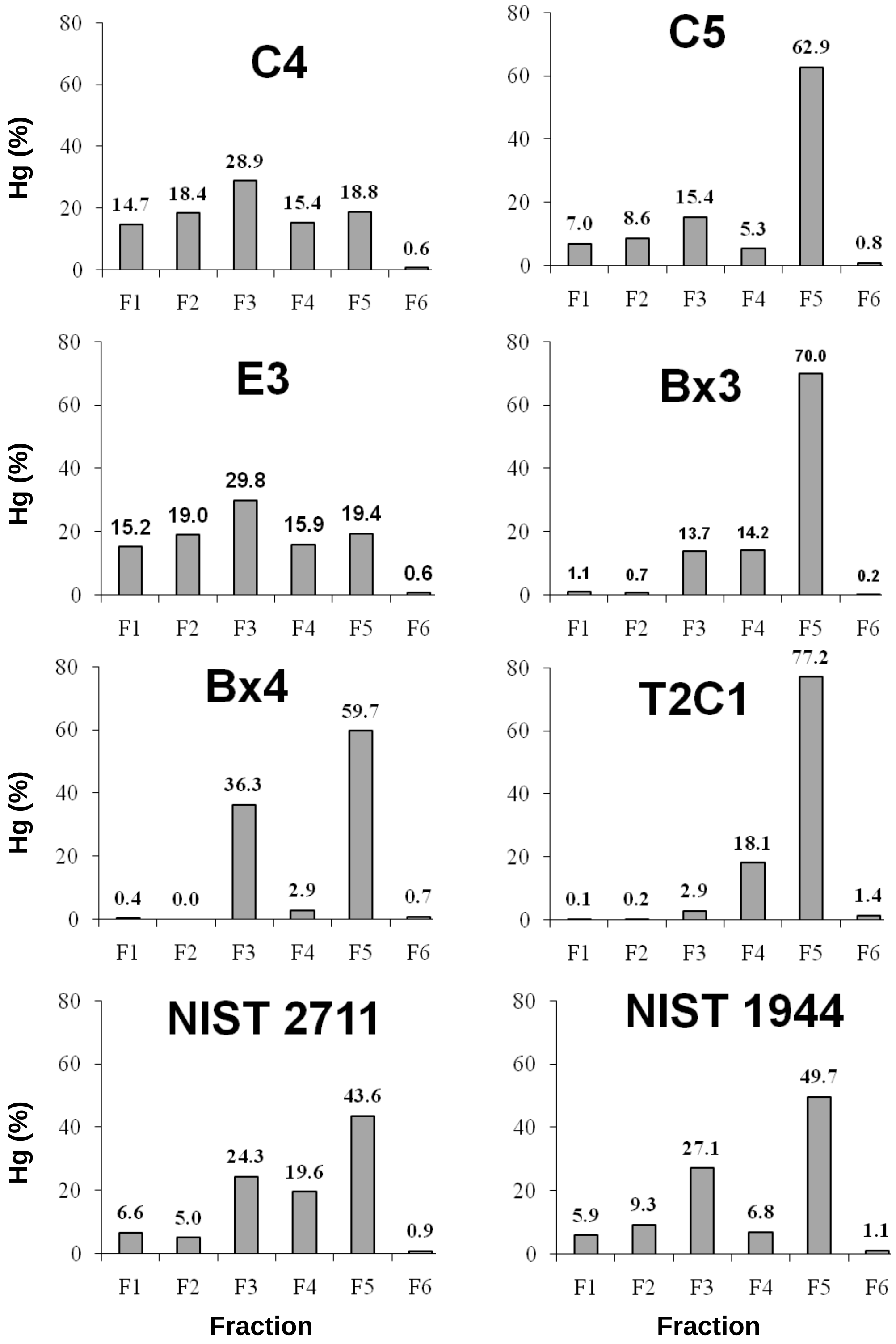

Figure 1. Percent of Hg extracted in each step of the fractionation.

The certified samples (NIST 2711 and NIST 1944) also exhibited higher concentrations of Hg in F5. With the exception of C4 and E3, all the other samples had a higher Hg concentration in this extraction step. It can also be observed that the C4 and E3 samples had a higher percentage of Hg in the more labile fractions. Coincidently, these samples also had the lowest concentration of THg probably because the Hg present is weakly bound to them. The certified samples exhibited similar profiles for the percentage of Hg in each fraction. The highest percentages of Hg in the certified samples were found in F5: 43.6% in NIST 2711 and 49.7% in NIST 1944.

The inclusion of the fifth extraction step was especially important because the majority of Hg would have been extracted in the residual fraction if this step had not been performed. The concentration of Hg in the residual fraction (F6) was very low in all of the samples studied. Kocman et al. (2004) expected that aqua regia will mainly extract Hg in cinnabar. According the technical report published by CDTN/FEAM (2005), the mineralogical data obtained through X-ray diffraction for the soil in the Descoberto contaminated site do not reveal the existence of cinnabar. However, these researchers do not discount the presence of other sulfide minerals in the location. The same report showed that the soil at the site is rich in hematite, gibbsite, and goethite, which explains the higher concentration of Hg in F5.

The thermograms (Fig. 2) show that there is a predominance of Hg^{2+} in the contaminated soil, even though the source of Hg at the site is Hg^0 from gold mining activities. This conclusion was drawn from the absorption signal observed at temperatures higher than 200 ºC, which is characteristic of Hg^{2+} (REIS et al., 2012). The absorption signal at temperatures less than 200 ºC is characteristic of reduced Hg species and was found to be significantly smaller compared with the signals above 200 ºC (VALLE et al., 2005; 2006).

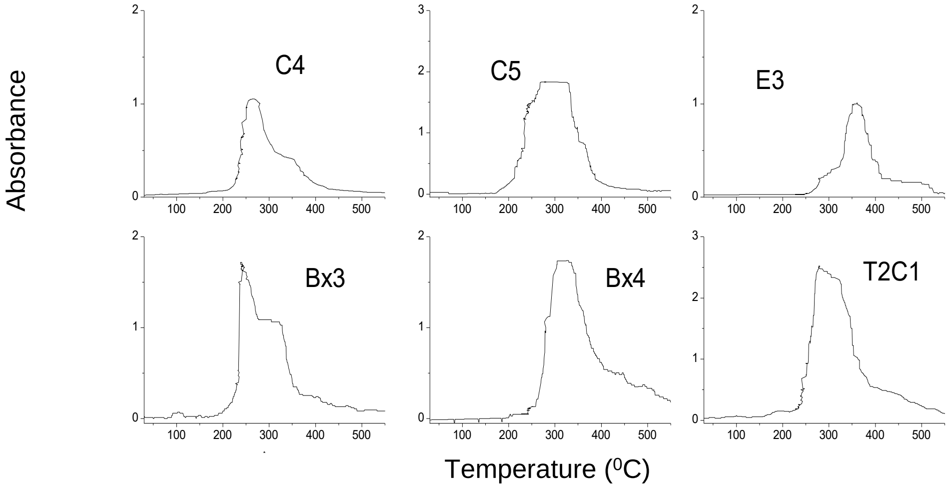

Figure 2. Thermograms of soil samples.

The concentration of Hg, which is present as the source of the soil contamination, that is not released to the atmosphere suffers oxidation over the years, and Hg^{2+} may be adsorbed on clay minerals, complexed with OM, and even transported by rainwater to watercourses. The desorption signal for Hg in the samples with a higher concentration of THg, such as Bx3, Bx4 and T2C1, appeared slightly below 300 °C and reached a temperature higher than 450 °C. The high- temperature Hg signal indicates that some of the metal is strongly bonded to the soil constituents. Thus, this finding helps explain why there is little mobility of the metal in the sequential extraction of Hg.

The peak of Hg bound to mineral phases appears at temperatures from 200 to 350 ^{0}C (VALLE, 2006). The thermograms show that the samples C5, Bx3, Bx4 and T2C1 present a peak with maximum release of Hg at about 300 ^{0}C (Fig. 2), indicating Hg bound to mineral phases. Similar results were reported by other researchers elsewhere (BIESTER et al., 2002; SÁNCHEZ et al., 2005). The comparison of these data to the results obtained from the Hg fractionation experiment revealed that these samples exhibit a greater percentage of Hg in F5 extraction step (Fig. 1).

In fact, comparisons of the results of the qualitative analysis of the Hg species by TDAAS and the sequential extraction method are very complex because the chemical fractionation of Hg identifies the compounds that are solubilized by the employed extraction solutions and not the Hg species. TDAAS does not allow the estimation of the mobility of Hg in the fraction that is soluble in water, which can be achieved through sequential extraction (BIESTER e SCHOLZ, 1997). This system principally distinguishes Hg^0 from Hg^{2+} in solid matrices and also evaluates the strength with which the metal binds to the soil constituents.

It is important to state that the surface soil at the upper part of the contaminated site can be transported to water systems by rainwater. These water systems may have conditions that are more suited to Hg methylation and may form more toxic species of the metal.

3.2. Correlations

The concentration of Al varied between 0.79 and 3.17% (w/w), and the concentrations of Fe and Mn varied between 2.15 and 10.14% (w/w) and between 67.96 and 307.91 mg kg^{-1}, respectively (Table 2). The concentration of Hg in the samples studied varied between 1.03 and 68.93 mg kg^{-1} (Table 3). Some correlations can be clearly observed between the values obtained. For example, the sample with the highest concentration of THg (T2C1) also had the highest concentrations of Al, Fe and Mn.

The Pearson correlation coefficient test was used to evaluate the correlation between the concentrations of THg, Al, Fe and Mn, the percentages of Hg in the different extraction steps, and the percentage of OM in the soil. The correlation matrix obtained is given in Table 4. The values in bold are statistically significant ($p < 0.05$). Amongst the correlations observed, there was a significant positive correlation between the concentration of THg and the sum of F4, F5, and F6 ($r = 0.819$). These data show that Hg is more abundant in the less labile soil fractions, i.e., in the extractions with 12 mol L^{-1} HNO_3 (F4), 6 M HCl (F5), and aqua regia (F6). The inverse, which is the contribution of the more labile fractions (F1 + F2 + F3), were negatively correlated with the concentration of THg ($r = -0.830$). For example, the T2C1 sample, which had the highest concentration of THg (Table 3), had the lowest percentage of Hg in F1, F2, and F3. Those samples with lower concentrations of THg, such as E3, had the highest percentage of Hg in the more labile fractions.

Table 4. Pearson correlation matrix of all the determined parameters in the soil samples.

	F1	F2	F3	F4	F5	F6	F1+F2	F4+F5	F5+F6	F1+F2+F3	F4+F5+F6	OM	Fe	Al	Mn	Hg
F1	1															
F2	**0.9996**	1														
F3	0.43265	0.41901	1													
F4	0.26814	0.27574	-0.45297	1												
F5	**-0.94069**	**0.93631**	-0.65639	-0.2195	1											
F6	-0.22453	0.19701	-0.45075	0.15314	0.30694	1										
F1+F2	**0.99987**	**0.99992**	0.42505	0.27243	**-0.93833**	-0.20914	1									
F4+F5	**-0.89805**	**-0.8917**	-0.78404	0.02097	**0.9708**	0.3522	**-0.89458**	1								
F5+F6	**-0.93968**	**0.93493**	-0.6599	-0.21631	**0.99991**	0.3199	**-0.93711**	**0.97148**	1							
F1+F2+F3	**0.88675**	**0.87971**	**0.80032**	-0.05454	**-0.96205**	-0.37237	**0.88289**	**-0.99929**	**-0.96307**	1						
F4+F5+F6	**-0.89662**	**0.88989**	**-0.78653**	0.02311	**0.97019**	0.36503	**-0.89294**	**0.99991**	**0.97106**	**-0.9995**	1					
OM	-0.70864	0.71618	0.24156	-0.74133	0.54257	-0.04284	-0.71293	0.37371	0.53952	-0.34692	0.37112	1				
Fe	-0.35073	0.32588	-0.67983	0.45697	0.42651	**0.90856**	-0.33685	0.54945	0.43762	-0.5758	0.5599	-0.14146	1			
Al	-0.24282	0.21575	-0.64781	0.33535	0.37103	**0.95649**	-0.22768	0.46268	0.38308	-0.48688	0.47429	-0.21427	**0.95741**	1		
Mn	-0.19534	0.17051	**-0.81101**	0.32843	0.42832	**0.82235**	-0.18145	0.51969	0.43819	-0.54092	0.52903	-0.25621	**0.84892**	**0.89031**	1	
Hg	-0.69979	0.68319	-0.71875	0.35282	0.70874	0.70008	-0.69056	**0.81305**	0.71559	**-0.83029**	**0.81905**	0.14814	**0.89246**	0.77551	0.66445	1

The values in bold are statistically significant ($p < 0.05$)

There is also a significant negative correlation between the concentration of Hg bonded to OM (F3) and the concentration of Mn (r = -0.811). This correlation indicates that the contribution of OM-bound Hg is lower when the interaction of Hg with Mn oxyhydroxides is predominant. An example of this is T2C1 sample. Furthermore, the sample with the lowest concentration of Mn in the F3 fraction resulted in a higher extraction of Hg in this step (F3).

This was the case with, for example, sample Bx4. It is well known that clay minerals containing Fe and Mn have a large capacity of adsorption, can control the concentrations of other ions, such as Hg, and retain OM. In the present study, no strong correlation was found between the percentage of OM in the soil and any other parameter. However, as discussed earlier, the data in Table 2 and Fig. 1 show that the Bx4 sample, which exhibited a high percentage of OM (3.72%) amongst the samples studied, had the largest amount of Hg extracted in F3 (36.3%) and F5 (59.7%).

This finding indicates that the interaction of Hg with humus present in the samples is also relevant, although the interaction with clay minerals appeared to be more important in the characterization of this material. Another sample that showed this same profile was the certified sample NIST 1944, which had the highest OM mass percentage (6.45%) and a high percentage of Hg in the humic fraction (27.1%). These correlations between Hg and other metals with OM and clay minerals are well established.

For example, Guedron et al. (2009) found a high positive correlation between the quantity of the clay fraction and the concentration of Hg extracted in the fractions bound to Fe and Al oxyhydroxides and OM. According to the same authors, these high correlations can be explained by the fact that the clay fraction is mainly composed of Fe and Al oxyhydroxides and OM containing –S groups.

3.3. Thermal treatment as a technique for determining Hg^0

Table 5 shows the values of the THg concentration in the certified reference samples (NIST 2709 and NIST 2711) and their respective certified values, as well as the values obtained before and after the thermal treatment. This table also shows the values of the THg concentration in two soil samples (C6 and E4), which were collected from the contaminated site of Descoberto, before and after the two thermal treatments studied (180 °C for 48 h and 80 °C for 8 h).

The detection limit for the method was 0.05 mg kg^{-1}, and the sample mass was 1.0 g. The LQ value was found to be 0.18 mg kg^{-1}. The recovery values of Hg in the certified materials analyzed (NIST 2711 and NIST 2709) were 95.5% and 107.8%, respectively. These values agree with the certified values to a 95% confidence level (n=3).

If the THg volatilized by thermal treatment at 180 °C for 48 h was Hg^0, the results show a predominance of Hg^0 in all of the samples studied (Table 5). However, the contribution of Hg^0 to the total Hg concentration in highly contaminated soils can vary depending on the Hg source and/or the soil properties and/or the environmental conditions. It is therefore essential to choose the correct methodology for the determination of Hg^0 to obtain accurate results. For example, reports of studies on soils that were highly contaminated with $Hg(NO_3)_2$ using sequential extraction and did not detect Hg^0 (BLOOM et al., 2003).

However, studies utilizing thermal desorption and a thermal treatment to determine the concentration of Hg^0 and found higher concentrations of Hg^0 in soils contaminated with the same form of Hg (BOSZKE et al., 2008).

Table 5. THg contents and percentage of volatilized Hg due to thermal treatments.

Sample	Certified value C_{Hg} (mg kg^{-1})	Measured value C_{Hg}^* (mg kg^{-1})	Measured value after thermal treatment at 180 °C/48 h		Measured value after thermal treatment at 80 °C/8 h	
			C_{Hg}^* (mg kg^{-1})	(%) Hg volatilised	C_{Hg}^* (mg kg^{-1})	(%) Hg volatilised
NIST 2709	1.40 ± 0.08	1.51 ± 0.03	0.26 ± 0.04	82.78	1.27 ± 0.05	9.05
NIST 2711	6.25 ± 0.19	5.97 ± 0.29	0.59 ± 0.09	87.81	4.72 ± 0.10	18.93
C6	---	13.21 ± 0.98	1.61 ± 0.14	90.12	10.71 ± 0.46	20.94
E4	---	3.80 ± 0.64	0.91 ± 0.05	76.05	3.20 ± 0.28	15.79

[a] Mean ± S.D., n = 3

The amount of Hg eliminated by thermal treatment at 180 °C for 48 h in the four samples studied was in the range of 76.05% to 90.12% of THg. If we consider that this treatment eliminates only Hg^0, one can conclude that Hg^0 is the predominant specie in these samples. This hypothesis contradicts the previous results that were obtained using sequential extraction and thermodesorption analysis.

The association of Hg with metal oxides (Al_2O_3, MnO_2, and Fe_2O_3) and OM contributes to the stabilization of Hg in its oxidized form. Studies conducted by Durão Junior et al. (2009), revealed that Hg^{2+} is predominant in the Descoberto soil. It is also possible that part of the Hg^0 contaminating this location volatilizes during the summer, when the temperatures in this region are high, and the oxidized metal remains in the soil.

The other thermal treatment used in this study was heating at 80 °C for 8 h. Under this condition, the concentration of Hg volatilized from the samples studied varied between 9.05% and 20.94%. The certified sample NIST 2709, which had a lower concentration of THg (1.27 ± 0.05 mg kg^{-1}) also, exhibited a lower percentage of Hg volatilized at this temperature (9.05%). Studies of sequential extraction of Hg conducted using NIST 2711 (as described in section 3.1) reported a concentration of Hg in F4 of 1.15 ± 0.25 mg kg^{-1}, which corresponds to the extraction of Hg^0 (BLOOM et al., 2003). This value is equivalent to 19.6% of the THg concentration (Fig. 1). The concentration of Hg volatilized by thermal treatment at 80 ºC for 8 h in the same sample was 4.72 mg kg^{-1}, which corresponds to 20.94% of the THg volatilised. The comparison of the results obtained with the two methodologies used to quantify Hg^0 using Student's *t* test indicated agreement to a 95% confidence level. This milder heating condition thus appears to be the best methodology for the quantification of Hg^0 in these soils. However, it is also possible that some of the Hg^{2+} present is reduced and volatilized under this sample heating conditions.

The extraction of Hg by heating a sample of glass powder doped with $HgCl_2$ for 8 h at 80 °C confirmed that approximately 84% of the Hg was volatilized (SLADEK e GUSTIN, 2003).

Fig. 3a shows the thermograms for the certified reference samples (NIST 2711 and NIST 2709) before and after the three thermal treatments. All thermograms show the same Hg thermal release pattern of the samples submitted to the Hg fractionation study.

As has been mentioned previously, studies using a heating rate of 33°C utilizing the TDAAS system and spiking soil samples with different Hg species found that the thermal desorption band for Hg^0 occurs from room temperature to approximately 180 °C. The mercurous ion (Hg_2^{2+}) undergoes thermal desorption at higher temperatures (from 180 °C to approximately 240 °C). The thermal desorption of the mercuric ion (Hg^{2+}) occurs at temperatures higher than 200 °C (VALLE et al., 2006).

The thermogram of the NIST 2711 sample (Fig. 3a) shows that the thermal desorption signal for Hg appears at approximately 200 °C, which indicates that Hg^{2+} predominates. The thermal treatment of the sample for 3 h at 180 °C demonstrated that Hg was reduced from the oxidized state (it is possible to see an absorption signal appearing at lower temperatures, which is characteristic of the lower oxidation states). In this sample (NIST 2711), the desorption signal for the Hg starts to increase at approximately 100 °C. The thermogram obtained after the thermal treatment of the sample at 180 °C for 48 h shows that practically all of the Hg^{2+} was reduced and volatilized, as indicated by the almost complete disappearance of the absorbance signal. When the sample was thermally treated at 80 °C for 8 h, the Hg desorption signal in the thermogram appeared at approximately 200 °C. The same Hg desorption profile was observed in the thermogram of the sample that was not subjected to any thermal treatment.

The analysis of the NIST 2709 sample (Fig. 3a) revealed that the integration area signal in the thermograms decreased for the samples that were thermally treated at 180 °C compared with the samples that were not subjected to any thermal treatment. It can be observed that Hg^{2+} ($T > 200$ °C) predominates in the untreated samples. The thermogram of the sample that was treated at 180 °C for 3 h shows that Hg was reduced and volatilized. An increase in the sample heating time (180 °C for 48 h) resulted in a more significant loss of Hg, and the desorption signal appeared at a higher temperature (approximately 300 °C). The proposed experiment showed that part of the Hg^{2+} was reduced from its oxidation state and was volatilized, leaving only Hg^{2+} more strongly bound to the matrix.

Fig. 3b shows thermograms of the two soil samples (C6 and E4) collected in Descoberto, before and after the studied thermal treatments. The Hg desorption signal of the two samples before thermal treatment appeared at approximately 200 °C. Therefore, Hg^{2+} predominates in the two samples studied. A very small quantity of Hg^0, which was below the technique detection limit (0.1 mg kg^{-1}), was observed, i.e., Hg^0 was not detected in the untreated samples (WINDMÖLLER et al., 1996).

The thermograms of the samples subjected to thermal treatment at 80 °C for 8 h showed a profile like the untreated samples, but with a smaller signal integration area. The determination of the Hg speciation using TDAAS after the sample was heated in an oven at 180 °C for 3 h gave thermograms with a small Hg signal starting at a temperature less than 200 °C. This experiment showed that the heat treatment of the sample causes reduction of the metal. The decrease in the integration area is further evidence that the Hg reduced is lost by volatilization. The same result was obtained when the samples were treated at 180 °C for 48 h. The Hg signal area of desorption decreased significantly after the two samples were subjected to this thermal treatment.

The use of a thermal treatment at 180 °C for 48 h to determine the elemental Hg was also investigated by Guedron et al. (2009). In these studies, samples of marine sediments did not exhibit significant desorption of Hg, whereas nearly 70% of the THg in sandy soils was desorbed under the same procedure. It is assumed that, in addition to Hg^0, the OM-bound Hg was partially desorbed during the thermal treatment.

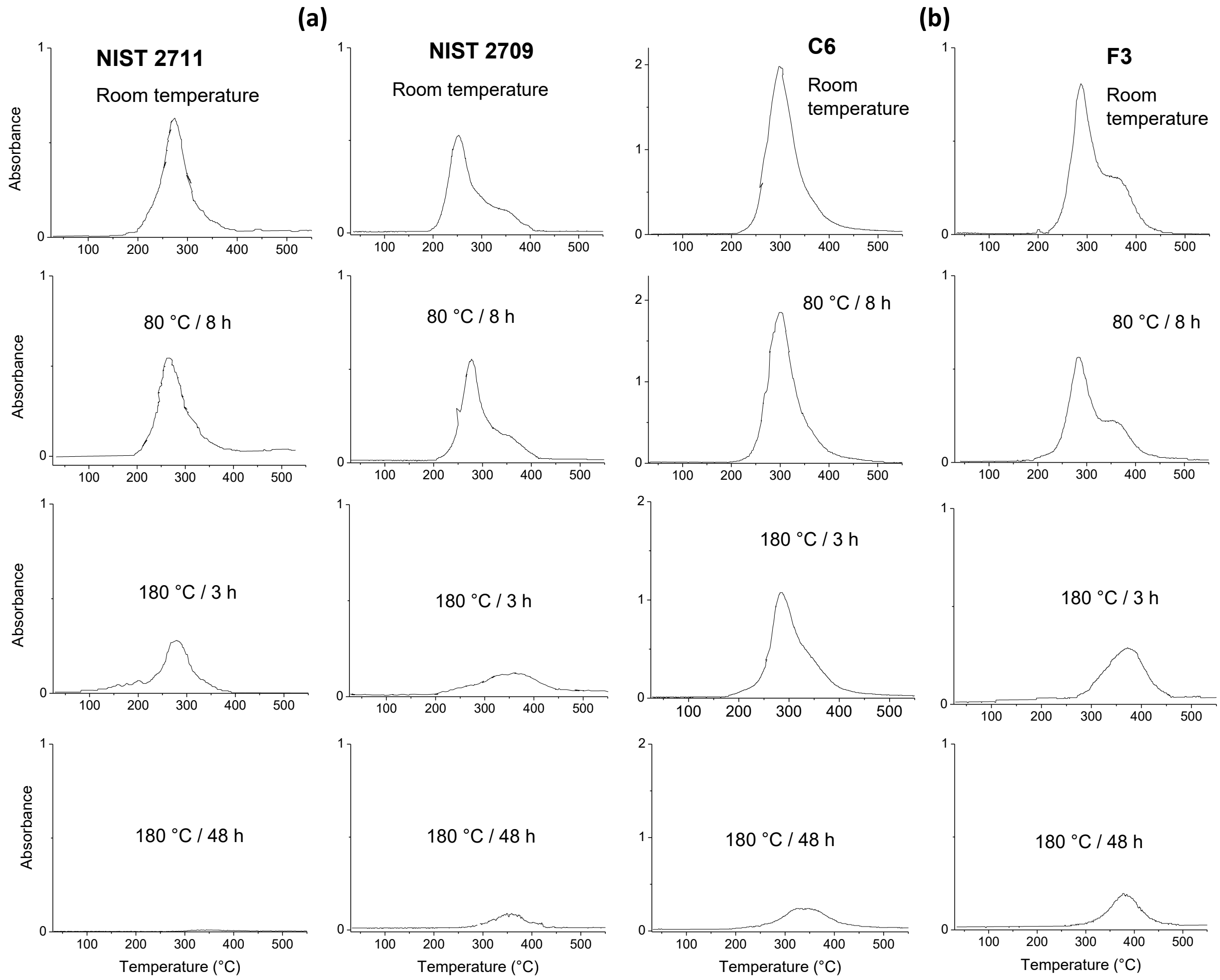

Figure 3. Thermograms of CRM (a) and of soil samples (b) submitted to thermal treatments.

4. Conclusion

This work studied soil samples from the gold mining activities in the XIX century. The results of sequential extraction showed that the Hg present in Descoberto is only slightly available to the solubilisation processes that can occur in the environment. A large part of the metal, which had contaminated the environment as Hg^0, oxidised and is principally bound to Fe, Mn and Al oxyhydroxides. Some of the Hg^0 probably volatilised during high temperature periods at this site and mainly oxidised metal remains in the soil. Some of this Hg is also bound to the organic matter, in some cases reaching 30%. Although Hg showed low mobility as a soluble form, it is important to consider that the related area is very steep. Therefore, the surface soil of the contaminated site is capable to be carried over to other water systems by rainwater. More suitable conditions to Hg methylation might occur and therefore might form most toxic species of the metal.

The use of the thermal treatment to determine Hg^0 concentration showed that the heating at 180 °C for 48 h promoted the reduction of Hg and its subsequent volatilisation, that means this condition is not appropriated. Although there is not much research that uses milder temperatures, such as at 80 °C for 8 h, they are more proper to this evaluation. These findings also indicate that it is possible to use the thermal treatment to decontaminate the soil from this and probably other areas without needing high temperatures.

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