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RESEARCH ARTICLE

Sustainable remediation of mercury contaminated soils by thermal desorption

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Abstract Mercury soil contamination is an important environmental problem that needs the development of sustainable and efficient decontamination strategies. This work is focused on the application of a remediation technique that maintains soil ecological and environmental services to the extent possible as well as search for alternative sustainable land uses. Controlled thermal desorption using a solar furnace at pilot scale was applied to different types of soils, stablishing the temperature necessary to assure the functionality of these soils and avoid the Hg exchange to the other environmental compartments. Soil mercury content evolution (total, soluble, and exchangeable) as temperature increases and induced changes in selected soil quality indicators are studied and assessed. On total Hg, the temperature at which it is reduced until acceptable levels depends on the intended soil use and on how restrictive are the regulations. For commercial, residential, or industrial uses, soil samples should be heated to temperatures higher than 280 °C, at which more than 80 % of the total Hg is released, reaching the established legal total Hg level and avoiding eventual risks derived from high available Hg concentrations. For agricultural use or soil natural preservation, conversely, maintenance of acceptable levels of soil quality limit heating temperatures, and additional treatments must be considered to reduce available Hg. Besides total Hg concentration in soils, available Hg should be considered to make final decisions on remediation treatments and potential future uses.

Keywords Soil contamination · Total mercury · Available mercury · Remediation · Thermal desorption · Solar furnace

Introduction

Mercury (Hg) is one of the most toxic heavy metals and is considered as a global contaminant. Hg^0 is the predominant form of Hg in the atmosphere and has a long residence time in it (from 6 months to 2 years). Therefore, it can be transported and deposited to remote places away from the source (Adriano 2001). This element has left an important record in the history of humankind (Gochfeld 2003).

Hg is released to atmosphere from natural sources, including volcanoes and geothermal activities, wild fires, and weathering of rocks and soils, and from anthropogenic sources. Human activities that release Hg into atmosphere are silver and gold mining, chemical industry, metal smelting, combustion of fossil fuels, waste incineration, chloro-alkali production, or Hg mining district (Xu et al. 2015). Furthermore, Hg that has been deposited from the atmosphere can be repeatedly emitted again in various ways (United Nations Environment Programme (UNEP) 2008). Hg mining has left a record in Europe because more than half of the total Hg produced and extracted in the world has been mined in European mines (Schroeder and Munthe 1998). Among them, Almadén has been the greatest

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and oldest Hg mining site in the world producing one third of the globally mined Hg in two millennia of activity (Hernández et al. 1999; Hernández Sobrino 2007; Higueras et al. 2006; Arrayanes SA 2015). The Almadén Hg mining district included cinnabar extraction sites, storage areas, and metallurgical plants. The mine closed down completely in 2003.

Hg is scarce in the lithosphere, and normal soils are expected to have Hg levels up to 0.3 mg kg^{-1} (Adriano 2001; Alloway 2013) because of a cross-border effect that makes numerous sources of Hg emissions to cause an increasing of Hg levels in soil, water, and sediments globally (Biester et al. 2002). In the case of the Almadén mining district, their soils have significant contents of Hg even in zones far from pollution sources because of the anthropogenic impact besides lithological features of the area. Several authors (Higueras et al. 2006; Lingberg et al. 1979; Millán et al. 2011, 2006; Schmid et al. 2003; Sierra et al. 2012) measured total Hg concentrations in surface soils ranging from 0.5 to 8889 mg kg^{-1}.

According to the particular problem that we face, different treatment processes such as stabilization/solidification techniques, in situ vitrification, electrokinetic technique, soil washing, phytoremediation, or thermal desorption among others have been used for the remediation of a specific Hg-contaminated soil (He et al. 2015; Negrete and Barboza 2013; Wang et al. 2012; Xu et al. 2015). Stabilization is the process of converting Hg into chemical forms that are stable and highly insoluble over wide ranges of pH and redox conditions in soil (United States Environmental Protection Agency (US EPA) 2007). Solidification is the encapsulation of the stabilized Hg forms in a rigid and durable (López et al. 2015; Mulligan et al. 2001). Vitrification involves heating of contaminated soils to melting point and cooled to form a solidified, chemically inert, vitreous mass wherein the contaminants are immobilized (United States Environmental Protection Agency (US EPA) 1997a). These techniques are costly and can increase the volume of the contaminated area or may pose risks in a longer term (He et al. 2015). The electrokinetic technique uses a low-intensity direct current between a cathode and an anode imbedded in the contaminated soil (United States Environmental Protection Agency (US EPA) 1997b; Virkutyte et al. 2002) to facilitate the movements of ions, charged small particles, and water. Anions move toward the positively charged electrode (anode) and cations move toward the negatively charged electrode (cathode). In the case of Hg-contaminated soils, this technique can be difficult because Hg has a low solubility in most natural soils (Cox et al. 1996). Soil washing involves extraction of contaminants from soil using an appropriate washing solution such as water, containing chemicals, or an organic extractant (United States Environmental Protection Agency (US EPA) 1997a). To improve Hg removal efficiency because it strongly adsorbs to soils and/or is present in insoluble complexes, chemicals are usually added (He et al. 2015). Subirés-Muñoz et al. (2011) found that washing soil from an Almaden (Spain) mining district with high mercury concentration (1000 mg kg^{-1}) could achieve 35 % Hg removal. Phytoremediation makes use of plant growth to degrade or remove pollutants from a contaminated area (He et al. 2015). Finally, thermal treatment involves heating to remove Hg from soil through volatilization. It is based on the unusual high volatility of this heavy metal and is usually carried out ex situ. It converts mercurial compounds into the volatile Hg. By raising the soil temperature, the vapor pressure of the contaminant increases producing a mass transfer into the gas phase which is collected and further treated (Chang and Yen 2006; Chang et al. 2009; Navarro et al. 2009; United States Environmental Protection Agency (US EPA) 2007) to avoid the Hg transfer from one environmental compartment to another. A typical thermal desorption unit for Hg removal operates at temperatures from 320 to 700 °C (United States Environmental Protection Agency (US EPA) 2007), and it is one of the few methods that are effective for very high Hg concentrations (Xu et al. 2015). There are previous preliminary studies that have demonstrated the viability of the Hg release at temperatures between 127 and 600 °C (Chang and Yen 2006; Chang et al. 2009; Matsuyama et al. 1999; Navarro et al. 2009, 2014; Palmieri et al. 2006). Hg will be released at different temperatures depending on the phase to which it is linked (Navarro et al. 2009, 2014). Studies about the remediation of Hg-polluted soils by thermal desorption at low temperature have shown Hg removal of over 99 % in sand matrices (Kunkel et al. 2006); negligible values in mining soils and residues which have a great percentage of pyrite and cinnabar in their composition; 76 % in mining soils and residues which have the most of Hg from atmospheric deposition (Navarro et al. 2009); and the thermal treatment of an Hg-contaminated soil (69 mg kg^{-1}) with a common chloridizing agent ($FeCl_3$) at a reduced temperature (400 °C) reduced to a level below the maximum mercury concentration allowed for soil in China (Fujun et al. 2014). The cost of this technique is high because of the high temperature process and the specialized facilities required, but it also has high efficiency. In this way, use of solar energy instead of conventional non-renewable energy sources has been proposed recently (Navarro et al. 2009; Wang et al. 2012) in order to lower that cost.

This work proposes using solar energy as primary energy source to carry out thermal desorption of Hg by solar furnace on soils from Almadén with different land uses. This technology could be applied in many developing countries where solar energy is one of the most sustainable and cheap energy sources, and where, nowadays, Hg is a real and serious environmental problem that affects to the population in artisanal gold mining areas, Hg mines, chlor-alkali plants, among others (Bose-O'Reilly et al. 2010; Veiga et al. 2014).

The natural mobilization of Hg from soil by incident solar radiation is well-known in a theoretical way (Gustin et al.

2002), but there are scarce works about evaluating the use of solar energy as an option for the treatment of Hg-contaminated soils. Navarro et al. (2009, 2014) implemented it to Hg-contaminated soils from Valle del Azogue and Bayarque mines. Those works only focused on the solar furnace operation and the percentage of Hg released during process while the present work goes one step further. It focuses on the study and evaluation of physico-chemical characteristics and distribution of Hg (total, soluble, and exchangeable) in soils from field after heating them to different temperatures in order to assess the effectiveness of the thermal desorption process considering their future use. To get that objective, two scenarios were compared: an agricultural soil with high Hg background and a marginal soil from an abandoned Hg metallurgical site. Given that soil is a natural resource that is being lost irreversibly and progressively worldwide, there is a need to protect it, as far as possible, and pay more attention to search more friendly soil decontamination techniques. Therefore, the final goal of this pilot scale study is to develop scientific bases to evaluate the optimal range of temperatures at which an Hg-contaminated soil would be remediated considering the future soil use, protecting as far as possible soil quality characteristics and minimizing risks for human and environmental health.

Material and methods

Selection and characterization of the study soils

The Almadén mining district, situated in the province of Ciudad Real in Southwest of Spain, has been the greatest and oldest Hg mining site in the world where Hg is mainly in cinnabar form. Considering this latter fact, physico-chemical characteristics and land uses of different sites within Almadén (Millán et al. 2011, 2006; Sierra et al. 2011, 2012; Burt and Soil Survey Staff 2014), two different soils from each other, were selected to implement thermal desorption of Hg by solar furnace.

The first soil belongs to an abandoned metallurgical site in Almadenejos (12 km from Almadén) where cinnabar (HgS) was roasted by furnaces to obtain primary Hg. Intense Hg activity was carried out in this site in the eighteenth century. Nowadays, this plot is partly covered with slags and cinnabar mine tailings, and village habitants use it to keep livestock. This soil has a high Hg concentration (10,496±1564 mg kg^{-1}). On the one hand, this Hg has a natural origin because of the geological anomaly in Almadén district; on the other hand, it has an anthropogenic origin because of the past cinnabar roasting in the furnaces and the storage of mining residues.

The second soil (background soil) was from "Dehesa de Castilseras" which is an open Mediterranean forest in the Almadén area where livestock graze. The main origin of Hg in this soil is natural (geochemical background levels of Hg) since this site used to have less anthropogenic involvement by mining activities than the other chosen soil. Its average Hg concentration is 34±7 mg kg^{-1}.

Compound soil samples of each chosen site were collected, and they were physico-chemically characterized before and after their treatment by solar furnace. For this goal, soil samples were air-dried and sieved to obtain the fine fraction of <2 mm. The soil physico-chemical characterization was performed measuring the following: pH (H_2O, 1:2.5) and electrical conductivity as saturated paste extract (EC_e) (Burt and Soil Survey Staff 2014), organic matter (OM) according to the Walkley-Black method, cation exchange capacity (CEC) according to the EPA 9081 method (NaOAc 1N, pH 8.2), soil texture using the Bouyoucos method according to standard procedures (Page et al. 1987), color determination according to Munsell Soil Charts (Munsell Color 2009; Soil Survey Division Staff 1993) and redness rating according to Torrent et al. (1983), and the percentage of hematite by X-ray diffraction (X'Pert-MPD, Philips). EC_e was determined by measurements of EC (Burt and Soil Survey Staff 2014) multiplied by a factor of 6.4 (Loveday et al. 1972).

Soil thermal desorption by solar furnace

The experimental work was performed into a pilot scale solar rotary kiln located in "Plataforma Solar de Almería" (PSA-CIEMAT, Almería, Spain) and developed by its staff. It consists of a new design of solar rotary reactor with an inner volume of 13 L with a ceramic insulation interior chamber, where the energy supply to the soils is achieved by solar concentrated radiation through a quartz window located at the front of the reactor which is attached to the reactor body by an iron flange (Pinilla et al. 2012a, b).

The reactor design allows air flowing through its interior, with a slight overpressure, from its front part, next to the quartz window, to the inner/posterior region of the reactor. In the center of the back wall of the reactor, there is an outlet pipe which allows gasses to leave the reactor. Gasses are evacuated throughout the activated carbon trap once the soils were treated within the reactor.

The experimental work was performed with each study sample at different temperatures into the solar furnace used as a batch reactor. In each case, the amount of 350 g of the study soil was introduced inside of the reactor and the quartz window was closed to begin the solar treatment. The temperature ramp at which the study soils were subjected was as follows: 60 °C (potential volatilization of Hg^0 under field conditions), 160 °C (volatilization of Hg^0), 220 °C (Hg thermal desorption from Hg_2Cl_2 or $HgCl_2$), 280 °C (Hg thermal desorption from OM), 360 °C (Hg thermal desorption from HgS), 560 °C (Hg thermal desorption from HgO, $HgSO_4$, and pyrite), and 650 °C (Hg thermal desorption from sphalerita and/or remained Hg from pyrite and cinnabar), and finally, the solar furnace was heated to 750 °C. The furnace was opened to take samples at each temperature waiting until the temperature was below 40 °C due to the nature of volatile compounds. Both the ramp rate to reach each target temperature and the corresponding hold time were 1 h.

This ramp of temperature was chosen considering the literature which shows the thermal desorption curves of standard Hg compounds and the theoretical desorption temperatures for Hg associated to different fractions (Biester et al. 2002; Bombach et al. 1994; Palmieri et al. 2006; Windmoller et al. 1996).

Hg distribution in soil and its analysis

Total Hg in soil was measured and, in order to obtain the available Hg, the two first steps of the seven-step sequential extraction procedure (soluble H_2O and exchangeable Hg NH_4Cl 1M, pH=7) (Sánchez et al. 2005) were applied to each soil sample.

Hg concentration in all samples was measured using an atomic absorption spectrophotometer specifically designed for Hg determination (AMA254, LECO Company). Certified reference materials (CRM) were used for determining the accuracy and precision of the measurements and validating the applied methods.

Both the solid and liquid samples were measured without a need of sample chemical pre-treatment and with an Hg detection limit of 0.01 ng except when soil samples showed a high Hg content out of the equipment range limit (>600 ng). In this case, they were pre-processed by an acidic digestion following the EPA 3052 Method (US EPA 1996). The process was performed in a microwave ETHOS 1 (Milestone SRL). Recovery percentage for CRM 051 was 99 %.

Statistical analysis

The software package used to perform the statistical analysis was SPSS for Windows (version 11.5). Standard descriptive analyses as well as Kendall's tau-b correlation tests were applied. Correlation was significant at the 0.05 level.

Results and discussion

Evolution of different soil parameters of the study soils with temperature

The physico-chemical characterization of the initial soils (background soil and abandoned metallurgical soil) before thermal desorption treatment is shown in Table 1. The obtained pH values in both cases were adequate to support plant life. Regarding values of EC_e, background soil was not saline soil and abandoned metallurgical soil was very slightly saline soil (Soil Survey Division Staff 1993). The higher EC_e value of the abandoned metallurgical soil could be because of the wastes from livestock and because of occasional unloading of urban wastes. In both cases, OM was higher than 2.75 % which, in a region with semi-arid Mediterranean climate, is considered high value. CEC was in accordance with OM values. Both soils had sandy loam texture. Finally, regarding soil color and redness rating, background soil was more enriched in hematite than in abandoned metallurgical soil.

The soil parameters mentioned above were also measured along the temperature ramp of desorption treatment. Their evolution with temperature is described below.

Regarding soil pH variation with temperature, Fig. 1a shows that, in general, the pH value of the abandoned metallurgical soil was always kept lower than the pH value of the background soil. This fact could be related with the higher OM percentage of the first soil with respect to the second one that was steeper in the soils heated from ambient temperature to 160 °C (Table 1, Fig. 1c). Soil OM is mineralized releasing CO_2 that is easily transformed in HCO^{3-}. This reaction releases protons which decreases soil pH. Besides that, the large amount of urea excreted by the livestock kept in the abandoned metallurgical study plot could be another factor to be considered (Zapata Hernández 2004). Furthermore, the trend along the temperature ramp of both soils was similar. Values of pH decreased with increasing temperature from ambient temperature to 160 °C, which was related to desiccation and heating effects which favored proton-reducing oxidation reactions (Sertsu and Sánchez 1978). However, pH values increased from 160 to 360 °C which could be because of the displacement of H^+ from exchange sites of clay and OM by base cations released by heating effect (Terefe et al. 2008). The results show that there was a significant correlation between the values of pH and OM along the temperature ramp in both soils (background soil $r=-0.667$, $p<0.05$; abandoned metallurgical soil $r=-0.535$, $p<0.05$).

Both soils heated from ambient temperature to 220 °C were moderate acid to neutral, which could be considered suitable for agriculture. The latter rating of pH was kept in all temperatures in the case of the abandoned metallurgical soil despite the direct anthropogenic influence, whereas pH increased from strong to very strong alkaline (extreme conditions) in the case of the background soil heated from 280 to 750 °C. These extreme pH values also indicate soil structure loss. Furthermore, in the latter temperature range, the OM values were too low, reaching an almost total organic carbon removal at 360 °C, which is in agreement to Terefe et al. (2008). Thus, there would be difficulties in the agricultural management of the background soil heated from 280 to 750 °C because of their alkaline reactions and OM lack. Meanwhile, the abandoned metallurgical soil heated to this temperature range could not be considered suitable for agriculture only because of OM values.

Table 1 Physico-chemical characterization of the initial soils (DC and AJ) before thermal desorption treatment

Soil	pH	EC_e (dS cm^{-1})	OM (%)	CEC (cmol kg^{-1})	Soil Texture	Soil color	Redness rating
DC	6.9	1.05	2.8	18.4	Sandy Loam	7.5YR 4.5/7	2.5
AJ	6.1	3.93	3.7	37.3	Sandy Loam	10YR 3.5/2	0

AJ abandoned metallurgical soil, *DC* background soil

Regarding the differences between the pH evolutions of the studied soils, it is interesting to discuss the influence of old mining use (Hg roasting furnaces) on the abandoned metallurgical soil. Oxidation of the sulfides (Online Resource 1) inherited from cinnabar roasting gave acidity, but according to the obtained results, it was buffered. The metallurgical process of cinnabar roasting used melting compound in the form of calcium and magnesium oxides which provides soil with extra basic cations. Furthermore, the materials used in the construction and reparation of metallurgical site installations could have also provided soil with Ca^{2+} and Mg^{2+}. These basic cations would be responsible for the observed buffer (Online Resource 1).

Moreover, regarding the OM differences between both studied soils (Fig. 1c), in the case of the abandoned metallurgical soil, the obtained results show that there has been a permanent presence of organic wastes (animal and urban) long ago. Hence, the highest presence of nitrites in the initial abandoned metallurgical soil (up to 166 times more than in background soil) was converted into nitrates by a nitrification process (Fig. 2c). Furthermore, the large amount of organic residues in this site (higher than in background soil) was mineralizing by temperature treatment and becoming NH^{4+} which was totally volatilized from 560 °C (Fig. 2a). In the case of the background soil, the content of organic wastes was lower and more recent, therefore the source of NH^{4+} was little (Fig. 2a). This fact was confirmed with the negligible content of nitrites (Fig. 2b) in the initial soil and the highest chloride content (25 mg kg^{-1}).

The evolution of soil CEC with temperature was obviously related to OM (background soil r=0.722, p<0.01; abandoned metallurgical soil r=0.833, p<0.01). Figure 1d shows an initial slight increase of this parameter from soils at ambient temperature to soils heated to 60 °C. Afterwards, CEC gradually decreased to 750 °C because of a gradual loss of OM and clay collapse.

The abandoned metallurgical soil reached low values of CEC when they were heated to 650 °C while the background

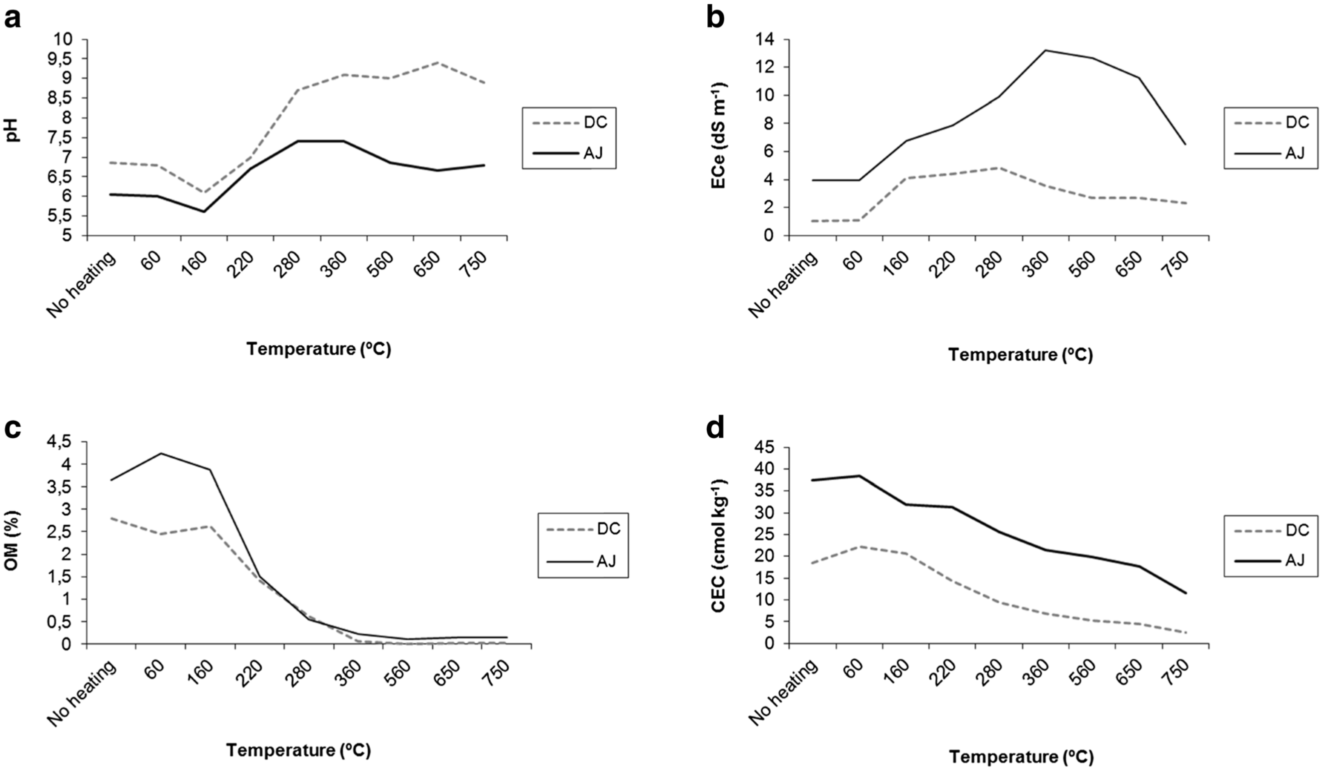

Fig. 1 Evolution of different soil parameters along the solar heating treatment of the study soils: **a** pH; **b** ECe; **c** OM; **d** CEC. *AJ* abandoned metallurgical soil, *DC* background soil

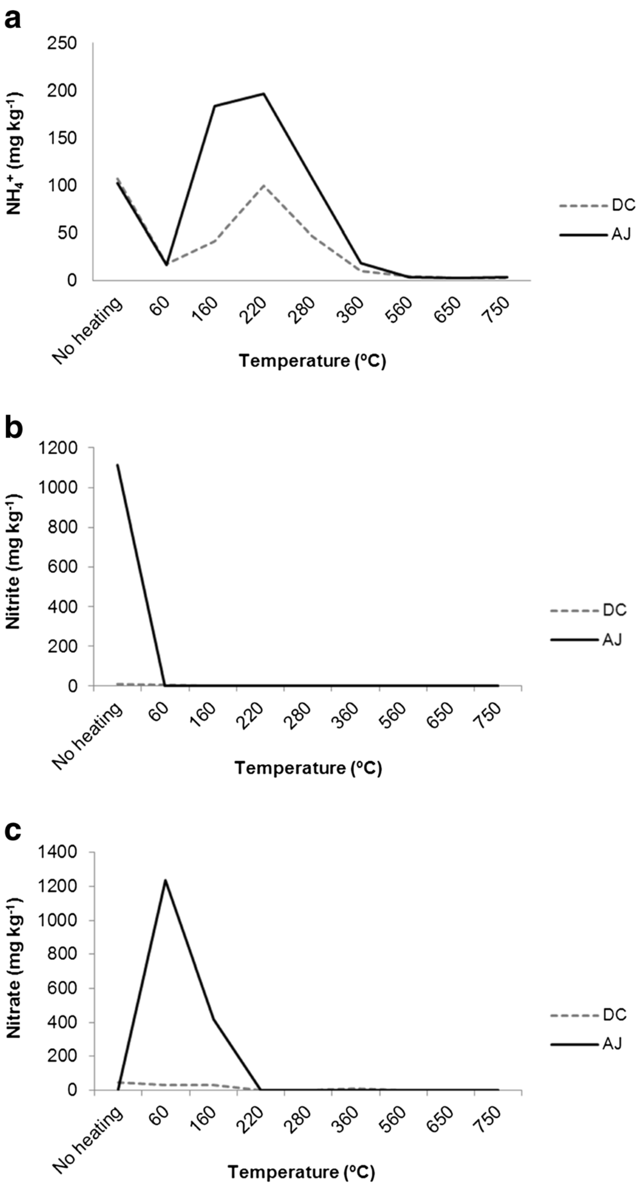

Fig. 2 Evolution of different nitrogen inorganic forms along the solar heating process of the study soils: **a** NH4+; **b** nitrite; **c** nitrate. *AJ* abandoned metallurgical soil, *DC* background soil

soils reached them when they were heated to 280 °C. Decrease of CEC entails decrease of water and nutrient holding capacity of soil and consequent loss of soil fertility (Hepper et al. 2008). Thus, the abandoned metallurgical soil could be heated up to higher temperatures than the background soil, keeping an agricultural suitable CEC value.

Regarding soil EC_e variation with temperature, Fig. 1b shows that values increased in soils heated from 160 to 280–360 °C (abandoned metallurgical soil and background soil, respectively), which could be due to the progressive release of base cations. Increase of EC_e was accompanied by decrease of OM and disappearance of clay by high temperatures, which is in agreement with Hepper et al. (2008) or Sertsu and Sánchez (1978). Since that temperature point, the EC_e values began to decrease. The collapse of clay minerals, the formation of oxides with some of the bases previously released, and the generation of coarse sand size particles, which can enclose base oxides, could explain the above EC_e decrease (Terefe et al. 2008).

Moreover, taking into account EC_e, the abandoned metallurgical soil heated from ambient temperature to 60 °C and the background soil heated from ambient temperature to 160 °C and from 360 to 750 °C could be considered suitable for agriculture. In these ranges, salinity effects would be negligible (Soil Survey Staff 2006). The highest EC_e values in the abandoned metallurgical soil along the temperature ramp seems to be related with the higher contents of ions like Na^+ or SO_4^{2-} compared to the background soils (from 1.5 to 5 times higher and from 2 to 7.5 times higher, respectively).

Regarding the variation of soil texture with temperature, according to Martínez (2001), clay fraction decreases while sand fraction increases at temperatures above 275 °C. Thus, the study soils heated from 280 to 750 °C would become sandy soils which have low water and nutrient holding capacity and therefore poor structure which could entail high susceptibility to wind erosion and consequent easier contaminant dispersion.

Regarding the color of the study soils, there was a reddening and an increase of chromas because of the transformation of iron hydrous oxides into maghemite and then hematite (Cornell and Schwertmann 2003; Mullins 1977; Taylor and Schwetmann 1974; Ulery and Graham 1993). Thus, in this heating process, there was an increase of crystallization and a strong decrease of specific surface area. In summary, it could be the result of the enrichment in hematite (from trace levels at all lower temperatures to 2 %, 4–5 % at 650–750 °C in the case of the background soil and the abandoned metallurgical soil, respectively) with a very high chroma and a high reddening power (Ketterings et al. 2000; Schwertmann 1993; Schwertmann and Taylor 1989). From the agricultural point of view, heating process does not affect Fe solubilization (from very low solubility of Fe to extremely low solubility of Fe); therefore, soils do not significantly lose fertility considering the availability of Fe.

In both study soils, the evolution trend of the studied parameters was the same but the values were different with each other. Thus, the pH, EC, and CEC values measured in the study soils from an old metallurgical area (abandoned metallurgical soil) were higher than in the case of agricultural soil (background soil) along the whole temperature ramp. On the other hand, the OM values measured in the background soils were higher than in the abandoned metallurgical soils until being of the same level when the OM began to mineralize at 220 °C. In summary, there was a fertility loss in the studied soils as temperature increased, but properties of the soil heated from ambient temperature to 220–280 °C could be considered suitable for agriculture, although in some cases soils could need to be gradually recovered by organic soil amendments and appropriate watering soil. From that temperature, these soil quality parameters could be irreversibly affected. Further studies focusing on the soil evolution over time would be interesting.

Evolution of Hg concentration in the studied soils with temperature

In order to evaluate the effectiveness of Hg thermal desorption by solar furnace, total Hg was measured along the heating treatment in both study soils (Table 2). In both study soils, more than 80 % of total Hg was released from initial soil once soil sample was heated to 280 °C. The rest of Hg, about 19 %, was released by heating the soils to 360 and 560 °C. These data were consistent with the evolution of OM; thus, total Hg had a significant, positive correlation with OM values (background soil $r=0.833$, $p<0.01$; abandoned metallurgical soil $r=0.778$, $p<0.01$) and with CEC (background soil $r=0.778$, $p<0.01$; abandoned metallurgical soil $r=0.944$ $p<0.01$).

Authors mentioned above (Biester et al. 2002; Bombach et al. 1994; Palmieri et al. 2006; Windmoller et al. 1996) gave theoretical values of temperature at which some Hg forms are desorbed from soils. The results obtained in the present work are discussed according to them.

Figure 3 shows that the percentage of Hg with respect to the total Hg from the initial abandoned metallurgical soil released at 60 and 280 °C was higher than that released in the case of the background soil. The trend was the contrary in the rest of the temperatures. The proportion of Hg^0 in the initial soil is higher in the case of the abandoned metallurgical one which is confirmed with higher values of Hg released at 60 °C. This fact is related to the direct influence of cinnabar roasting in furnaces carried out in the mentioned site along centuries. These furnaces had low efficiency which meant Hg^0 losses that impacted to a greater extent in the close area because Hg contamination decreases with distance from the source. In the case of Dehesa de Castilseras (background soil), the proportion of Hg^0 was lower because of the indirect influence of mining activities since this site was not close to any anthropogenic source. Meanwhile, the almost three times higher Hg released at 280 °C (Hg thermal desorption from OM) is also related to the higher Hg deposition in this area from those Hg losses in the furnaces. Part of this Hg^0 was oxidizing (chemically or microbiologically) to Hg^{2+} along the time, and this form was forming complexes in soil mainly with OM because of the great affinity of its sulfur functional groups to Hg (Skyllberg et al. 2006). Furthermore, this fact is according to the highest OM values in the abandoned metallurgical soil.

The percentage of Hg released at temperatures higher than 360 °C from background soil was almost two times higher than in the case of the abandoned metallurgical soil. It implies that the Hg present in the background soil was strongly linked to soil matrix.

Besides total Hg data, soluble and exchangeable Hg concentrations were determined along with heating treatment (Fig. 4a, b). These data provide easily available Hg for plants which is the essential Hg from the agricultural point of view. Kucharski et al. (2005) investigated the remediation of Hg-contaminated soil using thermal desorption with operating conditions of 100 °C for 10 days and found that the most mobile and toxic Hg species were removed. In the present work, it is observed that another factor to consider besides time is the temperature increase since the concentration of these species changes with it. Figure 4 shows a significant increase of soluble and exchangeable Hg concentration at 220 and 280 °C. Thus, the cultivation of the study soils heated to those temperatures would be a risk due to the fact that crops could uptake this Hg (Millán et al. 2013, 2006; Sierra et al. 2008, 2009, 2011, 2012).

The temperature at which total Hg concentrations of the study soils were reduced until acceptable levels according to international regulation (Canadian Council of Ministers of the Environment 2007; De Miguel et al. 2002; Ministerie van

Table 2 Mercury concentrations in the experimental soils (DC and AJ) after achieving the different temperatures into the Solar furnace

DC		AJ	
Heating temperature (°C)	Hg (mg kg^{-1})	Heating temperature (°C)	Hg (mg kg^{-1})
No heating	34.4±7.2	No heating	10497±1564
60	27.4±2.1	60	7599±158
160	22.7±5.6	160	6184±594
220	9.1±1.7	220	3152±163
280	6.6±0.4	280	1174±82
360	3.3±0.2	360	257±6
560	0.29±0.06	560	5.3±0.7
650	0.22±0.05	650	5.2±0.5
750	0.42±0.06	750	0.88±0.11

AJ abandoned metallurgical soil, *DC* background soil

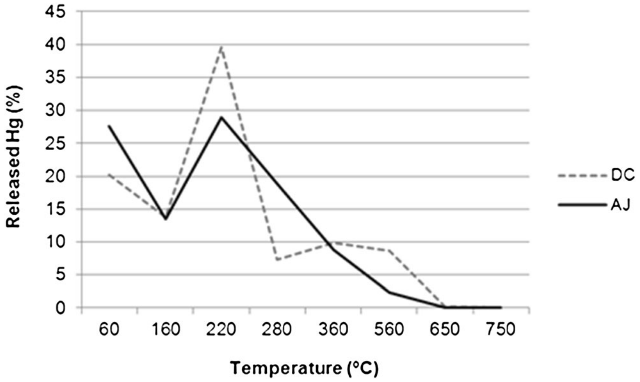

Fig. 3 Evolution of percentage of released Hg along solar heating treatment. *AJ* abandoned metallurgical soil, *DC* background soil

Volkshuisvesting and Milieubeheer 2009) depends on the intended soil use and how restrictive the regulation is. Thus, if the intended use for the study soils was agricultural, the background soil should be heated to 560 °C and the abandoned metallurgical soil to 750 °C according to more restrictive regulations, but in both cases, the soil functions and properties would be lost irreversibly; therefore, these soils would not be recoverable and they could not be used for agriculture. In the case of the background soil, it could be heated to 220 °C for protecting soil quality characteristics and another complementary technique such as induced phytoremediation could then be applied in order to decrease total Hg concentration until legal levels taking advantage of the increase of available Hg concentration (Fig. 4a). If Hg availability increases, plants can absorb it more easily. Thus, in the study case, plants that tolerate and accumulate Hg could be grown in the background soil in order to decrease total Hg by the uptake of the available Hg.

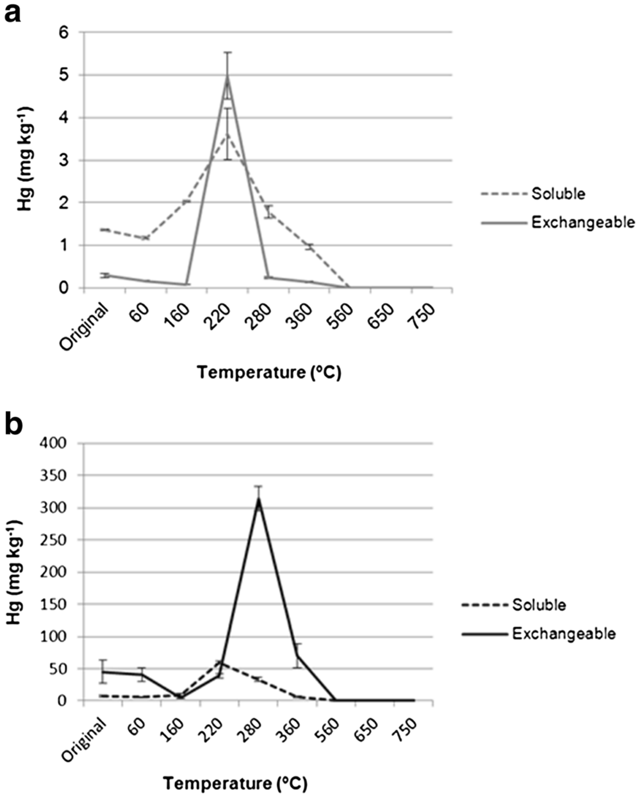

Fig. 4 Evolution of soluble and exchangeable Hg along the solar heating process of the study soils: **a** DC soil; **b** AJ soil. *AJ* abandoned metallurgical soil, *DC* background soil

For other uses such as industrial, commercial, or residential, soil quality and soil health are not important, so the study soil should be heated until the total Hg level established by the specific regulation is reached. Even if the study soils would need to be heated to 220–280 °C for these uses in order to reach the legal levels, they should not be used directly due to the very high soluble and exchangeable values (i.e. higher risk of leaching and groundwater contamination). Therefore, in those cases, the study soils should be heated to higher temperatures to avoid and minimize the possible human and environmental risk in a more efficient way.

Conclusions

This study, performed at pilot scale, evaluates how to determine the optimal temperature at which Hg-contaminated soils would be remediated. For that, it considers soil properties and total, soluble, and exchangeable Hg, as a limiting factor, depending on the future use of the soil and the established legal limits. In the case of land uses other than agricultural use or soil natural preservation, soil properties are not as important as Hg concentrations. Total Hg concentration should be lower than the established limit for a particular land use. The study soils should be heated to temperatures higher than 280 °C at which more than 80 % of the total Hg is released and eventual risks derived from high available Hg concentrations obtained at that temperature are avoided. In the case that the future use is agricultural, the maintenance of acceptable levels of soil quality is as important as Hg concentrations. The study soils should be heated to 280 °C to avoid losing soil health and quality irreversibly and apply to them additional treatments to reduce available Hg. In summary, when thermal desorption is applied to soil for Hg decontamination besides soil quality and total Hg concentration, available Hg should be considered to make final decisions on remediation treatments and potential future uses.

Further experimental works at a larger scale including different sources of Hg contamination would be interesting for developing a complete database since this technology could be applied in many developing countries where solar energy is one of the most sustainable and cheap energy sources, and where, nowadays, Hg is a real and serious environmental problem affecting the population.

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