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# Mercury Availability by Operationally-Defined Fractionation in Granulometric Distributions of Soils and Mine wastes from an Abandoned Cinnabar Mine

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Mercury contamination from historic cinnabar mines represents a potential risk to the environment. Asturias, in Northern Spain, was one of the largest metallurgic and mining producer areas of Hg in Europe during the 20th century until the end of activities in 1974. Mining operations have caused Hg release and dispersion throughout the area. In this study, soils collected from calcine piles and surrounding soils at an abandoned Hg mine and metallurgical plant in Mieres (Asturias, Spain) were distributed in different particle-size subsamples. Fractionation of Hg was performed by means of a Hg-specific sequential extraction procedure complemented with the selective determination of organic Hg fraction by a specific extraction method. Extremely high concentrations of total Hg were found in calcine piles. Concentrations and mobility of Hg decreased markedly with distance in soils located 25 m both above and below the chimney of the metallurgical plant. The sequential extraction results indicated that Hg is primarily found as elemental Hg followed by sulfide Hg in the finest subsamples. However, this distribution is inverted in the coarser grain fractions where sulfide Hg prevails. Calcine piles exhibited exceptionally high values of mobile Hg (up to 5350 µg.g$^{-1}$ in the finest subsample). Accumulation of Hg in the elemental Hg fraction was observed at decreasing grain size which is indicative of deposition of Hg vapors from the metallurgical plant. Enrichment of sulfide Hg was found in the finest subsamples of soils sampled below the chimney (up to 99 µg g$^{-1}$). Significant organic Hg contents were observed in soil samples (up to 2.8 µg g$^{-1}$), higher than those found in other abandoned Hg mining sites. A strong correlation was observed between organic Hg and Hg humic and fulvic complexes, as well as with the elemental Hg fraction. This indicates that both humic and fulvic material and elemental Hg must be the primary variables controlling Hg methylation in these soils.

## Introduction

Historic cinnabar mines represent persistent mercury sources to the environment. They include both subsurface sources associated with underground mine workings, and surface sources associated with the treatment facilities and disposal of mine wastes. This mercury can be mobilized under a variety of environmental changes. The runoff under low pH conditions or severe wind erosion can result into the transport of mercury present in wastes to the surrounding soils and streams. Additionally, the percolation of rainwater through spoil heaps can mobilize reactive mercury, putting it into solution, which can flow into local watercourses.

Asturias is a region located in Northern Spain with abundant Hg ore deposits, which has been an important Hg producer on global scale[1, 2]. The most important Asturian Hg mines were La Peña and El Terronal (Mieres). The Hg mineralization in this site shows lenticular morphology and it is distributed in conglomeratic-brecciated bodies constituted by clasts of siliceous nature of Carboniferous age. Mercury appears generally in the form of cinnabar, though metacinnabar and native Hg are also occasionally found[3]. Mining activity in the area goes back to the presence of the Romans at the Iberian Peninsula (centuries I and II AD), when their activities were restricted to mining the upper mineralized levels[4]. The modern extraction of Hg at La Peña-El Terronal site was made by drift mining inside an underground mine which was exploited in 12 levels. During the late 1960s and early 1970s, production in excess of 500 flasks month$^{-1}$ (1 flask = 34.5 kg Hg) was achieved at La Peña-El Terronal mine, constituting at this time the second most productive Hg mine in Spain, and the eighth most productive Hg mine in the world.

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There has not been any mining activity at this site since 1974 when both mines were closed as a consequence of the decline of the Hg price, due to international health concerns over this metal. The legacy of the historical mining activities remains in the form of abandoned industrial installations (shaft, mining buildings, roasting furnace, chimney, etc.) and significant quantities of mining and metallurgical wastes stocked in piles on the surface. The atmosferic and waterborne dispersion of these materials have involved for decades an important source of Hg pollution in the area[3]. No preventive measures to avoid these effects were undertaken until 2002, when 300,000 tons of spoil heap wastes (constituted by tailings and variable granulated materials) were isolated in an on-site security landfill.

The mobility, bioavailability and toxicity of mercury depend upon its specific chemical forms and their interactions with the different soil and sediment constituents. Mercury present in soils can be mobilized due to different factors[5-7]. Consequently, detailed information about the interactions between this metal and the soil and/or sediment matrix is required to judge its environmental impacts. In addition, the retention and accumulation of mercury in soils and mining wastes is closely related to grain size fractions[5-8]. Anions as sulfates and negatively charged surfaces of Fe, Al and Mn oxyhydroxides or organic carbon groups complex Hg by electrostatic forces[9-12]. The concentration of Hg and other heavy metals in soils and sediments generally increased with decreasing grain size, because of the affinity of metals to bind with finer particles[13]. Finer size particles are mainly composed of weathering-resistant, net positively charged minerals of Fe and Al[10]. In sandy soils with lack of organic matter, quartz and feldspar minerals retain cationic Hg species which are found predominantly in medium to coarse particle sizes[14, 15].

Sequential extraction is a frequently used approach to evaluate mercury distribution into different chemical forms present in a solid phase. In the last decades, several authors have developed specific sequential extraction methods in order to establish a logical mercury fractionation according to its mobility and environmental behavior in soils and sediments[16-23]. Conceptually, sequential extraction categorizes mercury associated with chemically homogeneous fractions that, ultimately, affect mercury availability. The strength of the binding between mercury and soil phases eventually controls its bioavailability.

The purpose of this study is to evaluate the fractionation of mercury in soils and wastes from an old mining area in Asturias (Spain). Special emphasis has been placed on the Hg distribution within grain size subsamples in order to achieve a better understanding of Hg accumulation and mobility. This can improve predictions about potential contamination of environments surrounding abandoned cinnabar mines. A new mercury-specific four stage sequential extraction procedure was used to discriminate mercury bound to different phases and to evaluate the potential mobilization and transport of mercury in this area[23]. The four phases considered are: labile Hg, Hg associated to humic and fulvic acids, elemental mercury and crystalline oxides and sulfide mercury and refractory species. In order to evaluate the influence on the grain size distribution on mercury fractionation, sequential extraction in bulk as well as in size-particle subsamples were performed. In addition, an estimation of organic mercury fraction based on a selective extraction procedure was carried out for bulk samples and grain size subsamples.

# Experimental

## Sample collection

Soil samples were collected in the vicinity of El Terronal mine (Figure 1). Samples were taken at a depth of 30 cm (B horizon), using a standard Auger sampler. Originally, 3 points were selected and sampled closely to the chimney placed ascending up the slope of the valley, which was used to evacuate the exhaust vapors generated during the pyrometallurgical treatment of the ore. Sample CP was located directly in contact with the remains of the chimney whereas samples DS and US were taken, respectively, at about 25 m topographically below and above it. Sample CP can be considered as a mixture of original soil, chimney remains and ore roasting residues. The other two samples correspond to natural, quite well-developed, alluvial soils. Thus, it is expected that Hg in the CP sample should be anthropic (native Hg droplets can be observed at the chimney), and Hg in the DS and US samples could be partly “natural”, related to the presence of this metal in the local soils before mining produced an additional pollution effect. Soils in the area are characterized by being moderately acidic (pH 3 to 6), containing 3 to 13% of organic matter, and up to 10% of clay, with illite and kaolinite as major components[3]. Developed on the subjacent alluvial substrate, the sandy mineral fraction is the dominant one in these soils. Each soil sample was composed by four subsamples of 500 g taken at the extremes of a Greek cross of 1 m of side. These were later homogenized and blended in the same proportion to become just one representative sample.

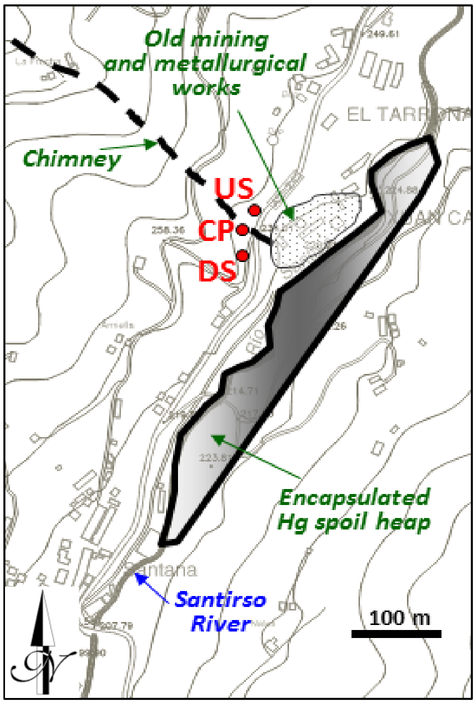

**Fig 1** Location of the studied area (El Terronal mine) and sampling points (CP, DS, US). UTM coordinates (European Time Zone 30 North Datum ETRS89) of sample CP: X=274643.3, Y=4794360.6

### Sample preparation

In the laboratory, samples were dried for 48 h at a temperature below 40 ºC to minimize loss of volatile elements, such as Hg. After drying, stones and other large particles were removed, and the components of the samples were gently disaggregated.

A fractionation was carried out by sieving into different particle-size ranges, by means of standard Tyler sieves. Table 1 summarized the type of strainers, the corresponding particle-size range and the percentage obtained for each subsample. The 5 resulting subsamples (s1-s5) were ground to a size finer than 147 µm. These samples and also the original samples (O) were quartered by means of an aluminium rifler (which was cleaned between samples using a jet of compressed air) to provide representative subsamples for analysis.

Organic matter was determined by means of the Large-scale burette titration method, using an Organic Matter Test Model ST-OR 5020 LaMotte Company kit. The pH in soils was measured by the saturated paste method[24]. The different grain-size subsamples were subjected to organic matter content and pH determination, as well as to chemical and mineralogical analyses. In the latter case, samples were dusted over adhesive paper and metallized to make them electrical conductors.

### Total Hg and Organic Matter in soils

Total Hg determinations in soils samples were performed using a DMA-80 instrument (Milestone, Sorisole, Italy) following the recommendations given by EPA 7473 method[25].

Organic matter contents (OM) were determined following the protocol described in the standard UNE 103204:1993, based on soil oxidation with potassium permanganate[26].

### Sequential extraction method

A sequential extraction method was used to categorize mercury binding to different minerals in the samples and in the particle-size subsamples. This is a new sequential extraction procedure developed specifically to evaluate Hg fractionation in solid environmental samples, according to the unique physical and chemical properties of numerous Hg species. The procedure divides the content of mercury in solid samples in four categories: *Labile mercury species* (Hg Lab), *Humic and fulvic complexes* (Hg Hum/Ful), *Elemental Hg and crystalline oxides* (Hg Elem/CrystOx) *and sulfide Hg and refractory species* (Hg Sulf/Ref), as shown in Table 2. To ensure the quality of the results, the sequential extraction method was applied to CRM NIST 2710 Montana soil (with elevated trace element concentrations), whose certified Hg content is 32.6 ± 1.8 $mg.kg^{-1}$. The sum of Hg concentrations extracted in every fraction was 30.9 ± 2.4 $mg.kg^{-1}$, which is in good agreement with the certified value at 95% confidence level (t-test).

Extractions were conducted in 50 ml centrifuge tubes with 0.5 g of dried soil. After each extraction step, samples were centrifuged at 4000 rpm for 10 minutes. The supernatants were removed using a Pasteur pipette and transferred to a vial. The residue was washed with 5 mL of MilliQ water after each extraction. Wash solutions were combined with corresponding extracts, filtered through 0.45 µm cellulose paper, diluted with water to a final volume of 50 mL and then analyzed by Electrothermal Atomic Absorption Spectrometry using the DMA-80 instrument, Milestone, Sorisole, Italy.

### Organic mercury fraction

A procedure for the selective determination of the organic mercury fraction in soil samples, which gives an estimation of the highly available and toxic MeHg species was used for this work. This procedure uses successfully the DMA-80 mercury specific analyzer advantages. The proposed method is based on a previous one developed for soils[27]. Essentially, it consists on the releasing of organic mercury compounds by a $CuBr_2$ solution and simultaneous extraction with $CH_2Cl_2$ in a single step. The evaporation of the organic phase aliquot onto a quartz boat in the presence of an N-Acetyl-L-Cysteine solution allows the determination of extracted organic mercury by the direct mercury analyzer DMA-80. Validation of this procedure was performed by its application to BCR 580 (estuarine sediment), with a certified MeHg content of 75.5 ± 3.7 $ng.g^{-1}$. The obtained value was 72.8 ± 2.8 $ng.g^{-1}$ which is in good agreement at 95% confidence level (t-test) with the certified value.

**Table 1** Description of particle-size subsamples

| Subsample | Strainer Tyler No. | Particle-size (mm) | Sample CP (%) | Sample DS (%) | Sample US (%) |
|---|---|---|---|---|---|
| s1 | 10 | > 1.651 | 43.4 | 65.8 | 66.4 |
| s2 | 20 | 0.833 - 1.651 | 15.1 | 10.2 | 13.4 |
| s3 | 35 | 0.417 - 0.833 | 14.1 | 7.4 | 9.0 |
| s4 | 100 | 0.147 - 0.417 | 16.3 | 7.9 | 7.0 |
| s5 | Pass-through | <0.147 | 11.1 | 8.7 | 4.2 |

**Table 2** Sequential chemical extraction procedure

| Step | Fraction | Extractant |
|---|---|---|
| 1: Hg Lab | Labile Hg species | 20 mL of 0.2M $HNO_3$, 50 ºC, combined rotary-ultrasonic agitation, 2h |
| 2: Hg Hum/Ful | Humic and fulvic complexes | 10 mL of 0.1M $Na_4P_2O_7$, r.t., end-over-end shaking, 18h |
| 3: Hg Elem/CrystOx | Elemental Hg and crystalline oxides | 20 mL of 50% v/v $HNO_3$, end-over-end shaking, r.t., 21h |
| 4: Hg Sulf/Ref | Sulfide Hg and refractory species | 10 mL of 0.03M KI in 50% v/v HCl, occasional ultrasonic agitation, 70ºC, 45 min |

r.t. = room temperature (aprox. 20ºC)

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## Results and discussion

### Hg fractionation in bulk and grain size subsamples

The distribution of Hg in the particle-size subsamples of the chimney-ore roasting residues (sample CP) as well as below (sample DS) and above (sample US) soils are presented in Figure 2. The recovery of Hg obtained as the sum of Hg contents in every fraction varied between 93% and 102% for each subsample indicating that the sequential extraction procedure may be successfully used to assess the partitioning of Hg in soil samples.

*Chimney-ore roasting residues*

Sample CP corresponds to the area in the immediate vicinity of metallurgical exhausts and deposition of residues. Results from sample CP are shown in Figure 2a. As it was expected, most of Hg is accumulated in the finest subsamples[28, 29]. All subsamples present extremely high concentrations of Hg Lab, which represents the most available Hg. Similar contents of Hg Lab were found in the coarser fractions (s1, s2, s3) as well as the finest subsample (s5). However, the highest Hg Lab concentration was found in subsample s4 (0.147 - 0.417 mm). It indicates an accumulation of reactive Hg species in this grain size subsample, corresponding to fine to medium sand. This high concentration may be explained since Hg would be accumulated in the material associated to amorphous Fe and Mn oxy(hydroxides) which is presumably extracted in the Hg Lab fraction[30]. The presence of reactive Hg compounds in calcine piles is explained since these compounds are formed during Hg retorting process due to the inefficient cinnabar conversion[31, 32]. As a consequence, highly available species as chloride-bearing Hg or Hg sulfates can be formed. Extreme high concentrations of water leached Hg and simulated gastric fluid leached Hg were reported in calcine piles from Almadén (Spain)[33].

Hg Hum/Ful fraction was globally similar for all the grain size subsamples, representing 7.1%-11.4% of total Hg. These data is consistent with the organic matter content (Table 3), since no drastic differences were found for this parameter among the considered grain size fractions (ranging between 3.2 and 4.4%). No significant correlation was found between Hg concentations in Hg Hum/Ful fraction and organic matter (r=0.33; Table 4). Such lack of positive correlation has been found in other mining districts and polluted soils and may be attributed to the presence of non Hg complexes forming groups, different than humic and fulvic acids, in the soil organic matter[15, 34]. Hg concentration in Hg Elem/CrystOx fraction presented a bimodal distribution over particle-size fractions. It seems that Hg extracted in this fraction accumulated in the silt/clay subsample (s5 < 0.147mm) and fine sand (s4 0.147-0.417 mm). However, Hg in both subsamples could have a different origin. The presence of elemental Hg in coarser subsamples is due to Hg native droplets originated as processing losses during the pyrometallurgic treatment of the ore, which is still possible to observe it on the ground of the hillside near the chimney. On the contrary, its presence in the finest subsamples may be related to the association of Hg with Fe crystalline oxides. The strong association of Hg with Fe oxyhydroxides has been previously reported for soils from Almaden mining area[35]. It has been demonstrated that Hg(0) adsorption increase at decreasing particle size[36]. The measurements of Hg after the fourth extraction (Hg Sulf/Ref), interpreted as an estimate of total Hg in cinnabar particles, were similar for the three coarser grain subsamples (s1, s2, s3) and appeared significantly enriched in the finest ones (s4, s5).

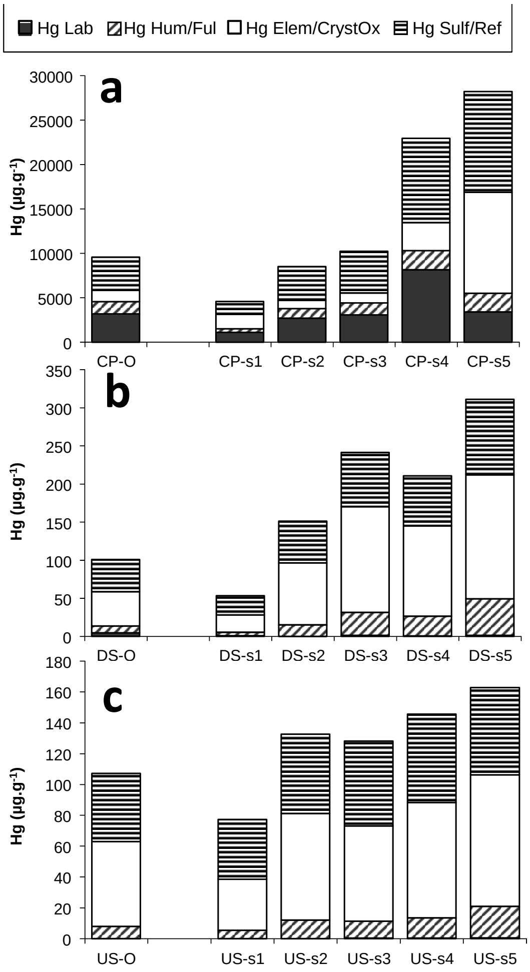

**Fig 2** Relative distributions of Hg in the original sample (O) and among the different grain-size subsamples (s1-s5) from samples CP (a), DS (b) and US (c). Hg Lab = Labile Mercury Species, Hg Hum/Ful = Humic and Fulvic Complexes, Hg Elem/CrystOx = Elemental Hg and sorbed on crystaline Fe and Mn oxyhydroxides, Hg Sulf/Ref = Bound to sulfide Hg and refractory species

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**Table 3** Concentrations and percentages of organic Hg fraction and organic matter in the original sample (O) and the grain-size subsamples (s1 to s5).

| Sample | Organic Hg ($\mu g\ g^{-1}$) | Organic Hg (%) | Organic Matter (%) |
|---|---|---|---|
| CP-O | 49.0 ± 6.8 | 0.48 ± 0.07 | 4.4 |
| CP-s1 | 22.4 ± 3.0 | 0.47 ± 0.06 | 3.2 |
| CP-s2 | 52.1 ± 4.5 | 0.62 ± 0.05 | 2.9 |
| CP-s3 | 64.9 ± 3.8 | 0.62 ± 0.04 | 4.4 |
| CP-s4 | 191.3 ± 13.9 | 0.82 ± 0.06 | 4.4 |
| CP-s5 | 236.0 ± 16.7 | 0.81 ± 0.06 | 3.8 |
| DS-O | 0.4 ± 0.1 | 0.39 ± 0.07 | 4.9 |
| DS-s1 | 0.3 ± 0.1 | 0.58 ± 0.08 | 4.1 |
| DS-s2 | 0.7 ± 0.1 | 0.43 ± 0.05 | 4.9 |
| DS-s3 | 1.4 ± 0.1 | 0.56 ± 0.04 | 5.8 |
| DS-s4 | 1.1 ± 0.1 | 0.48 ± 0.05 | 6.7 |
| DS-s5 | 2.8 ± 0.1 | 0.86 ± 0.03 | 7.3 |
| US-O | 0.5 ± 0.1 | 0.46 ± 0.04 | 10.2 |
| US-s1 | 0.5 ± 0.1 | 0.46 ± 0.05 | 9.9 |
| US-s2 | 0.9 ± 0.0 | 0.66 ± 0.03 | 10.5 |
| US-s3 | 0.8 ± 0.1 | 0.58 ± 0.06 | 10.2 |
| US-s4 | 0.7 ± 0.1 | 0.51 ± 0.09 | 11.6 |
| US-s5 | 1.3 ± 0.3 | 0.80 ± 0.12 | 9.3 |

**Table 4** Correlation coefficient between organic Hg and organic matter (O.M.), total Hg and Hg fractions (n= 18, level of significance α = 0.01 and the critical value is 2.584)

| | O.M. | Total Hg | Hg Lab | Hg Hum/Ful | Hg Elem/CrystOx | Hg Sulf/Ref |
|---|---|---|---|---|---|---|
| **Sample CP** | | | | | | |
| Hg Hum/Ful | 0.33 | | | | | |
| Org. Hg | 0.24 | 0.99* | 0.35 | 0.69 | 0.75* | 0.98* |
| **Sample DS** | | | | | | |
| Hg Hum/Ful | 0.86* | | | | | |
| Org. Hg | 0.74* | 0.84* | 0.64 | 0.95* | 0.76* | 0.89* |
| **Sample US** | | | | | | |
| Hg Hum/Ful | 0.96* | | | | | |
| Org. Hg | 0.18 | 0.75* | 0.67 | 0.91* | 0.79* | 0.01 |

*Statistically significant

*Soils sampled below and above the chimney*

Hg distributions in soils below (Sample DS) and above (Sample US) the chimney are plotted in Figures 2b and 2c, respectively. Total Hg concentration in sample US is slightly higher in the finer subsamples, ranging from 110 to 163 $\mu g\ g^{-1}$. In the sample DS, Hg shows a marked tendency to be accumulated in the finest subsamples. This may be indicative of deposition of Hg fine grained material from the pollution source[37].

Contrary to that occurs in sample CP, none of the DS or US subsamples present significant Hg concentration in the Hg Lab fraction, with the exception of subsample DS-s5 with 3.9 $\mu g\ g^{-1}$. In addition, all these studied grain-size subsamples displayed appreciable Hg concentration in the Hg Hum/Ful fraction. This fraction increases at decreasing particle size as well as organic matter does. The strong chemical affinity of soil organic matter for Hg is typical of well-developed soils[38]. This tendency was also confirmed by the very high correlation ($R^2$ = 0.86 and 0.96) between Hg Hum/Ful concentration and organic matter content in samples DS and US, respectively (Table 4).

Hg Elem/CrystOx fraction was the most abundant fraction in all subsamples with the exception of the coarsest subsamples (DS-s1, US-s1). This fraction ranges from 23 $\mu g\ g^{-1}$ for subsample DS-s1 to 160 $\mu g\ g^{-1}$ for subsample DS-s5. In both sampling points, this fraction represents approximately 50% of total Hg present in subsamples s2, s3, s4 and s5 and 42% of total mercury in subsample s1. This means that Hg is these soils may be present mainly as elemental Hg as well as associated to crystalline Fe oxyhydroxides. The relatively high elemental Hg percentages are not surprising since similar percentages of this Hg species have been found in other cinnabar districts. In soils from Idrija mercury mining region located in the vicinity of mining and smelting works, elemental Hg represents 30–60% of total Hg content[34]. In the case of sample DS, Hg Sulf/Ref concentration considerably increases at decreasing grain size, ranging from 25 µg g$^{-1}$ to 99 µg g$^{-1}$. This fraction in the coarsest subsamples (s1) may be mainly attributed to its natural cinnabar content. The significance of this fraction in the finest subsamples (s2 to s5) may be due to the dispersion of small ore particles from the chimney residues. In contrast, Hg Sulf/Ref concentration in above (US) subsamples does not vary significantly with size, as cinnabar is present in this soil mainly as natural constituent rather than accumulated from mining wastes.

### Organic mercury fraction in bulk and grain size subsamples

Concentrations of organic mercury in sampled soils are presented in Table 3. Appreciable organic Hg contents were observed in all samples and grain subsamples. Organic Hg contents vary between 0.4% and 0.9%. As expected, the highest organic Hg concentrations are found in sample CP. At this point, organic Hg varies between 22 µg g$^{-1}$ in the coarsest subsample (CP-s1) and 236 µg g$^{-1}$ in the finest one (CP-s5), being the content in the bulk sample (CP-O) as high as 49 µg g$^{-1}$. These concentrations found in the ore roasting residues are exceptionally high in comparison with other similar studies reported in the literature. MeHg concentrations up to 1.5 µg.g$^{-1}$ were found in calcine piles from abandoned mines in Texas (USA)[39]. Slightly higher concentrations were found by Gray *et al.* (2004), who detected concentrations of 3.1 µg g$^{-1}$ in mine waste calcines from Almadén (Spain)[40]. Both samples collected at certain distance from the chimney also exhibited important organic Hg contents, ranging from 0.3 to 2.8 µg.g$^{-1}$. These concentrations significantly exceed known values for soils or sediments from cinnabar mining areas. To our knowledge there are only a few studies about methylmercury and other organomercurials in old cinnabar mine soils. Up to 0.2 µg.g$^{-1}$of MeHg were found in soils from Idrija mine site[41]. Bailey *et al*. (2001) found MeHg concentrations of 41 ng g$^{-1}$ in soils collected near an old cinnabar mine in Alaska (USA)[42].

Concentrations of organic Hg are strongly correlated with concentrations of total Hg (Table 4) which is in agreement with other studies[17, 38]. In order to evaluate factors controlling the presence of organic mercury in these soils, relationships between organic Hg and organic matter and elemental Hg were examined. It has been reported that organic mercury and microbial activity in soils plays an important role in the bioavailability and methylation of inorganic mercury[43, 44].

In this case, organic Hg concentrations showed no significant relationship with concentrations of organic matter (Table 3), with the exception of soils sampled below the chimney (Table 4). However a strong correlation between organic Hg and Hg Hum/Ful concentrations were found for soils sampled both below and above the chimney. This behavior was expected since the methylation potential of humic and fulvic Hg complexes, by methylating bacteria, has been previously reported[45-47.] These observations indicate that humic and fulvic material rather than total organic matter may be a factor controlling organic Hg content in the studied soils. On the other hand, it has been suggested that the presence of elemental Hg could be an important factor in mercury methylation in soils from mining sites[40.] Elemental Hg present in calcines and other deposits can be converted to reactive Hg (II) species by oxidation processes that are bioavailable for microbial transformation to MeHg[48, 49]. The obtained data revealed significant positive correlations (Table 4) between organic Hg and Hg Elem/CrystOx concentrations, which may be assumed as an estimation of the elemental Hg present in the soil. This suggests that elemental Hg content is also a primary variable controlling the content of organic Hg in the investigated soils. In addition, similarly to elemental Hg, the general remark is that the concentrations and percentages of organic Hg increase with the decreasing grain size. This fact supports the argument that elemental Hg present in the soils may have an anthropogenic origin due to the adsorption of elemental Hg coming from the mine wastes. Strong correlations were also found between organic Hg and Hg Sulf/Ref in CP and DS samples. However, since it is widely accepted that cinnabar is not prone to suffer methylation reactions[17, 50], these correlations have not a geochemical significance.

## Conclusions

The obtained data may allow recognition of potential environmental hazards derived from anomalous Hg concentrations of the “El Terronal” mine site in Asturias (Northern Spain).

The results of this study indicate a heavy contamination of Hg in residues from the old chimney used for pyrometallurgy treatment of Hg ore. Calcine residues constitute a pollution source for the local environment. The amounts of Hg leached in Hg Lab and organic Hg fractions are outstanding and emphasize the environmental hazard of these calcine residues. Concentration and availability of Hg considerably decrease with distance from the chimney. In samples of well-developed soils Hg is probably retained by other existent ligands that potentially lead to decrease Hg availability. Sequential extractions revealed that elemental Hg, Hg associated to Fe crystalline oxyhydroxides and cinnabar prevail in these soils. The amount of elemental Hg and Hg associated to Fe crystalline oxyhydroxides gradually increases at decreasing grain size. Regarding Hg sulfide content, significant differences were observed between soils sampled below and above the chimney. Former soil presents a clear enrichment of fraction Hg Sulf/Ref at decreasing grain size which may be related to the presence of small ore particles from the source together with natural cinnabar content. On the other hand, Hg concentrations in Hg Sulf/Ref fraction of soil sampled above the chimney keep approximately constant in all grain subsamples which indicate that Hg may be present mainly as natural cinnabar. The significant Hg concentrations in Hg Hum/Ful fraction confirmed that binding to humic and fulvic substances constitute a significant process of Hg sorption in well-developed soils.

Even though the major source of Hg in the sampled soils is inorganic Hg, it was observed that significant concentrations of organic Hg are also present. The transformation into organic Hg seems to be controlled mainly by possible methylation of humic and fulvic Hg complexes and the presence of important amounts of elemental Hg which acts as a primary source for Hg methylation.

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