

Seasonal and spatial distribution of mercury in stream sediments from Almadén mining district



Efrén Garcia-Ordiales^{1*}, Pablo Higuera², Jose M. Esbrí², Nieves Roqueñí¹ & Jorge Loredó¹

¹ ISYMA Research Group, Mining, Energy and Materials Engineering School, University of Oviedo, Oviedo, Spain

² IGEA, Biogeochemistry Laboratory of Heavy Metals, University of Castilla La Mancha, Almadén, Ciudad Real, Spain

E.G., 0000-0001-9138-7076

*Correspondence: garciaefren@uniovi.es

Abstract: The spatial and temporal distributions of Hg in different fractions of sediment samples from the Valdeazogues River (Almadén) were investigated. Almadén is widely known as the world's largest Hg mining district. A total of nine sites during six time periods were monitored using a BCR (Community Bureau of Reference) sequential extraction procedure. The results showed that Hg is mainly present as residual cinnabar but there is another important organic fraction in which Hg is primarily incorporated. Higher proportions of Hg in the residual fraction were found in wet seasons, while the opposite is true in the organic fraction. The exchangeable/carbonate and Fe-Mn oxide phases are the minor Hg fractions, and they were found less susceptible to seasonal changes. The potential risk for the aquatic medium was evaluated based on the proportions of non-residual (exchangeable/carbonate + Fe-Mn oxides + organic) fractions. The high proportions of Hg potentially (bio)available, together with the Hg total concentrations, indicated an important risk, especially in areas close to the mines. Although the risk is important in all seasons, it is particularly noticeable during dry periods due to the increase in the organic fraction, which may favor potential transference from the sediments to the environment due to the physic-chemical river conditions.

Keywords: mercury; sediments; fractionation; BCR sequential extraction; spatial-temporal distribution; Almadén

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Contamination of aquatic ecosystems by mercury is a global concern due to the potentially severe consequences for biota and human health (Mergler *et al.* 2007). This element is enriched in the environment primarily through natural atmospheric emissions (and subsequent deposition) as well as through gaseous, solid or liquid contributions from anthropogenic point sources (Dhanakumar *et al.* 2015). In the environment, Hg can be biogeochemically processed into toxic species, which present a high risk to biota, becoming bioconcentrated and biomagnified in food webs (Souza-Araujo *et al.* 2016). Among several possible anthropogenic activities, mining is one of the most significant sources of the introduction of Hg to riverine systems (Johnson & Hallberg 2005; Byrne *et al.* 2013). Connection to surface water ecosystems from these sources has been recognised in many areas around the world (Macklin *et al.* 2006; Monna *et al.* 2011; Gray *et al.* 2015). A peculiarity of mining-related contamination is that mine wastes, including tailings, slags, waste piles, yellowish-brown sediments, as well as contaminated floodplains, continue to act as secondary sources of the mined element(s) in the drainage basin for hundreds of years after the closure of the mine (Gray *et al.* 2015). In addition, the extent of the contamination is not strictly limited to the vicinity of the sources. Contaminated materials may be physically remobilised in high-flow conditions (Pattelli *et al.* 2014), thus dispersing contaminants over hundreds of kilometres downstream from historical mining sites (Frohne & Rinklebe 2013; Chiarantini *et al.* 2016), even affecting the marine system remote from the source area (Horvat *et al.* 1999; Garcia-Ordiales *et al.* 2018).

According to the Water Framework Directive (2000/60/EC) (with its aim to achieve a good ecological status of water bodies) riverine sediment conservation is a priority, due to the importance of this environmental compartment in the flow and storage of trace metals on the scale of a drainage basin (Yuan *et al.* 2014). In aquatic

environments, contaminants in general, and Hg in particular, are easily adsorbed by fine suspended particles (Duan *et al.* 2010). A portion of these fine particles will eventually be deposited and fixed onto bed sediments. Due to its low solubility, Hg tends to precipitate as solid phases in association with organic matter (OM) and various inorganic compounds such as oxides and carbonates, and thereby it can be stored in sediments, although in metastable conditions. Depending on the mineralogical and granulometric characteristics of sediments, *in-situ* environmental conditions and the biological components living in the area, these adsorption processes can be more or less effective. Alternatively, once the Hg is incorporated into sediments, it can be recycled by biogeochemical processes, which may release Hg first into the porewaters and then again into the water column (Tao *et al.* 2016). As part of the sediments, Hg can exist in various forms: soluble, exchangeable, occluded in Mn and/or Fe oxyhydroxides, bound to OM, in association with suspended minerals (such as carbonates, phosphates, sulphides, oxides/hydroxides), or bound to phyllosilicates or their colloidal precursors. Indeed, Hg mobility and bioavailability depend on the chemical forms or species rather than the total concentration of the element. Sequential extraction procedures based on specific chemically leaching agents have become a useful approach to investigate trace element speciation (Malandrino *et al.* 2011) and to achieve the necessary information to assess the potential environmental risk, based on the (bio)availability of the elements (Chen *et al.* 2010).

In the present study, stream sediments from the drainage basin of the Valdeazogues river, draining the Almadén mercury mining district, were investigated in order to understand if they behave as a source and/or sink for Hg in this aquatic environment. This manuscript is complementary to the previously published work from Garcia-Ordiales *et al.* (2016a) as part of an in-depth study on the aquatic ecosystem of the Almadén mining district. The BCR

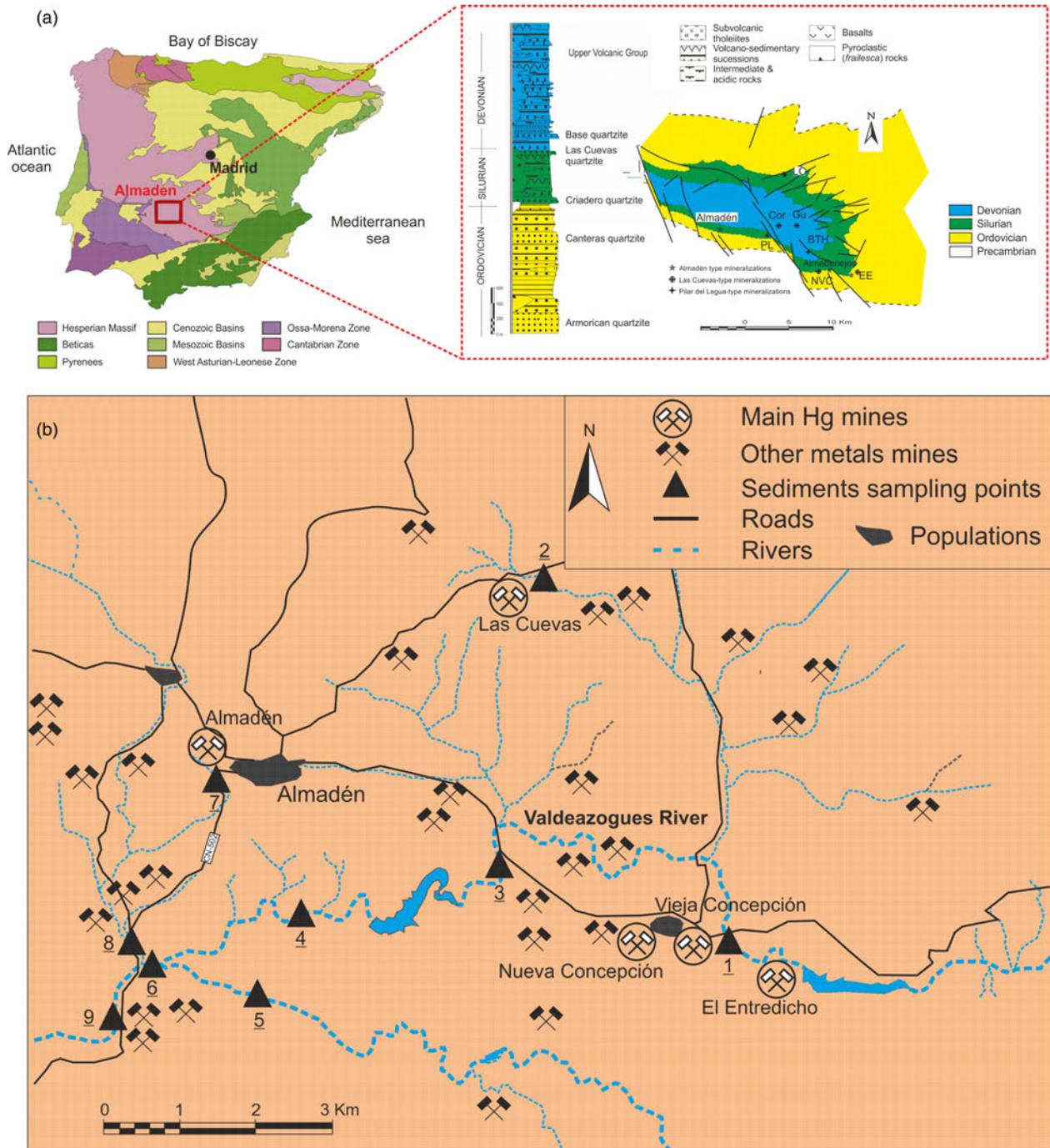


Fig. 1. Geological settings of (a) the study area and (b) and stream sediments sampling sites.

(Community Bureau of Reference) sequential extraction procedure was applied to examine all the biogeochemical forms of Hg and to better understand their potential availability. Finally, an attempt was also made to outline the important implications to be considered for a better assessment of the ecological risk. The results provide relevant information that enable the development of appropriate strategies to plan environmental management of Hg mining-affected drainage basins.

Materials and methods

Study area

The Almadén mining district, located in the Province of Ciudad Real in south-central Spain (Fig. 1), has been well-known as an important Hg mining district since the times of the Roman Empire

(Higuera *et al.* 2006). From this area, one third of the total global production of this element in the world was produced (Hernández *et al.* 1999). The mining district belongs to the Rio Valdeazogues drainage basin, which covers a total area of 1.213 km², where c. 240 km² include the area clearly affected by the Hg extraction activities. Streams flow through the district, which in general exhibits low slope and erodibility (4–5‰) and their hydrological conditions are mainly determined by seasonality and controlled by the semi-arid climate of this part of the Iberian Peninsula, with a rainy mild winter and a severe hot and dry summer season. The mean annual rainfall is within the range of 500–525 mm, and the mean annual temperature is 15–16°C, whereas the mean potential evapotranspiration is 963 mm (Schmid *et al.* 2003).

From a geological point of view, rocks outcropping in the Almadén area are mainly siliciclastic. The materials correspond to Palaeozoic (meta)detritic rocks with a significant volume of

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Table 1. Distribution of mercury in different fractions. Data in $\mu\text{g g}^{-1}$

Date	Sampling Points	Total Recovery (%)	Exchangeable/Carbonate (F1)	Fe-Mn oxides (F2)	Organic (F3)	Residual (F4)
2011–5	1	98.2	9.6	18.5	52.5	101.1
	2	100.6	12.3	16.2	55.7	86.2
	3	98.5	3.5	14.3	22.9	65.0
	4	102.1	3.6	13.7	39.6	33.7
	5	98.8	0.1	0.4	1.4	4.0
	6	96.3	3.4	4.6	18.0	56.9
	7	93.1	17.0	22.9	57.7	93.3
	8	100.9	5.0	7.2	29.2	73.8
	9	93.3	8.3	15.8	28.3	45.6
2011–11	1	93.8	7.6	21.1	22.2	133.9
	2	98.6	9.0	36.0	67.1	122.5
	3	95.7	3.0	9.1	16.7	62.7
	4	100.6	1.9	7.0	10.8	49.4
	5	100.2	0.1	0.5	0.5	3.8
	6	101.6	2.6	5.8	26.1	59.4
	7	95.9	6.1	24.0	35.9	114.3
	8	95.9	3.7	11.8	22.9	51.9
	9	93.9	1.9	9.4	27.8	68.9
2012–2	1	95.1	4.8	15.1	19.0	127.5
	2	98.5	5.2	17.1	56.8	105.9
	3	102.3	2.3	8.8	30.6	86.8
	4	102.9	1.1	3.3	10.2	32.8
	5	100.9	0.1	0.7	1.1	4.2
	6	98.7	2.3	8.4	25.9	68.3
	7	93.5	8.6	19.4	48.1	163.1
	8	95.9	2.2	8.9	24.4	59.1
	9	92.4	4.2	12.8	23.5	83.7
2012–6	1	101.4	25.9	16.1	87.0	77.5
	2	99.4	17.5	30.9	64.6	162.9
	3	99.3	4.7	27.6	37.4	67.8
	4	96.5	3.2	8.4	24.6	32.6
	5	98.7	0.1	0.8	1.4	4.8
	6	101.2	3.0	3.9	23.3	56.2
	7	100.7	16.8	33.3	76.3	57.1
	8	95.3	3.8	4.3	25.1	34.1
	9	97.8	5.8	17.4	42.7	72.1
2012–12	1	95.7	3.1	10.4	22.0	127.1
	2	97.6	3.8	12.3	63.3	109.6
	3	98.9	2.6	7.6	31.0	59.1
	4	101.9	2.1	6.0	17.5	43.4
	5	93.3	0.1	0.4	0.5	2.9
	6	97.9	1.3	8.6	14.2	45.8
	7	93.2	4.2	17.5	36.1	109.3
	8	97.6	4.5	11.1	24.8	58.3
	9	93.3	1.8	9.6	18.8	75.5
2013–6	1	98.7	15.6	18.6	113.3	80.5
	2	100.2	14.0	17.6	86.7	98.1
	3	101.2	2.6	11.2	43.0	79.8
	4	102.2	7.1	13.1	30.3	38.1
	5	98.4	0.1	0.4	1.2	4.2
	6	100.7	6.3	5.1	24.9	47.8
	7	96.8	9.1	12.0	88.7	82.9
	8	94.0	8.3	7.1	32.7	63.2
	9	94.5	6.9	12.3	32.0	51.4

interbedded magmatic rocks (Higuera *et al.* 2013) forming a tectonic structure, known as the Almadén syncline (Hernández *et al.* 1999). The district was historically affected by massive mining activities, developed over more than two millennia, including more than 52 decommissioned Hg mines of very different sizes, and scattered throughout the district. The main Hg ore deposits consist of the dissemination of cinnabar (HgS) stratabound in the so-called *Criadero* Quartzite formation (Lower Silurian age), together with cinnabar veins and replacements of volcanic rocks which are not

coupled with specific stratigraphic layers (Higuera *et al.* 2013), along with polymetallic (Pb-Zn-Cu-Ag-W) hydrothermal vein fillings related to the late stages of placement of Hercynian granites.

Sampling and analysis

Stream sediment samples were collected from nine selected sites (Fig. 1). A total of six field campaigns were carried out in different months over three years (2011–13); a total amount of 54 samples

Table 2. Mean proportions of mercury in different fractions over the six time periods

Fractions of mercury	Proportion of fractions (%)					
	2011–5	2011–11	2012–2	2012–6	2012–12	2013–6
Exchangeable/Carbonate (F1)	5.3	3.2	2.6	6.2	2.5	5.7
Fe-Mn oxides (F2)	10.6	10.9	8.8	11.6	9.2	8.5
Organic (F3)	28.5	20.4	21.6	33.2	22.4	34.6
Residual (F4)	55.6	65.4	67.0	49.0	66.0	51.2

were collected and processed. Samples were recovered using a plastic shovel, paying attention to minimize the cross-contamination among the sites. Samples were stored in disposable zip-bags and kept refrigerated at 4°C in the field.

In the laboratory, sediments were air-dried for two days at room temperatures (20–25°C) to avoid possible loss of easily volatile elements such as Hg. The dried samples were then sieved through a 2-mm mesh to remove pebbles, coarse organic fragments and shells. The remaining material (<2 mm) was homogenised and split into subsamples. An optimised BCR sequential extraction procedure was applied to partition the total Hg concentrations into their loosely bound (non-detrital) and residual (detrital) fractions in the samples. This method was described in detail elsewhere (Quevauviller *et al.* 1997) and adapted to a four-step scheme by Sahuquillo *et al.* (1999). Following this last publication, the method applied essentially consists of four extraction steps, namely: (1) Step 1, extraction with 0.11 M acetic acid to recover the easily exchangeable and carbonate-bound species (F1); (2) Step 2, extraction of the residue from the previous step with 0.5 M hydroxylamine hydrochloride at pH 1.5 to recover the species associated with Fe-Mn oxides (F2); (3) Step 3, reaction with 8.8 M H₂O₂ followed by extraction with 1.0 M ammonium acetate at pH 2 to recover species bound to organic matter (F3); and (4) Step 4, the final residue is dissolved using aqua regia + HF for recovery of refractory species (F4), including mostly cinnabar, the main Hg ore (HgS). It was applied to 1.0-g sediment subsamples in triplicate; the metal concentrations of the extracts obtained in the four steps of the procedure were analysed by ICP-MS. The quality of the analytical data for the BCR sequential extraction procedure was assessed by comparing the recovery percentage of the elements with respect to the total concentration already reported by Garcia-Ordiales *et al.* (2016a).

Results and discussion

Concentrations of the BCR steps at each point are shown in Table 1. Within the sampling sites, three different groups can be differentiated according to their location. The first group comprises the sampling sites 1, 2 and 7, which are close to mine sites. These sites show the highest total Hg concentrations of the district and high variability in the different BCR steps as a consequence of their location. The second group comprises only Site 5, which exhibits the lowest concentrations of the district, because there are no direct Hg contributions to this site since no Hg mines are located in its hydrographic basin. Thus, Hg contributions to this site come mainly from natural sources and consequently, variability of the concentrations in the different BCR steps is very low. Finally, the third group (sampling sites 3, 4, 6 and 9) comprises the rest of sites downstream of the mine areas. These sites show that Hg concentrations decrease with distance from the source as a consequence of the input of fresh uncontaminated materials to the sediments.

Measurements of the proportions of Hg in the four fractions in the six periods considered show that the residual fraction (F4) was systematically dominant, with mean proportions from 49.0% to 67.0% (Table 2). The organic fraction (F3) ranked second to the

residual fraction, with mean proportions ranging from 20.4% to 34.6%, while the exchangeable/carbonate (F1) and Fe-Mn oxide fractions (F2) had the lowest proportions with mean percentages from 2.6% to 6.2%, and 8.8% to 11.6%, respectively. The dominance of the residual fraction indicates that cinnabar, present in the mineralized rocks and in mine wastes, is a mineral resistant to local weathering conditions (Esbrí *et al.* 2010), and so it constitutes the main source of Hg into the sediment, in the form of detrital mineral. Besides, the relatively large proportion in the organic fraction indicates that non-detrital Hg has a strong ability to be incorporated into organic matter (OM) as a primary sink.

The seasonal variation in mercury fractions among the nine sampling periods is shown in Figure 2. A comparison of the temporal variations in the fractions during the study period shows a differential allocation of Hg bound to organic and residual fractions during the wet and dry seasons. The residual fraction (F4) proportions are greater during the wet seasons (November 2011, February 2012 and December 2012) than in the dry seasons (May 2011, June 2012 and June 2013). In contrast to the residual fraction (F4), the proportion in the organic fraction (F3) is higher during the dry seasons than the wet seasons. The exchangeable/carbonate (F1) and Fe-Mn oxides (F2) fractions hardly vary between periods. An ANOVA analysis performed on the dataset show similarities for the organic (F3) and residual (F4) fractions between the months considered dry (May 2011, June 2012 and June 2013; $P > 0.05$) and also show similarities between the months considered wet (November 2011, February 2012 and December 2012; $P > 0.05$), but not between seasons ($P < 0.05$), supporting the differential allocation of Hg as a consequence of seasonality. For the exchangeable/carbonate (F1) and Fe-Mn oxide (F2) fractions, the ANOVA test does not show significant differences between months and seasons.

The resuspension of sediments due to higher water velocity during the wet seasons reduced the amount of finest fraction in the sediment and therefore the residual fraction reaches its greatest proportions as a consequence of its association with the coarser sizes of the sediments (Garcia-Ordiales *et al.* 2016a, b). In contrast, during the dry seasons the lower water velocity favours a major proportion of finest grain sizes in the sediments. In the district, concentrations of OM negatively correlate with the quantity of sand fractions (Garcia-Ordiales 2016) and, as a consequence, major proportions of OM may exist in the sediments during dry periods. The association between Hg and OM, especially its association with reduced S-containing ligands in humic acids, is well known and widely reported in the literature (Bernaus *et al.* 2006; Graham *et al.* 2013). In the Almadén area, due to the local semi-arid climate, the river flow may cease temporarily and oxygen depletion or anoxia at the river/lake bottom may occur during long periods of drought. These reductive environmental conditions, produced as a consequence of the climatic conditions, can induce the presence of larger amounts of OM (Siepak 1999), which is reactive and may act as a complexing agent for Hg; the rest of predominant materials, mostly siliceous, do not act as effective Hg sinks in the concerned sediments (Anderson 1979). No significant variation was found among the exchangeable/carbonate and Fe-Mn oxide fractions over

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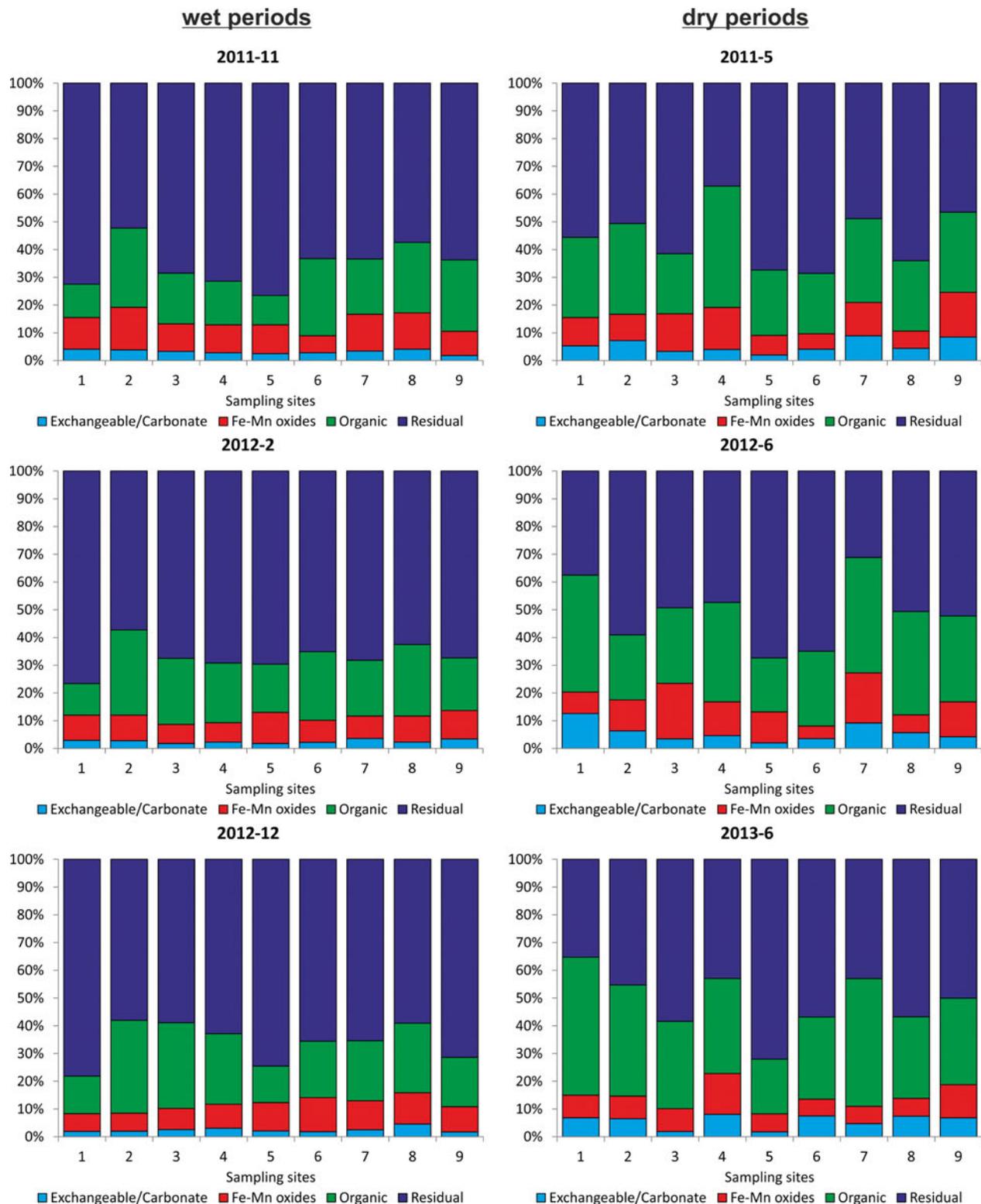


Fig. 2. Seasonal proportion of mercury fractions among the nine sampling.

wet and dry seasons. This result can be explained by the labile properties of these two fractions and the complex physiochemical processes that occur in the rivers of the district (Garcia-Ordiales 2016).

The geographical distributions of residual and organic fractions are relatively irregular because their distribution and transportation depend primarily on changes in the sediment physico-chemical conditions, since both fractions are relatively stable in the sediments in natural oxic conditions (Feng *et al.* 2014). Hydrodynamic

conditions in the district are extremely variable and complex due to the semi-arid climate of the area (Garcia-Ordiales 2016), resulting in irregular inputs to sediments and thus affecting the distributions of the organic and residual fractions (Fig. 2). However, a higher concentration of the organic fraction is found in the adjacent areas of Las Cuevas and Almadén Mines (Sites 2 and 7), which can be explained by the presence of a large cattle farm and sewage pipes, respectively. Different proportions of Hg in the non-residual fractions (F1 + F2 + F3) were found at different sites in different

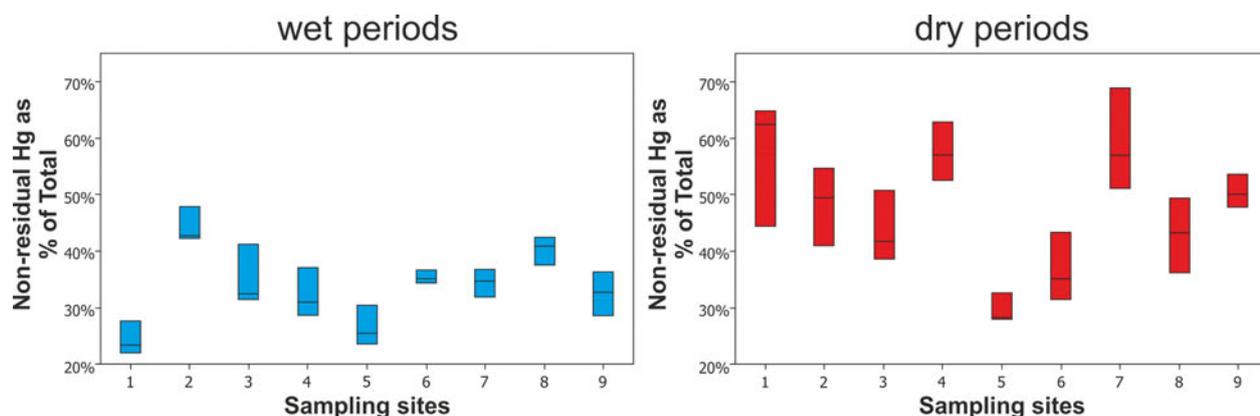


Fig. 3. Comparative of the non-residual fraction among periods.

seasons, as shown in the histogram (Fig. 3). This is especially noticeable at Sites 1 and 7, which show the greatest variations of the residual and organic fractions between wet and dry periods. Both sites are located close to the spoil heaps of El Entredicho and Almadén mines, which can be considered the main or even exclusive source of this variability. During wet periods, the major proportion of the residual fraction is attributed to the rain contributions, which transport coarse sizes, rich in cinnabar, from the spoil heaps, while in summer, as the runoffs disappear and the river trends to a null flow, Hg bound to the organic fraction gains prominence in the sediments. In contrast, lower variability corresponds to Site 5, in which fractions are almost constant between different periods because the river is not directly affected by Hg mining, as it occurs in the rest of sites.

The distribution pattern of the total concentration of Hg in the district was shown in detail by Garcia-Ordiales *et al.* (2014), demonstrating that the areas near mine sites present the higher total contents of Hg and, based on this, they should be the areas of higher ecological risk. However, the total Hg concentration cannot reliably represent the ecological risk of the area because this parameter does not take into account the actual mobility and (bio)availability of metals. Conversely, the sequential extraction procedure seems to be the most realistic approach for assessing the mobility, (bio)availability and the associated potential risk for the aquatic medium (Chen *et al.* 2010). Some authors consider the Risk Assessment Code (RAC) as an appropriate index to evaluate the potential ecological risk of trace metals, based on the use of the combined percentages of exchangeable and carbonate fractions (e.g. Marrugo-Negrete *et al.* 2017). However, other fractions such as Fe-Mn oxides

and organics, which are more stable compared to exchangeable and carbonate fractions (Lambertsson & Nilsson 2006), must also be taken into account since changes in the environmental conditions (e.g. redox, pH) can also produce bioavailable and bioaccessible elements associated with both fractions. Thus, evaluation of the non-residual fraction (exchangeable/carbonate + Fe-Mn oxide + organic) is a more realistic method to assess the bioavailability and the associated potential risk for the aquatic medium. Also, for a proper consideration of this potential risk, the values of the non-residual fraction and their comparison with standards reported in the bibliography have been taken into account.

The non-residual (NR) fraction values (Fig. 4) for the six periods indicates that the entire area generally has high proportions of Hg potentially (bio)available and the NR concentrations widely surpass the worst recommended standards reported by reference agencies such as US NOAA (Severe Effect Level: $2 \mu\text{g g}^{-1}$). Special attention must be paid to data obtained in May 2011, June 2012 and June 2013, because these periods had higher NR values than the other seasons as a consequence of the higher proportions of organic fractions. According to the results, organic fractions were influenced by the season, whereas the other fractions that form the NR fraction showed no obvious seasonal relationship. Thus, the organic fractions seem to be the more realistic factor that can increase or decrease the (bio)availability of Hg in the medium. The organic fraction plays an important role in the methylation process when serving as an Hg sink and as a food for methylation bacteria (Kocman *et al.* 2004; Frohne *et al.* 2012). In the district, methylation processes have already reported in the local sediments (Gray *et al.* 2004), and the transference of methylmercury to the food chain also

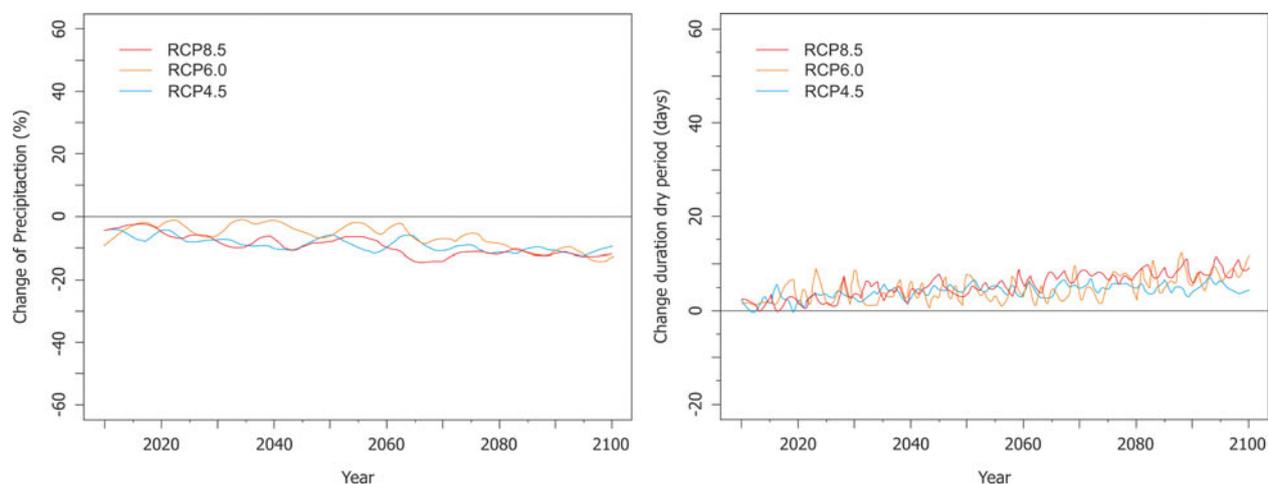


Fig. 4. Predictions of changes in precipitations and duration of dry in Ciudad Real province (IPCC 2014).

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has been verified (Berzas Nevado *et al.* 2003; Moreno-Jimenez 2008). Thus, potential risks seem to be higher in dry periods than in wet ones, according to these results. Although the studied periods were short, and no apparent trends were found, the results indicate that seasons may have directly or indirectly affected the Hg fractions by changing the natural conditions. Seasonal changes physico-chemical conditions in the rivers could mainly have affected the precipitation/absorption processes, which may also have been altered by the flow velocity and the resuspension/deposition of sediments. This seasonality is especially relevant in future climatic scenarios for the area, such as those shown in Figure 4, extracted from the Intergovernmental Panel on Climate Change (IPCC 2014). Mercury levels in the sediments of the district have declined over time as a consequence of the mining closure and natural attenuation (García-Ordiales *et al.* 2016a). However, nowadays concentrations are still far from natural geochemical values (García-Ordiales *et al.* 2014). According to total Hg concentration trends in the district sediments and to the results of this study, the future climatic scenarios for the region, in which dry periods will be intensified, seem to suggest an increase in the potential risk for the environment due to a hypothetical rise in the non-residual fraction.

Conclusions

The large amounts of Hg present in the sediments of the Almadén mining district are mainly governed by their partition between the organic and residual fractions. Both fractions show obvious distribution patterns downstream from the mine sites and seasonality plays an important role in their predominance. Non-residual fraction values, taken as mechanisms for a preliminary assessment of the potential risk for the aquatic medium, show that significant amounts of bioavailable Hg are stored in the sediments. While in wet periods the residual fraction is dominant, in dry periods the non-residual fractions gain prominence and, consequently, higher amounts of potentially bioavailable Hg are present in the sediments. As the non-residual fraction is mainly governed by the organic fraction, during dry periods the peculiar/singular environmental conditions of the district, with oxygen depletion or anoxia at the river bottom, may imply negative effects on the ecological system and human health. Climate change scenarios for the region suggest that dry periods will be more frequent in the future, and therefore the potential risks could be increased according to the results of this research.

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