

Heavy metal contamination in sediments of an artificial reservoir impacted by long-term mining activity in the Almadén mercury district (Spain)

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Abstract Sediments from the Castilseras reservoir, located downstream on the Valdeazogues River in the Almadén mercury district, were collected to assess the potential contamination status related to metals(oids) associated with river sediment inputs from several decommissioned mines. Metals(oids) concentrations in the reservoir sediments were investigated using different physical and chemical techniques. The results were analyzed by principal component analysis (PCA) to explain the correlations between the sets of variables. The degree of contamination was evaluated using the enrichment factor (EF) and the geoaccumulation index (Igeo). PCA revealed that the silty fraction is the main metals(oids) carrier in the sediments. Among the potentially harmful elements, there is a group (Al, Cr, Cu, Fe, Mn, Ni, and Zn) that cannot be strictly correlated to the mining activity since their concentrations depend on the lithological and edaphological characteristics of the materials. In contrast, As, Co, Hg, Pb, and S showed significant enrichment and contamination, thus suggesting relevant contributions from the decommissioned mines through fluvial sediment inputs. As far as Hg and S are concerned, the high enrichment levels pose a question

concerning the potential environmental risk of transfer of the organic forms of Hg (mainly methylmercury) from the bottom sediments to the aquatic food chain.

Keywords Heavy metals · Sediments · Reservoir · Almadén mining district

Introduction

Contamination of sediments by metals(oids) and organic chemicals is one of the major threats to aquatic ecosystems, and it may lead to serious environmental problems as it causes, for instance, acute and chronic toxicity to organisms (Sin et al. 2001; Skordas et al. 2014). Trace metals can be introduced into freshwaters in gaseous, dissolved and particulate phases and from several sources, which may be either natural or anthropogenic. Generally, most of the metals in uncontaminated aquatic ecosystems are lithogenic as they are derived from rock and soil weathering and are present at very low concentrations, preferentially associated with sediment particles (Varol and Sen 2012). The most significant anthropogenic sources of metals are activities related with mining and smelting, municipal and industrial effluents, dry and wet deposition, or fertilizers and pesticides in agriculture (Zhao et al. 2013; Hashmi et al. 2013; Li et al. 2014). Consequently, sediments are essentially repositories of the contamination status of the aquatic environment and they represent an excellent tool for assessing spatial and temporal effects of the anthropogenic sources (Ioannides et al. 2015).

Within catchment areas, dam construction alters the natural water flow and this, in turn, modifies the sediment inflow and outflow mass balance due to depth increases and flow velocity

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decreases. Artificial reservoirs play an important role as they act as an accumulation trap for sediments. A wide variety of contaminants, heavy metals included, that are introduced upstream of the reservoir encounter ideal conditions to settle down in these basins in conjunction with particles. The contaminants are buried in bottom sediments, and this leads to anomalous enrichments compared to natural backgrounds. Any change in the biogeochemical conditions within the reservoir, such as eutrophication or thermal stratification, may have a detrimental effect on the natural ecosystem, since sediments may become secondary sources of metals and metalloids in the water column (Gray et al. 2000, 2003; Zheng et al. 2008; Sarmiento et al. 2009; Torres et al. 2014). The investigation of metal contents and speciation in reservoir sediments belonging to contaminated catchment areas should be a high-priority task to assess the potential threat to the health of humans and aquatic organisms. Concentrations of the most bioavailable forms of metals that occur in the sediments are needed to predict metal toxicity.

The present study focuses on the Castilseras reservoir, an artificial water body located along the course of the Valdeazogues River (mercury valley is the literal translation from Spanish), which flows south from the Almadén mercury mining district and receives significant inputs from several cinnabar (HgS) mines in the area (Hernández et al. 1999). In addition to these Hg-rich inputs, the river also receives Pb-Zn and related metal(oid)-rich lixiviates from a number of minor deposits of these metals within the district.

The aim of this study was to carry out a preliminary evaluation of the role played by Castilseras reservoir as a sink for heavy metals associated with freshwater sediments that originate within the drainage area seriously affected by the presence of several types of decommissioned mines, in order to acquire necessary information about the metal contents, and the main factors associated with their dispersion for future corrective action plans. The contamination characterization of sediments in the area was followed by calculation of the geoaccumulation index, and this was supported by statistical analysis to examine the extent and the degree of heavy metal contamination in the reservoir sediments.

Materials and methods

Study area

The Almadén mining district (South Central Spain) is well known as the most important mercury (Hg) district in the world. The district consists of a wide region that was historically affected by the massive mining activities developed over more than two millennia, where more than 52 decommissioned mines are located and where mineral traces of Hg are widely dispersed (Puche 1989). In a general

geological context, the district is mainly formed by siliciclastic rocks with ages ranging from Ordovician to Late Devonian. Lithological materials are mostly orthoquartzite, sandstone, and slate with igneous rocks cropping out as dykes, sills, diatreme bodies, and well-bedded volcano-sedimentary layers (Hernández et al. 1999; Higuera et al. 2013). The area is characterized by a semiarid climate where the annual precipitation rate falls between 500 and 525 mm, the average temperature is about 15–16 °C, and the average evapotranspiration amounts to 963 mm (Schimid et al. 2003).

The catchment area of Almadén includes different streams and creeks, with the main stream being the Valdeazogues River. Along the river course, the Castilseras reservoir (4°47' W longitude and 38°44' N latitude) in the southern part of the district is located downstream with respect to four of the five most important Hg mines and other polymetallic mines scattered in the region (Higuera et al. 2012; Palero 1991; Palero and Lorenzo 2009). The reservoir was built in 1983 and has a storage capacity of 5 Hm³ of water. The catchment area of the reservoir covers 574 Km², and the average surface area of the reservoir is 97 Ha. The artificial lake is classified as holomictic, and physical mixing occurs between the surface and the deep waters during autumn and winter months. Conversely, during wet periods, the water layers do not intermix and thermal stratification appears to determine anoxic conditions in the hypolimnion layer. The average stream flow is 55.1 Hm³ year⁻¹, although very high discharge rates can occur during occasional winter floods. In addition, during these flood events, large amounts of particulate material eroded from the riverbed and from run-off are transported into the reservoir. In the recent past, the reservoir was used for hydroelectric power generation and crop irrigation using a pipe that removed sediments from the bottom. The reservoir is now used to regulate water resources and for recreational purposes such as picnics, fishing, and bathing.

Sample collection and physico-chemical analysis

Sediment sampling was planned and designed taking into consideration the characteristics of the reservoir. Samples were taken from the head of the reservoir downstream from the dam along its main axis. Twelve sampling points (labelled Cs) were eventually considered in this study (Fig. 1). Surface sediments were collected using a Van Veen grab. The first two centimeters of sediments were scraped off with a plastic shovel, homogenized on board, transferred into pre-conditioned containers with a double closing device, and stored in a refrigerator. Once in the laboratory, samples were further homogenized and split in several subsamples before being frozen (< -20 °C) and then lyophilized (48 h). Dry samples were sieved through a 2 mm mesh to remove the coarse gravelly fraction (>2 mm).

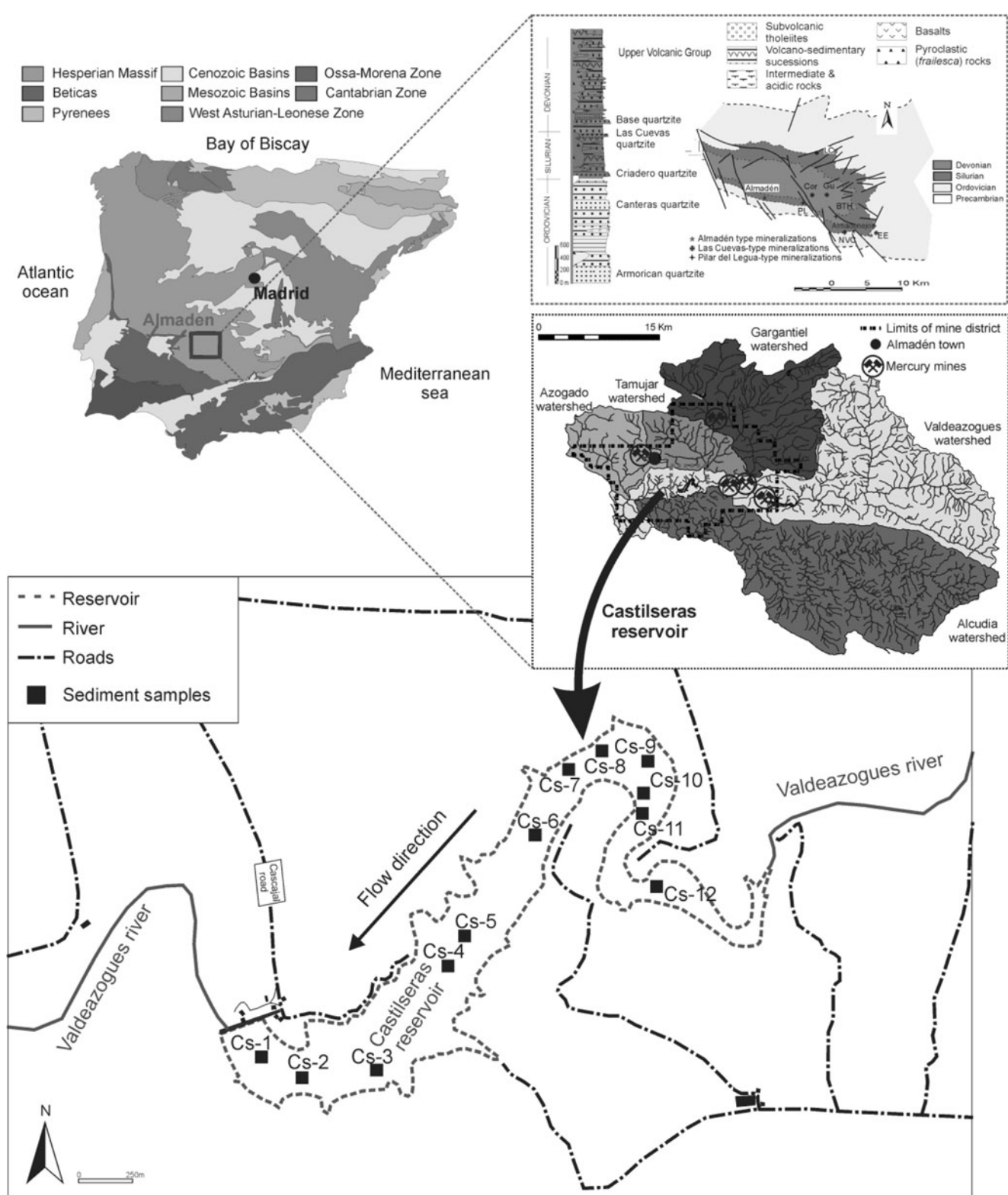


Fig. 1 Sketch maps of the study area and location of the sampling points

Grain-size analysis was performed on the <2 mm fraction of each sample. Sediment samples were treated for 48 h with hydrogen peroxide (H₂O₂) to

remove excess organic matter. The analyses were conducted using a Malvern Mastersizer 2000 laser granulometer.

For chemical analyses, dry samples were homogenized and crushed using an agate mortar and an agate grinding mill to obtain particles with a size of less than 63 μm mesh. The prepared samples were stored in refrigerator prior to analysis in order to avoid chemical alteration.

The pH was determined using a glass electrode in a suspension (1:5 v/v) of sediment/deionized water and potassium chloride (KCl) solution according to the ISO 10390:1994 standard method (ISO 1994). To determine the total organic carbon content (TOC), sediment samples were treated with hydrochloric acid and analyzed by combustion catalytic oxidation at 680 $^{\circ}\text{C}$ (TOC-V CSH Shimadzu). Total carbon (C_{total}) was determined by direct combustion (950 $^{\circ}\text{C}$) with the same equipment used for TOC, and the inorganic carbon (C_{inorg}) was calculated as the difference between C_{total} and TOC. The quality control of the results was ensured by measuring duplicate samples and by glucose and sodium bicarbonate pattern analysis according to the manufacturer's instructions.

Total Hg content in sediments was determined by thermal decomposition atomic absorption spectroscopy (AAS) with gold amalgamation (LECO[®], model AMA-254). Samples were analyzed in the solid state according to the methodology proposed by Costley et al. (2000). Quality control was tested using certified reference materials PACS-2 (Hg $3.04 \pm 0.25 \text{ mg kg}^{-1}$), CRM026-050 (Hg $2.42 \pm 0.32 \text{ mg kg}^{-1}$), and CRM042-056 (Hg $46.7 \pm 8.09 \text{ mg kg}^{-1}$). The recovery percentages for these materials were in the range 93–109 %, and the calculated relative standard deviation in % (RSD) for three replicates of each sample was less than 10 %. Organic mercury was analyzed with the same equipment following the methodology proposed by Válega et al. (2006). Briefly, sediment samples were first treated with an acid solution ($\text{KBr}/\text{H}_2\text{SO}_4/\text{CuSO}_4$) followed by extraction of the organic mercury halide with toluene and back-extraction with an aqueous sodium thiosulfate solution.

The major and trace elements were determined after digestion of 0.5 g of sample in hot *aqua regia* (95 $^{\circ}\text{C}$). Three replicates of each sample were digested and analyzed at Acme Analytical Laboratories Ltd. (Vancouver, Canada) by inductively coupled plasma atomic emission spectroscopy (ICP-AES) and inductively coupled plasma mass spectrometry (ICP-MS). The detection limits were 10 mg kg^{-1} for Al, Fe, Ca, Mg, Na, and K, 3 mg kg^{-1} for Pb, 2 mg kg^{-1} for Mn and As, and 1 mg kg^{-1} for Cu, Zn, Ni, Co, and Cr. The accuracy of the elemental determination was verified using several certified reference materials (CRMs); STD OREAS45CA, STD DS8, and CRM042-056. Recovery percentages of the different elements were in the range 82–111 %, and the RSD was less than 7 %.

Data analysis

The results were analyzed by principal component analysis (PCA) according to criteria explained by Preacher and MacCallum (2002) and Abdi and Williams (2010) for small datasets. Also, Pearson's correlation matrix was obtained from the variables dataset using Minitab 15. PCA was performed with Varimax rotation for extract and derive factors, and the first 2 PCs with eigenvalue >1 (according to of Kaiser Criterion) were considered according to the aforementioned statistical criteria.

Two different methodologies were applied to assess the contamination level and the potential impact of mining activities on the sediments of the Castilseras reservoir. The first approach concerned the enrichment factor (EF), a numerical method based on the identification of anomalous metal concentrations by normalizing their contents to one element, which must be a significant constituent of one or more of the major trace metal carriers and reflect their granular variability in the sediments. The normalizing elements often considered are Fe (Çevik et al. 2009; Abraham and Parker 2010) and Al (Covelli et al. 2006; Zhang et al. 2009; Hu et al. 2013), although other less common elements, such as Sc, have also been employed (Ravichandran et al. 1995). In the study reported here, the comparison between Fe and Al contents in the reservoir sediments and in six independent background samples, taken upstream from the water reservoir (Garcia-Ordiales 2014), showed that the partition and the regression lines of the data (obtained from the uncontaminated samples and the Castilseras samples, respectively) were not coincident (Fig. 2). This fact can be attributed to slight enrichment in Fe in the reservoir, as consequence of the mining activities, due to the presence of iron minerals (mainly pyrite, FeS_2) in the neighboring ore deposits. Therefore, Al, whose origin in our sediments should be exclusively geogenic, was chosen as a grain-size proxy to normalize metal concentrations. The EF is defined as follows (Grant and Middleton 1990):

$$EF = \frac{\left(\frac{C_x}{Al_{ref}}\right)_{\text{sample}}}{\left(\frac{C_x}{Al_{ref}}\right)_{\text{background}}}$$

where $(C_x/Al_{ref})_{\text{sample}}$ is the concentration ratio of the heavy metal (C_x) and the normalization element (Al_x) in the sample, and $(C_x/Al_{ref})_{\text{background}}$ is the same ratio in a suitable background sample. The EF values are interpreted according to the metal pollution levels proposed by Chen et al. (2007): $EF < 1$ no enrichment, $EF = 1-3$ minor enrichment, $EF = 3-5$ moderate enrichment, $EF = 5-10$ moderately severe enrichment, $EF = 10-25$ severe enrichment, $EF = 25-50$ very severe enrichment, and $EF > 50$ extremely severe enrichment.

In addition, possible contamination by metals of the reservoir sediments was also evaluated in terms of the

geoaccumulation index (I_{geo}) (Müller 1969), which is expressed as follows:

$$I_{geo} = \text{Log}_2 \left(\frac{C_n}{1.5B_n} \right)$$

Here, C_n is the measured concentration of the metal (n) in the sediment, B_n is the background value for the metal (n), and the factor 1.5 is introduced to include possible differences in the background values due to lithological variations. The I_{geo} index was calculated using the same background values as applied to the EF, and the results are interpreted in accordance with the six levels of metal pollution suggested by Müller (1969).

Results

Main physico-chemical characteristics of sediments

The grain-size distribution of the main components of the Castilseras reservoir sediment is presented in Fig. 3. The silty fraction is usually predominant, and it showed the highest variability of the three components, ranging between 35.57 and 88.75 % (avg. 72.92 ± 66.44 %). The sandy fraction can be considered subordinate to the silty fraction (avg. 17.05 ± 16.94 %) whereas the clayey component is limited (avg. 10.03 ± 16.62 %). According to Shepard's classification (1954), sediments collected in the Castilseras reservoir are mainly dominated by sandy silt or silt. There is no evidence of a trend in terms of a decrease or an increase in the mean size, although one might expect such a trend for this type of reservoir, where sediments usually become finer and richer in clay content in the water flow direction and on approaching the dam barrier. This is especially true for samples collected between stations

Cs-12 and Cs-3, between which the grain-size varied significantly. However, in the sampling stations closest to the dam (Cs-2 and Cs-1), the relative abundance of the sandy coarse fraction was negligible (0.09 and 1.17 %, respectively), whereas the clay percentages increased (15.44 % in Cs-2 and 40.08 % in Cs-1). These data are consistent with flow simulation models for similar artificial basins, as reported by Ferrari (2010) and Lv et al. (2011) among others. During periods of heavy rainfall, freshwater flows through the overflow channel located at the head of the dam. This large volume of flowing water, together with the low depth of the reservoir (13 m maximum), produces an increase in stream speed from the bottom of the reservoir towards the spillway. As a function of the water flow transported by the river, the front of this re-suspension mechanism moves away from the dam and this leads to a variation in the grain-size fractions. Furthermore, as a consequence of the water speed gradient and the barrier effect of the dam, suspended fine particles in the water column are deposited at the sampling points closest to the dam (Cs2 and Cs1) and this leads to enrichment of the associated heavy metals.

The pH values of the sediments measured in aqueous suspension are in the range 6.37–6.72, which is systematically higher than the pH values measured in KCl suspension (5.58–5.87). In general, the measured values only vary slightly and significant differences in pH values between sectors of the whole reservoir were not found.

The C_{inorg} contents, which are in the range 3.28–8.49 %, reflect a substantial carbonate origin of the sediments from weathering of geological materials that are rich in secondary carbonate minerals, such as ankerite or calcite (Higuera et al. 2013). These C_{inorg} contents mirror the variability of the sandy component in sediments, as evidenced by the positive correlation observed between the coarser component and the amount of C_{inorg} in the sediments ($\rho=0.921$, $p<0.001$). The

Fig. 2 Relationships between Fe and Al contents measured in the reservoir sediments (*regression line*) compared to the same in the six background samples (*partition line*) belonging to the Valdezogues watershed (see text for explanation)

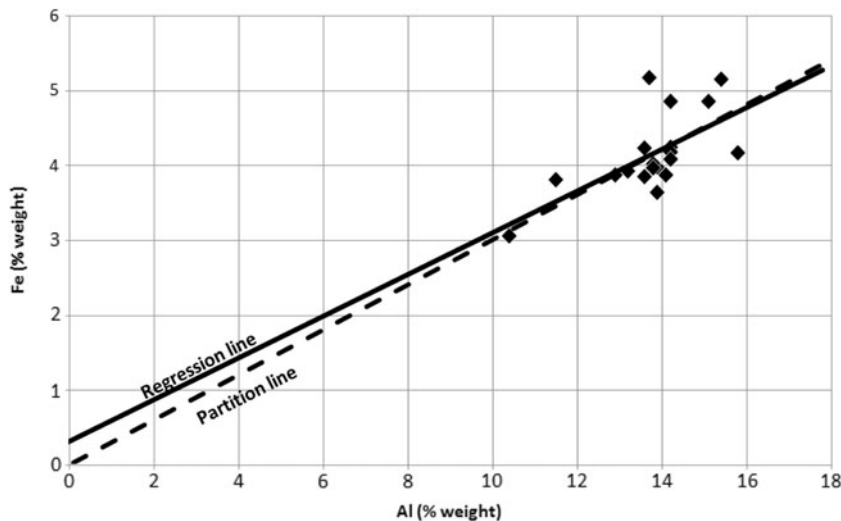
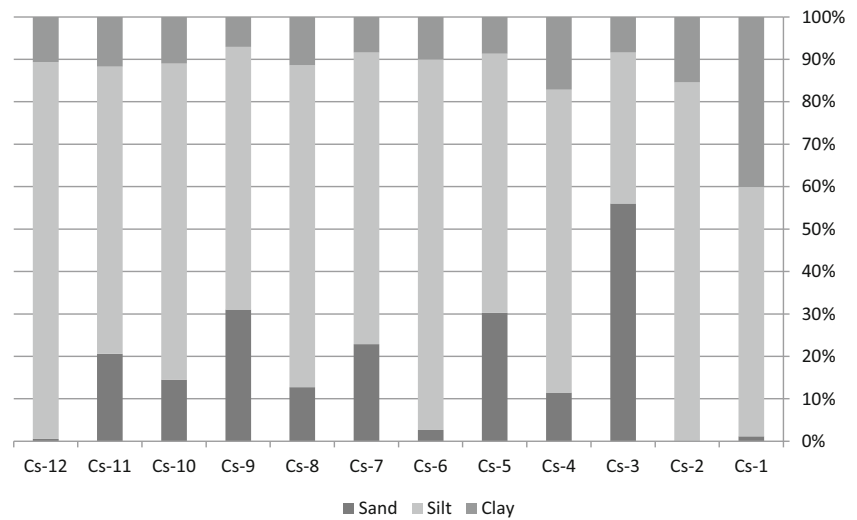


Fig. 3 Variability of the main grain-size components of sediments. Sampling stations are ordered from the head of the reservoir (Cs-12) to the dam (Cs-1)



contribution of TOC, with respect to total carbon, is in the range 10.73–49.69 %. With the exception of samples Cs-6, for which the TOC concentrations were comparable to the C_{inorg} contents, the organic carbon contribution is lower in all cases than the inorganic contents in the collected samples and this finding is consistent with the type of Mediterranean watershed of a semiarid climate (Cummins et al. 1989, Serrasolses et al. 1999). Overall, samples with high percentages of carbonates usually have low contents of TOC as a result of their geological origin.

Chemical composition of the sediments

Major and trace elements

The chemical compositions of the collected sediment samples are presented in Table 1 and Figs. 4 and 5. In terms of the major elements (Fig. 4), Al is the most abundant (avg. 14.20 ± 1.34 %) and it is associated with the muddy fraction (silt+clay), which is largely prevalent in the sediments, but it shows

only a slight increase in gradient along the flow direction. The second most abundant element is Fe (avg. 4.29 ± 0.63 %), which is present at concentrations three times lower than Al; the Fe content varies significantly along the longitudinal profile of the reservoir. The concentrations of the other major elements are below 1 % by weight in all cases. Among them, the most abundant is Mg (avg. 0.42 ± 0.15 %), followed by Ca (avg. 0.23 ± 0.06 %), K (avg. 0.17 ± 0.02 %), S (avg. 0.11 ± 0.04 %), and P (avg. 0.09 ± 0.01 %). As far as the surface distribution is concerned, Mg is distributed homogeneously whereas Ca shows a negative gradient downstream, with the lowest concentrations reached in close proximity to the dam. Conversely, K, S, and P show a positive concentration gradient from the head of the reservoir and the maximum values are reached close to the reservoir's dam. In case of K and P, this gradient may be explained by the enrichment in fine fractions in the flow direction where clay minerals are predominant. Moreover, gradient for S may be attributed to the organic matter distribution in the sediments, since this element is well correlated to P ($\rho=0.707$, $p<0.05$) and TOC ($\rho=0.619$, $p<0.05$).

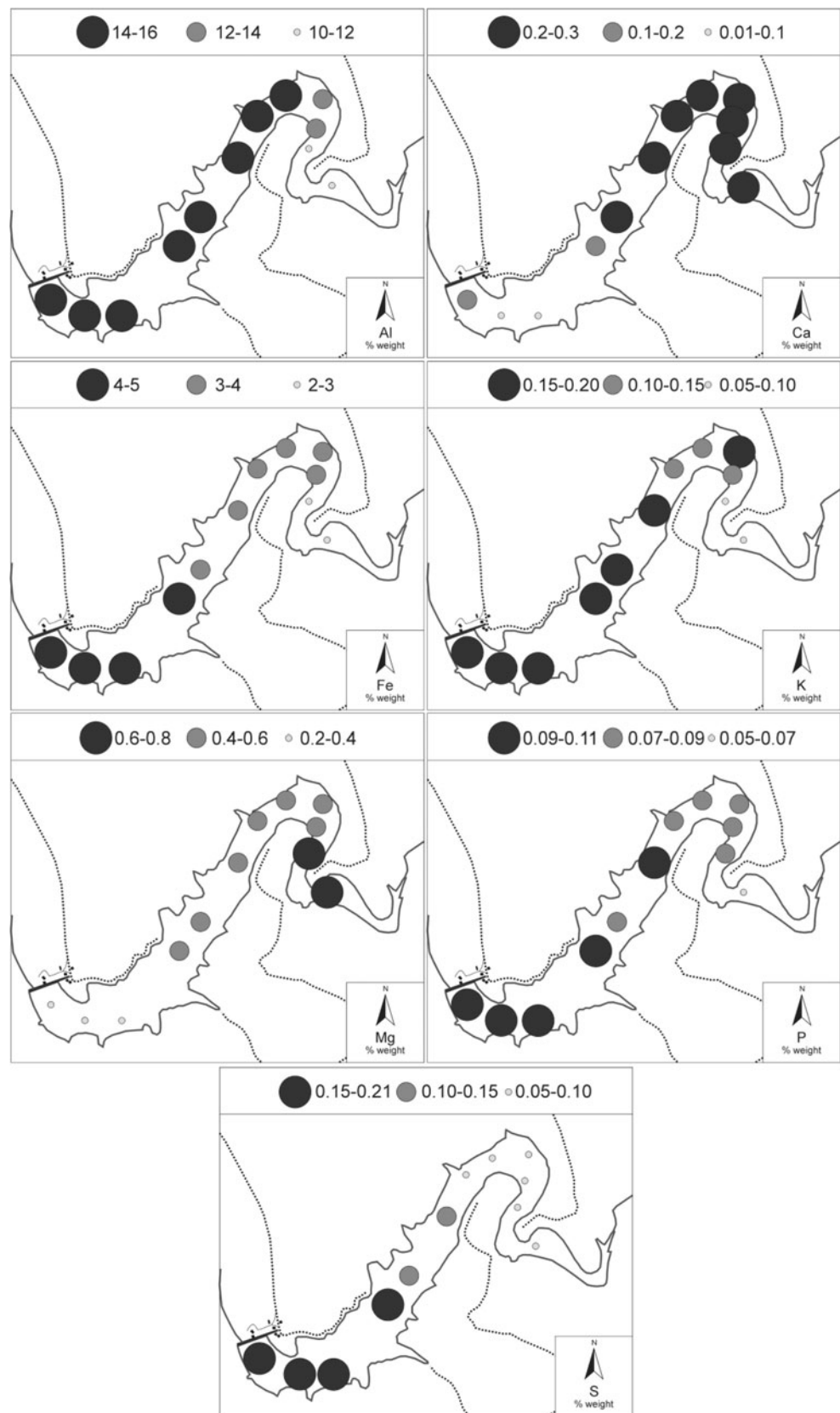
Table 1 Statistical summary of the measured parameters and elements

	Al	Ca	Fe	K	Mg	P	S	pH H ₂ O	pH KCl	IC	TOC
Median	14.07	0.24	4.2	0.17	0.41	0.09	0.10	6.47	5.71	5.33	2.87
Mean	14.20	0.23	4.29	0.17	0.42	0.09	0.11	6.47	5.72	5.61	2.81
SD	1.34	0.06	0.63	0.02	0.15	0.01	0.04	0.093	0.08	1.76	0.75
Variance	1.640	0.003	0.363	0.001	0.020	0.001	0.002	0.007	0.005	2.854	0.521
	As	Co	Cr	Cu	Hg	Mn	Ni	Pb	Zn		
Median	11.17	21.47	59.38	14.31	11.90	522.22	43.30	42.96	105.90		
Mean	11.253	21.52	64.44	14.58	11.78	539.12	43.44	40.72	103.58		
SD	11.50	2.57	10.89	3.87	3.68	78.80	6.81	7.71	14.51		
Variance	2.049	6.610	118.663	14.994	13.575	5692.002	46.425	59.505	192.956		

Units: major elements (Al, Ca, Fe, K, Mg, P, and S), IC and TOC expressed in % weight; trace elements expressed in $\mu\text{g g}^{-1}$

SD standard deviation

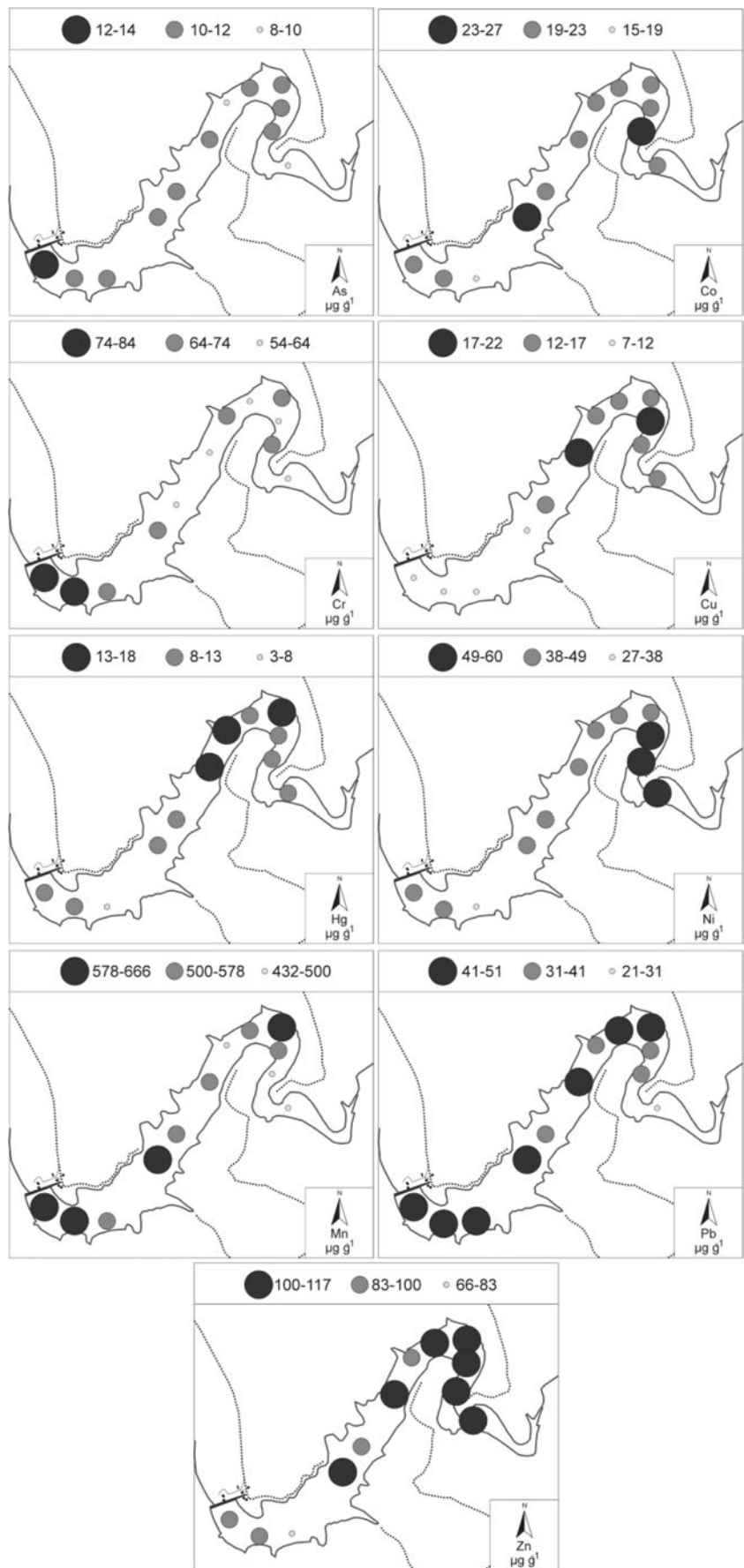
Fig. 4 Spatial distribution of the major elements total concentrations. Data are expressed as % (d.w.)



Among the analyzed trace elements (Fig. 5), the highest detected concentrations correspond to Mn (avg. $539.12 \pm$

$78.80 \mu\text{g g}^{-1}$) and Zn (avg. $103.58 \pm 14.51 \mu\text{g g}^{-1}$), whereas the lowest concentrations correspond to As (avg. $11.25 \pm$

Fig. 5 Spatial distribution of the total metal and metalloid concentrations. Data expressed as $\mu\text{g g}^{-1}$ (d.w.)



1.50 $\mu\text{g g}^{-1}$) and Cu (avg. $14.58 \pm 3.87 \mu\text{g g}^{-1}$). A decrease in the Cu, Zn, and Ni concentrations is observed along the water flow direction, and this finding suggests that these elements are preferentially associated with the sandy-silty fractions of the sediments. In contrast, the Cr, Pb, Mn, and As concentrations increase downstream, indicating that these elements are mainly associated with the finest clayey-silty particles. Finally, the Co concentrations only vary slightly over the whole reservoir.

Comparing the aforementioned results with those from similar studies of artificial reservoirs affected by different industrial inputs (Table 2), it appears that only the Rybnik Reservoir in Poland (Loska and Wiechula 2003), the Ruzin reservoir in Slovakia (Petrlakova et al. 2014), and the Aibi Lake reservoir in China (Abuduwaili et al. 2015) showed a higher metal load than Castilseras. This fact may be related to the absence of acid mine drainage (AMD) due to the buffering capacity of mafic and ultramafic volcanic rocks which are abundant in the Almadén district.

Mercury

The total mercury (Hg) concentration in the bottom sediments ranges from 2.49 to $17.30 \mu\text{g g}^{-1}$, and the highest concentration corresponds to the sampling point Cs-6, which is located at the center of the reservoir. However, the trend in Hg shows a general decrease on moving downstream along the reservoir. A comparison between Hg contents detected in the sediments of the Castilseras reservoir and those reported for similar artificial basins located just downstream of Hg districts throughout the world is shown in Table 3. Only in the Lahontan reservoir (Hoffman and Taylor 1998; Hill et al. 2008) Hg concentrations are higher than those found in Castilseras sediments. However, in both reservoirs, values are at least one order of magnitude higher than those observed in other case studies.

In general, most of the sediment samples contained organic mercury concentrations below the detection limit of the instrument, although the contents do tend to increase downstream. The highest value (10.30 ng g^{-1}) was observed at sampling point Cs-2, which is close to the dam. This point is also coincident with the greatest depth of the reservoir, and it suggests that the local physico-chemical conditions in the aquatic environment associated with depth may play an important role in favoring the production of organic Hg species in sediments. In the Almadén district, Hg is commonly present in sediments from freshwater courses (Berzas Nevado et al. 2003; García-Ordiales et al. 2014), either as cinnabar or as hydroxides (Esbrí et al. 2010). In the form of cinnabar, Hg is usually associated with fine sediments because of its high chemical stability but, due to the large number of abandoned mining operations in Almadén, cinnabar particles can be associated with other grain-size fractions such as sandy particles

Table 2 Comparison of metals(oids) contents in sediments between the Castilseras reservoir and other reservoirs around the world

	Fe	Al	Cu	Pb	Zn	Ni	Co	Mn	As	Cr
Castilseras reservoir, Spain (present study)	3.05–5.17	10.4–15.8	7.45–21.51	20.95–50.84	65.61–116.82	27.74–60.31	15.62–26.33	433.01–666.05	8.32–14.3	52.69–85.69
Ruzin reservoir, Slovakia (Petrlakova et al. 2014)	4.62–5.64	6.65–7.23	245.50–959.20	59.40–83.90	321.10–906.50	–	–	1200.00–1400.00	–	–
Manwan reservoir, China (Wang et al. 2012)	1.91–3.79	2.45–6.10	15.85–56.32	17.03–92.20	45.32–259.84	–	–	246.58–769.06	10.30–72.56	38.29–89.85
Hongfeng reservoir, China (Wang et al. 2015a)	1.36–8.57	–	14.40–93.60	1.20–89.20	–	–	–	–	0.10–49.10	34.10–141.00
Dongping Lake, China (Wang et al. 2015b)	–	–	36.50–86.10	29.20–41.30	79.90–115.40	–	–	–	19.20–38.50	67.20–102.80
Alqueva reservoir, Portugal (Palma et al. 2014)	0.80–22.40	–	3.40–124.90	<DL–197.4	14.80–354.50	7.60–159.30	–	1000.00–34,700.00	1.60–119.90	<DL–120.90
Agua Milpa, Mexico (Rangel-Peraza et al. 2015)	0.47–1.59	0.77–2.76	0.79–60.80	1.64–13.6	14.80–51.80	0.24–189.00	–	–	–	0.22–18.30
Rybnik reservoir, Poland (Loska and Wiechula 2003)	0.39–9.85	–	16.00–1116.90	11.01–315.00	50.80–2441.38	3.00–183.80	–	246.61–4215.43	–	14.27–739.11
Lianhua Mountain reservoir, China (Huang et al. 2015)	–	–	15.70–78.10	9.40–66.30	31.70–254.50	<DL–42.70	–	–	–	20.40–159.70
Drenova reservoir, Republic of Srpska (Tošić et al. 2013)	2.14–3.43	–	29.24–41.51	2.20–6.22	33.43–367.08	185.29–807.82	–	682.25–1384.90	3.66–11.84	64.95–339.03
Karla reservoir, Greece (Skordas et al. 2014)	–	–	18.00–50.70	13.20–66.00	13.20–58.00	101.00–392.00	10.90–44.80	–	–	127.00–392.00
Aibi Lake reservoir, China (Abuduwaili et al. 2015)	–	–	32.29–95.84	16.29–175.81	88.27–217.27	11.81–58.18	–	–	–	45.41–262.81
Ziqiab reservoir, Jordan (Al-Taani et al. 2015)	1.10–2.90	–	4.00–31.00	2.00–49.00	10.00–120.00	13.00–88.00	2.00–18.00	11.00–100.00	–	3.00–65.00

Units: major elements Al and Fe expressed in % weight; trace elements expressed in $\mu\text{g g}^{-1}$

Table 3 Comparison of Hg contents in sediments between Castilseras reservoir and other reservoirs located downstream from Hg mines. Data expressed as $\mu\text{g g}^{-1}$

Location	Hg	References
Castilseras reservoir (Almadén)	2.49–17.30	Present study
La Serena reservoir (Almadén)	0.44–1.8	Jiménez Moreno (2008)
Salmon Falls Creek reservoir (Idaho, USA)	0.023–0.083	Gray and Hines (2009)
Rye Patch reservoir (Nevada, USA)	0.004–0.15	Gray et al. (2002)
Lahontan reservoir (Nevada, USA)	0.01–100	Hoffman and Taylor (1998), Hill et al. (2008)
Guadalupe reservoir (California, USA)	0.42–7.29	Tetra Tech (2005)
Calero reservoir (California, USA)	0.10–0.84	Tetra Tech (2005)
Lexington reservoir (California, USA)	0.07–0.18	Tetra Tech (2005)

depending on the distance from the source (García-Ordiales et al. 2014). As the hydroxide, Hg is mainly related to aerial depositions and to leachates from mines and spoil heaps. In the surface waters of Almadén, as a consequence of the alkaline conditions (Berzas Nevado et al. 2003), Hg appears to be associated with the organic matter and is trapped by Fe and Mn oxides in the silt and clay fractions of sediments. At the sampling points located close to the dam (Cs-2 and Cs-1), where the water column and the contribution of the fine fraction are maximum, the total Hg concentrations are the lowest when compared to the rest of the reservoir. However, organic Hg, S, and Fe concentrations are at their highest at these sampling points (Cs-2 and Cs-1). These results, together with the amount of reactive organic matter (3.1 and 2.8 % TOC, respectively), suggest that sulfate-reduction processes may take place in the deepest zone of the reservoir where the high rate of organic matter degradation has consumed all of the former electron acceptors. The sulfate-reduction process activated by specific bacteria increases the risk of Hg transfer to biota living in the reservoir by promoting Hg methylation processes (King et al. 2000; Shao et al. 2012). The increase in the organic fraction is related to the formation of readily available organometallic species such as methylmercury.

Discussion

The application of PCA and Spearman's correlations (Table 4) to the geochemical data allowed the identification of element associations according to their geochemical behavior (Fig. 6). It can be seen from the results that four factors explain 84.6 % of the variance (Fig. 5). The first factor (F1) includes Al, Ca, Pb, and Zn, which are directly correlated with TOC and inversely correlated with IC and the sand contents of sediments. The second factor (F2) includes Mn, S, and clay contents in sediments, and this explains 18.5 % of the variance. The third factor (F3) includes Ni and As, and the fourth factor (F4) includes K and organic Hg. However, F3 and F4 explain less

than 15 % of variance which is not statistically relevant (Abdi and Williams 2010).

In relation to the first factor, the group of elements included shows that the geochemical composition of silt cannot be attributed exclusively to one contribution, but it is composed of a heterogeneous mixture of contributions from different sources that correspond to edaphological and geological materials. A correlation between Ca and Al ($\rho=0.754$, $p<0.05$) and between Fe and Mg ($\rho=0.703$, $p<0.05$) can be established. This evidence, along with the weakly acidic pH values, is consistent with the predominant composition of the sediments being clay and carbonate materials with low levels of sulfides and phosphates. The predominance of OH^- over H^+ ions in the media produces a buffering effect in the sediments. On the other hand, the presence of Al-rich kaolinite could be responsible for variations in the pH values measured in KCl (McLean 1982; Sumner 1994). A moderate correlation of Ca and Mg with IC ($\rho=-0.509$, $p<0.05$ and $\rho=-0.345$, $p<0.05$, respectively) was observed but, according to these data, it can be considered that lithological materials other than carbonates contribute to the enrichment of Ca and Mg in sediments. The second factor indicates a heterogeneous composition of the clay fraction, including siderophile and chalcophile elements related to the edaphologic and anthropogenic inputs. The third factor can be associated with geogenic processes and the fourth to biological methylation processes in sediments.

A careful examination of the relationships between the analyzed elements shows that Fe and Al stand apart from the rest because of their mineralogical contribution to fine fractions. In relation to Hg, the high correlation with TOC ($\rho=0.771$, $p<0.001$) is indicative of the important role played by the organic matter in Hg speciation. Furthermore, the relationship between Hg and Ca ($\rho=0.730$, $p<0.05$) suggests that carbonates are the main carrier of Hg in the sediments but, due to the lithological origin of carbonate minerals as a consequence of the volcanic processes in which the Hg ore deposits were formed, this hypothesis cannot be confirmed (Hernández et al. 1999; Higuera et al. 2013).

Table 4 Spearman correlation coefficient between analyzed parameters

	Fe	Ca	Mg	Al	K	Cu	Pb	Zn	Ni	Co	Mn	As	Cr	Hg	TOC	P	S	pH _{H₂O}	pH _{KCl}	IC	Sand	Silt	Clay	Hg _{org}	
Fe	1.000																								
Ca	-0.014	1.000																							
Mg	0.703	-0.103	1.000																						
Al	0.351	0.754	0.424	1.000																					
K	-0.116	-0.007	0.360	0.554	1.000																				
Cu	-0.109	0.462	0.208	0.075	0.078	1.000																			
Pb	0.501	0.159	0.524	0.772	0.687	0.035	1.000																		
Zn	0.753	0.441	0.445	0.374	0.007	0.308	0.517	1.000																	
Ni	0.403	0.268	0.154	0.078	-0.584	0.406	-0.014	0.538	1.000																
Co	0.683	0.138	0.237	0.107	-0.274	0.175	0.322	0.713	0.566	1.000															
Mn	0.238	-0.085	0.438	0.548	0.876	-0.091	0.832	0.161	-0.490	0.063	1.000														
As	0.567	-0.039	0.471	0.445	0.505	-0.119	0.713	0.601	-0.119	0.552	0.741	1.000													
Cr	0.389	-0.437	0.147	-0.089	-0.014	-0.322	0.035	0.070	-0.056	0.098	0.203	0.350	1.000												
Hg	-0.230	0.624	-0.074	0.312	0.073	0.673	0.025	0.126	0.322	-0.161	-0.112	-0.238	-0.221	1.000											
TOC	-0.007	0.730	-0.004	0.448	0.427	0.441	0.497	0.336	0.084	-0.049	0.371	0.175	-0.119	0.771	1.000										
P	0.540	0.293	0.592	0.371	0.314	0.151	0.609	0.606	0.270	0.193	0.385	0.413	0.403	0.137	0.448	1.000									
	0.428	0.349	0.342	0.567	0.467	-0.155	0.857	0.423	0.046	0.247	0.635	0.515	0.067	0.000	0.619	0.707	1.000								
pH _{H₂O}	0.589	0.332	0.139	0.203	-0.316	0.301	0.182	0.704	0.515	0.830	-0.081	0.382	-0.200	0.112	0.081	-0.053	0.018	1.000							
pH _{KCl}	0.735	0.153	0.250	0.242	0.063	0.074	0.399	0.593	0.049	0.600	0.346	0.557	0.406	-0.099	0.138	0.399	0.311	0.542	1.000						
IC	-0.140	-0.509	-0.345	-0.451	-0.323	0.039	-0.529	-0.196	-0.077	0.154	-0.287	-0.042	0.144	-0.235	-0.508	0.670	-0.797	0.233	0.004	1.000					
Sand	-0.378	-0.381	-0.313	-0.427	-0.128	0.161	-0.531	-0.315	-0.273	-0.014	-0.210	-0.091	-0.112	-0.144	-0.434	-0.067	-0.825	0.154	-0.123	0.921	1.000				
Silt	0.133	0.741	0.000	0.295	-0.164	0.217	0.168	0.322	0.476	-0.070	-0.210	-0.266	-0.294	0.641	0.657	0.392	0.402	0.133	-0.081	-0.676	-0.685	1.000			
Clay	0.722	0.060	0.435	0.206	0.032	-0.392	0.573	0.503	0.182	0.462	0.329	0.469	0.238	-0.483	-0.035	0.641	0.758	0.158	0.437	-0.546	-0.699	0.175	1.000		
Hg _{org}	-0.327	0.082	0.198	0.165	0.135	0.113	0.000	-0.483	-0.054	-0.538	0.029	-0.476	-0.269	0.408	0.240	-0.004	0.099	-0.417	-0.476	-0.484	-0.331	0.425	-0.171	1.000	

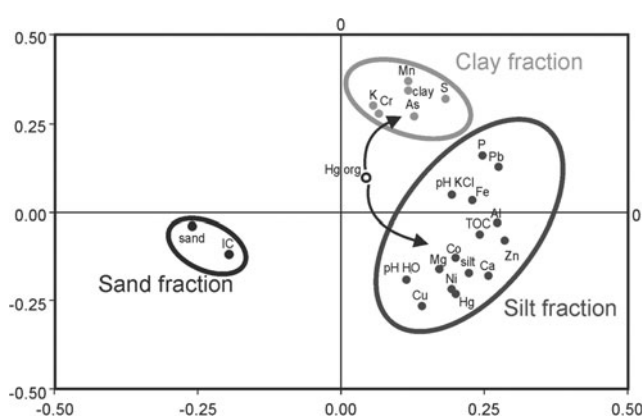


Fig. 6 Graphical results of PCA analysis applied to element concentrations, organic and inorganic carbon contents, and grain-size fractions of sediments

Finally, organic Hg is poorly correlated with the silty fraction ($\rho=0.425$, $p<0.05$) and IC ($\rho=-0.484$, $p<0.05$). From the PCA (Fig. 5), it is apparent that organic Hg is not included in any of the groups related to the fine grain-size fractions but it is close to both groups. Besides, the occurrence of organic Hg, including methylmercury, does not necessarily seem to be linked to the total Hg concentrations, but rather to several local biogeochemical factors to which grain-size appears to be subordinate. The production and accumulation of organic Hg, including methylation and demethylation processes, are complex environmental issues that would require further specific investigation in this aquatic ecosystem.

The resulting EF values (Fig. 7a) suggest that As, Co, Cr, Hg, Mn, Pb, and S can be considered as being enriched in the surface sediments of the Castilseras reservoir due to mining activities, whereas Ca, Co, Mg, Ni, and Zn have natural origin. As one would expect, the EF values for Hg are the highest among the analyzed metals. Values range from a moderate to a moderately severe enrichment related to the intensive Hg mining carried out in the district. The same EF factor applied on the Three Gorges Reservoir in China (Tian et al. 2013) showed EF values between 5.9 and 41.3, higher than EF values described on this work (1.3–6.7, see Fig. 7a for more details). The results also indicate that S has minor to moderately severe enrichments, which could be associated with the presence of polymetallic sulfide veins in the district and the precipitation of sulfates in sediments as a consequence of the alkalinity of the waters. Other elements, such as As, Co, Cr, Mn, and Pb, only exhibit minor enrichments. The differences in EF values for the different metals in the reservoir sediments may be due to the difference in the magnitude of the anthropogenic input for each metal in the sediment and/or the difference in the removal rate of each metal from the sediment.

The results obtained from the I_{geo} (Fig. 7b) indicate that surface sediments are not polluted with respect to Al, Ca, Cr, Cu, Fe, Mg, Mn, Ni, and Zn. The As, Co, and Pb levels range from unpolluted to moderately polluted. Sulfur and Hg have

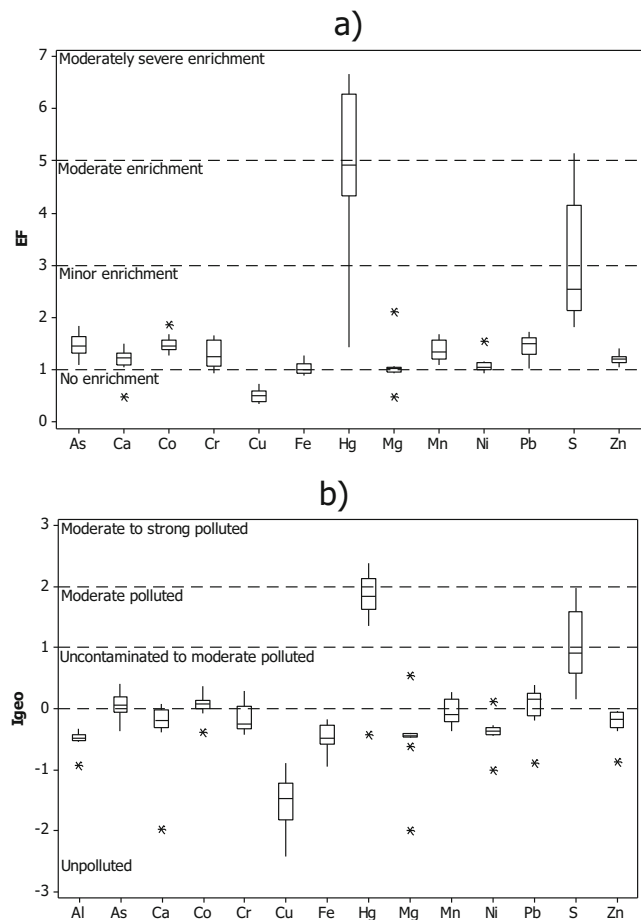


Fig. 7 a Variability (range, avg. value) for enrichment factors (EF) and b geoaccumulation index (I_{geo})

the highest levels and these range between moderately polluted and strongly polluted.

The two indexes applied indicate that both Hg and S contaminate the reservoir sediments. In fact, the calculated Hg I_{geo} for the Three Gorges Reservoir in China (Gao et al. 2014), was only slightly lower than the one found in Castilseras reservoir. Both elements show high concentrations in comparison to the geochemical background, and these high concentrations can be attributed to the mining operations carried out in the district. The high concentrations of Hg and S in sediments, together with the measured organic mercury concentrations, confirm the potential risk of methylation processes, which may occur in the reservoir sediments. Furthermore, both indexes show that As, Co, and Pb have only a low enrichment degree in sediments, and the origin of this enrichment can be attributed to long-term anthropogenic activities such as Hg mining, where As, Co, and Pb are accessory elements in the mineral paragenesis (Puche 1989). The rest of the elements, which have low values for both indexes, can be considered as not being enriched since their origin is lithogenic and is related to erosion of the rocky substrate and soil materials.

Conclusions

The work described here involved an examination of the role played by the Castilseras reservoir as an accumulation site for potentially harmful elements associated with freshwater sediments originating from the Almadén mining district. This reservoir acts as an efficient hydraulic trap for fine—mainly silty and, subordinately, sandy—particles. The evidence presented provides preliminary information on differences in contamination status related to the investigated trace metals in the bottom sediments. In fact, single concentration values alone do not explain the real impact of each element that is potentially related to mining activity in this aquatic environment. The choice of a suitable local background and the application of appropriate indexes, such as the EF and the I_{geo} , has proven to be useful for a correct assessment of the quality of reservoir sediments. They appear from moderately to moderately severe enriched in Hg (using EF) or from moderately polluted to strongly polluted (using I_{geo}), thus identifying Castilseras as one of the most Hg contaminated reservoirs all over the world. In association with Hg, other potentially harmful elements, such as As and Pb, can be attributed to environmental liabilities of decommissioned mines, actually identify a significant contamination degree due to the profound human alteration of the surface environment. Of particular concern is Hg, since favorable biogeochemical conditions at the reservoir bottom may facilitate methylation processes and the consequent transfer of Hg to the food chain, thus increasing its potential biological effects on edible aquatic organisms. Further investigation is therefore recommended to assess the toxicity levels of the reservoir sediments and also to evaluate the possible biological effects of these potentially harmful elements on fish, crustaceans (crayfish), and plants.

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