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Stream bottom sediments as a means to assess metal contamination in the historic mining district of Almadén (Spain)

Efrén Garcia-Ordiales*a*, Jorge Loredoa, Jose Maria Esbrib, Miguel Angel Lomincharc, Rocio Millanc and Pablo Higuerasb

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Located in the southern half of Spain, Almadén is the world’s largest Hg district and mercury has been mined there for over 2000 years. Its slag heaps and old metallurgy plants represent a risk to watercourses that flow through the district and receive the run-off from the mines. This study collected sediment samples along the length of the main watercourses in the mining district. High levels of heavy metals were detected, with Hg levels varying between 1.77 and 255.88 mg kg\(^{-1}\), Pb levels between 20.59 and 131.07 mg kg\(^{-1}\) and Zn levels between 59.06 and 131.07 mg kg\(^{-1}\). The dispersion of these heavy metals in rivers as a result of mining activities has caused sediment quality degradation. As such, when measured using reference indexes such as the SeQI and the EF, sediment quality for the entire district is practically poor, due to anthropogenic contributions, with the concomitant threat to the surrounding environment.

**Keywords:** Almadén; mercury; heavy metals; river bottom sediments; sediments quality index

**Introduction**

Decommissioned mercury mines represent a significant source of mercury (Hg) and also occasionally of other heavy metals in the environment as a result of the dumping of waste material originating from mines and metallurgy plants with a high concentration of Hg [1–5]. The metallurgical processing of Hg in mining districts has left a legacy of major mining liabilities as a result of the inefficient calcination of the mineral cinnabar. As this is an incomplete process, other types of soluble and insoluble compounds not originally present at the site, such as metacinnabar or mercury salts, are formed during the processing [6,7].

The run-offs originating from the mining liabilities have an adverse effect on the ecosystems of the areas surrounding the mercury mines [8–11]. Stream-bed sediments and bodies of water located downstream from the mercury mines are characterised by significant levels of Hg and heavy metals, which can persist for decades after mining activities cease [5,7,12].

The mining district of Almadén, located in south-central Spain, is the world’s largest geochemical mercury anomaly, and it has produced one-third of total global
production of this element [13]. The district includes a series of deposits with a range of structures and textures that share a relatively simple paragenesis whose dominant mineral is cinnabar, with pyrite present in lesser quantities. The most important mineralisation type, found in the mines of Almadén and El Entredicho, consists of strat-abound cinnabar disseminations in Criadero Quartzite (Lower Silurian) [13]. Other type of mineralisation present in the area is composed of cinnabar filling veins and replacements of volcanic rocks that cannot be associated with specific stratigraphic layers [14,15]. Throughout its history, the district has been the site of various mines and metallurgy facilities. In terms of mines, Almadén is by far the largest and it has been the one most heavily mined, followed by El Entredicho, Las Cuevas and Nueva Concepción. In terms of metallurgy plants, some of them exist along the district, but two are the most important, located close to Almadén and Almadenejos urban areas; although the one in Almadenejos is smaller than that of Almadén (both date back to the eighteenth and nineteenth centuries), it has been responsible for significant pollution in its surrounding area [9,16]. In addition to the large-scale mining of mercury, the area has many other small mines and there is widespread evidence of cinnabar in the area of influence (about 120 km²). Furthermore, in this area, there also exist a number of decommissioned Pb–Zn mines from other volcanic events that produced small polymetallic deposits, resulting, most notably, in the mining of Pb and Zn minerals.

The geology of these deposits is associated with hydrothermal fillings from the late stages of the placement of the Hercynian granites. The scale of the mining carried out in these deposits is not comparable with that of the mercury mines, but the number of mines and their dispersion are highly significant for the district. The most representative mines of this type are Quinto de Hierro, Jacinta, Nuestra Señora de la Encarnación and the mines of San José-Andrea.

The Almadén mercury mining district has been intensively studied for mercury environmental concerns, including the study of local water and sediments [17–19]. The present study is the first one that was carried out in the area that involves other potentially toxic heavy metals and metalloids related to all the mining activities. The research includes a study of the natural or anthropogenic origin, and their mutual relationships. In particular, this environmental research has been based on the study of the sediment compartment, due to its importance in the accumulation of heavy metals and the key role it plays in supporting life in aquatic ecosystems. As such, the study has focused on the main rivers and streams that provide drainage for the mining district. The main objectives of this study are as follows: (1) the evaluation of environmental dispersion and the sources of heavy metals in the drainage network, going beyond Hg to examine the prevalence of other heavy metals occurring as a result of mining liabilities that have not been sufficiently studied in the area [17–19] and (2) the assessment of heavy metals enrichment by applying an appropriate normalisation procedure and sediment quality indexes (SeQIs).

Materials and methods

Study area and sampling methods

The area under study is a section of the basins of the Valdeazogues, Alcudia, Tamujar, Gargantiel and Azogado rivers (Figure 1) within the boundaries of the Almadén mining district, determined by the presence of the largest mercury mines. The rivers flow through the district over impermeable materials (mainly composed of the slates that
make up the valleys and the quartzite present at higher altitudes) at a low speed due to the low average gradient of the watercourses (1%). As a result of droughts during the summer, the watercourses dry up and water ‘tables’ are formed, whereas during rainy periods, flooding gives rise to the suspension of a large concentration of sediments, which are transported downstream and deposited far from their source, resulting in significant dispersion of contaminants and the potential degradation of the aquatic environment.

To study the dispersion and quality of the sediment, 33 sediment samples were taken from the main watercourses of the area (Figure 2). The number of samples per watercourse was selected based on their importance in the hydrological network and the potential influence of mining on this network. Based on these criteria, the number of sample points per watercourse was as follows: 13 sediment samples from the Valdeazogues River, the main drainage watercourse in the area, receiving all the mining run-offs in the district; 8 samples from the Gargantiel Stream, the main recipient of run-offs from the Las Cuevas mine; 7 samples from the Azogado Stream, responsible for the drainage of the run-offs from the district’s largest Hg mine (Almadén); and 3 samples each for the Tamujar stream and the Alcudia River, neither of which is directly affected by Hg mining in the district; thus, these serve as low mercury reference streams.

Samples were collected from the field using a metal shovel. To avoid cross-contamination, the shovel was cleaned between samples using a 10% HNO₃ solution and rinsed three times using distilled and deionised water (DDI) [20]. Before taking the sample, the shovel was rinsed with water from the flow at the sampling point. The
sediment samples (approximately 1 kg) were stored in plastic bags using the dirty-hands/clean-hands method, which involves placing the sample bag inside a clean bag, which is then sealed by a different operator from the person taking the sample. The samples were cold stored in a portable refrigerator until they arrived at the laboratory, where they were kept chilled until analysis.

**Samples preparation and analysis**

All sediment samples were air-dried and sieved to < 2 mm (sand + silt + clay), discarding the gravel fraction (≥ 2 mm). The pH of the samples was determined using a glass electrode in a 1:5 (V/V) suspension of sediment in DDI and potassium chloride (KCl) solution in line with the procedure established in ISO 10390:1994 standard [21]. Total organic carbon (TOC) was determined after dry combustion using a TOC-V CSH Shimadzu instrument. To determine the content of organic carbon, the carbonates present in the sample were eliminated by treating the sediments with hydrochloric acid and then analysed by combustion catalytic oxidation at 680 °C. The quality control of the results was ensured by using duplicate samples and glucose and sodium bicarbonate pattern analysis in line with the manufacturer.

To determine the total content of major and trace elements, the sediments were ground to a fine powder using an agate ball mill. The total content of Hg in all the samples was measured by thermal decomposition and atomic absorption spectroscopy with gold amalgamation (LECO ® model AMA-254). The analyses were performed directly on the solid samples [22]. Certified reference materials, such as PACS-2 (total
Hg content of marine sediments $3.04 \pm 0.25 \text{ mg kg}^{-1}$, CRM026-050 (total Hg content of sandy loam $2.42 \pm 0.32 \text{ mg kg}^{-1}$) and CRM042-056 (total Hg content of loam $46.7 \pm 8.09 \text{ mg kg}^{-1}$), were used for quality control and assurance. For all materials, the percentages of recovery were between 94 and 108% and the relative standard deviation percentages (% RPD) calculated for three repetitions of each material were less than 10%.

The total Fe, Ca, Mg, Al, Na, K, Cu, Pb, Zn, Ni, Co, Mn, As and Cr in the sediments was measured by Acme Analytical Laboratories Ltd (Vancouver, Canada), an ISO 9002 certified company, using inductively coupled plasma atomic emission spectroscopy (ICP-AES) and inductively coupled plasma mass spectrometry (ICP-MS) after leaching 0.5 g of the samples in hot aqua regia ($95^\circ \text{C}$). The detection limits reported for the analysis of Al, Fe, Ca, Mg, Na, K, Cu, Pb, Zn, Ni, Co, Mn, As and Cr were $10, 10, 10, 10, 10, 10, 1, 3, 1, 1, 1, 2, 2$ and $1 \text{ mg kg}^{-1}$, respectively. Three repetitions of each sample were leached and analysed. The evaluation of the analytic quality of the results for the total concentration was carried out by analysing the certified reference materials STD OREAS45CA, STD DS8 and CRM042-056, which were provided by us for quality control. The recovery percentages of the various elements varied between 84 and 107%, and the relative percentage differences (%RPD) were less than 5%.

**Methods for estimating pollutant impact and ecological state of the environment**

The enrichment factor (EF) [23] and SeQI [24] methods, as described in the following sections, were used to quantify the degree of heavy metal enrichment and the ecological status of sediments. The EF is a standard method for estimating the anthropogenic impact on sediments [25–27]. This ratio for sediments can be used as a contamination index by comparing the concentrations of selected metals with their base levels in sediments or suspended particles in local or global rivers. The EF method normalises the metal concentrations with respect to a normalising element of the sample in order to eliminate the variations that occur as a result of the heterogeneity of the sediments [28–30]. The normalising elements used are Fe [31,32] and Al [30,33], although other less common elements such as Sc [34] are also used, all of which change according to the grain size and to the minerals associated to each grain size fraction. In this study, the EF is calculated using the following Formula (1):

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

where $\left( \frac{C_x}{C_{ref}} \right)_{\text{sample}}$ is the concentration ratio of the heavy metal and the normalisation element in the sample to be analysed (in this case the normalising element was Al due to the fact that it is not related and influenced by mining activities such as Fe), and $\left( \frac{C_x}{C_{ref}} \right)_{\text{background}}$ is the concentration ratio of a suitable background sample.

If the EF is between 0.5 and 1.5 ($0.5 < \text{FE} < 1.5$), metals are classed as naturally occurring, originating from crustal materials or natural weathering processes; an EF of 1.5 and above ($\text{EF} \geq 1.5$) indicates that metals are not naturally occurring and, hence, are the result of a significant anthropogenic contribution [35].

The SeQI method is based on the water quality index developed by Environment Canada (Ontario Region), the National Water Research Institute and the Canadian
Council of Ministers of the Environment (CCME) to evaluate the environmental quality of sediments [34]. The index is a mathematical combination of different factors (scope, frequency and amplitude) that allow a multi-variable environmental evaluation that gives greater precision than traditional indexes, and, due to the incorporation of different parameters, provides a method for comparing local levels with regional or national levels [36–38]. The mathematical index can be expressed in two ways, depending on the required evaluation. The first method developed for an area is calculated using the following equations:

\[ F_1 = \left( \frac{\text{Number of failed variables}}{\text{Total number of variables}} \right) \times 100 \]  
\[ F_2 = \left( \frac{\text{Number of failed test}}{\text{Total number of test}} \right) \times 100 \]  
\[ \text{excursion}_i = \left( \frac{\text{failed value}}{\text{reference value}} \right) - 1 \]  
\[ nse = \sum_1^n \text{excursion}_i \]  
\[ F_3 = \frac{nse}{0.01nse + 0.01} \]  
\[ \text{SeQI} = 100 - \left( \frac{\sqrt{F_1^2 + F_2^2 + F_3^2}}{1.732} \right) \]

In the second method, the SeQI is calculated station by station and only includes scope (F1) and amplitude (F3). In this case, the SeQI normalisation factor (1.732 in Equation 7) is recalculated to obtain the resulting values between 0 and 100. The two remaining factors are calculated using the following equation:

\[ \text{SeQI} = 100 - \left( \frac{\sqrt{F_1^2 + F_3^2}}{1.414} \right) \]

The index gives a number between 0 and 100 for both methods [24,39]. The results can be classified into five categories of ascending sediment quality based on the following intervals: 0 < SeQI ≤ 45 (grade 1), poor; 45 < SeQI ≤ 59 (grade 2), marginal; 59 < SeQI ≤ 74 (grade 3), fair; 75 < SeQI ≤ 89 (grade 4), good; and 89 < SeQI ≤ 100 (grade 5), excellent.

Results and discussion

Table 1 shows the concentration and descriptive statistics for Fe, Al, Ca, Mg, P, Cu, Pb, Zn, Ni, Co, Mn, As, Cr, Hg, Sr, as well as the TOC and pH for the sediment samples taken from the district. The results are expressed as a % weight for the elements Fe, Al, Ca, Mg and P, and in mg of metal extracted per kg of dry sediment for the other elements. All the results were calculated as the average value of three repetitions.
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**Major elements**

In terms of the highest levels, the Al content (average 15.99 ± 2.83%) is higher than Fe (6.17 ± 1.45%), Mg (0.53 ± 0.18%), Ca (0.38 ± 0.18%) and P (0.08 ± 0.02%) (Figure 3), making it the element with the highest average concentration detected in the sediments.

The watercourse with the highest average concentration of Al (17.78 ± 2.48%), which also had the maximum absolute concentration (21.5%), was Gargantiel (G-3), located downstream from the Las Cuevas mine. This is consistent with the clayey alteration characteristic of the Hg deposit at Las Cuevas [14]. The lowest average content was detected in the Alcudia River (12.60 ± 0.75%). The similar dispersion patterns detected in the watercourses suggest that the concentration of the element can be attributed to the district’s geology, the main elements of which are slates, quartzite and mafic magmatic rocks rich in Al [13].

The distribution of Fe is relatively homogeneous in the majority of the sediments. The element’s dispersion pattern is similar to the pattern for Al, with both the highest average concentration (7.49 ± 0.90%) and the maximum concentration (9.1%) occurring in the Gargantiel watercourse, and the lowest level occurring in the Alcudia River (4.45 ± 0.15%). At the nearest sampling points downstream from the mines, high values of Fe were detected compared to the background values for the district. This suggests greater mobilisation of the element at these sites as a result of the waste material grain size [40,41]. Its dispersion in the watercourses followed the same pattern as for Al and can be explained as a natural background phenomenon.

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*Figure 3. Maps of dispersion of Fe, Al, Ca and Mg in sediments.*
In terms of Ca and Mg, there are similar variations throughout the district, with the level of the latter being higher due to the geochemical enrichment of the element in the mafic and ultramafic volcanic rocks that characterise the area [42,43], these having been affected by significant regional alteration processes, including CO₂ enrichment [15,43]. The levels of P were similar throughout the district, with the local maxima occurring closest to the mines. The dispersion of the contents suggest that P is mainly introduced as a result of the erosion of the lithological materials made up of marine-origin rocks [40,41], as opposed to being a product of anthropogenic sources.

**Trace elements**

Among the trace metals, Mn has the highest average concentration (766.87 ± 264.04 mg kg⁻¹) followed by Zn (167.75 ± 73.58 mg kg⁻¹), Hg (87.29 ± 73.49 mg kg⁻¹), Cr (81.94 ± 16.58 mg kg⁻¹), Pb (59.56 ± 30.26 mg kg⁻¹), Ni (58.65 ± 22.44 mg kg⁻¹), Cu (28.55 ± 10.81 mg kg⁻¹), Co (25.34 ± 6.68 mg kg⁻¹) and As (13.01 ± 2.57 mg kg⁻¹) (Figures 4 and 5).

The presence of high levels of Mn in the sediments from the district can be attributed to volcanic alteration processes that are responsible for the pseudomorphic replacements of minerals such as olivine and pyroxenes with Mn-rich secondary minerals such as ankerite, calcite, chlorite and siderite [42,44]. The highest concentration was detected in the upper part of the district, at the sample points downstream from the El Entredicho (V-2) and Las Cuevas (G-3) mines, with the concentration

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Figure 4. Maps of distribution of metalloids (As) and heavy metals (Co, Cr, Cu) in sediments.
reducing when moving downstream from the mine sources. The lowest values were detected in the lower part of the district, suggesting that the processes of alteration are less significant in this area than at higher altitudes. A similar dispersion was observed with Co and Ni: both elements concentrations exhibited the same spatial distribution among the sediments, with the highest concentrations occurring in the upper part of the district, and the lowest concentrations occurring in the lower part, again suggesting that the origin of the elements is similar, resulting from volcanic alterations that favour the weathering of these elements.

High concentrations of Pb and Zn were discovered in the lower part of the district. The Alcudia River had the highest average concentration of these elements (Pb: $112.91 \pm 3.29$ mg kg$^{-1}$ and Zn: $251.09 \pm 45.77$ mg kg$^{-1}$) as a result of the large-scale mining of Pb–Zn carried out in its basin [45]. In the case of the Azogado watercourse, which had the second highest levels of Pb–Zn, high values were detected in the lower area, close to the confluence with the Valdeazogues River. These values can be attributed to the run-offs originating from the decommissioned Pb–Zn mines situated on the right bank of the river. In the area surrounding the Almadén mine, the average values, both upstream and downstream, were similar and, as such, they show that these elements are not introduced to the watercourse by the mine. In the case of the Valdeazogues River, the highest values were detected in the lower area, almost certainly originating from contributions from the Azogado stream and run-offs from the Nuestra Señora de la Encarnación and San José-Andrea mines located on its left bank.
The highest levels of arsenic were detected at sample points located downstream from the mines, decreasing in the flow direction from the sources. The detection of low concentrations, together with their limited variation (13.01 ± 2.57 mg kg\(^{-1}\)), suggests that the sediments were enriched with this metalloid due to local variations from the natural background. The case for Cr is similar, with the element following the same pattern as Al: its concentrations can also be attributed to the natural erosion of Cr-rich micas present in ultramafic xenoliths close to the mineral deposits [13].

The element Cu is widely dispersed throughout the district, although the average Cu levels measured for the Valdeazogues, Azogado and Gargantiel watercourses are higher than the values for the other courses. This suggests that this element may be mobilised faster in areas in which mines have been operated; however, the average values exhibit a regional statistical trend similar to Cr and As, without the existence of atypical values, and low variations that suggest a natural origin.

The dispersion of Hg throughout the area as a whole is significant due to past mining activity for cinnabar. The sediments in the areas surrounding the mines exhibit significant levels of enrichment when compared to the average values for the district as a whole. The maximum value for the district was detected at the sample point in front of the Almadén mine (Az-3), as a result of the run-offs from the large slag heaps present at the site. In general, Hg content decreases rapidly downstream.

**Major and trace elements behaviour in sediments**

To determine the relationships between the major and trace elements, a Pearson correlation analysis was undertaken (Table 2) to assess possible similar metal sources. The elements with a positive correlation have similar sources or similar deposit mechanisms such organic ligands or oxides and hydroxides retention.

The elements, Al and Fe have a high mutual Pearson correlation (\(r = 0.882\)), both precipitating as oxides and hydroxides that are mainly accumulated in the clay fraction. These local geochemical properties are supported by past studies of the district’s mineralogy, which has ore deposits rich in pyrite and clayey minerals [14,45]. The correlation between Ca and Mg (\(r = 0.845\)) is also significant, although they do not have a strong correlation with the other elements under analysis, with both elements sharing a similar geological origin that is unrelated to mineralisation. The element P has a medium correlation with Al (\(r = 0.678\)) and Fe (\(r = 0.658\)) suggesting that Fe and Al oxides and hydroxides are the main form of its retention in the sediments. Moreover not significant correlation of the elements with the TOC, Ca and Mg (organic ligands and carbonates principal constituents) support this supposition [46,47].

In terms of the pH values that were measured, the pH (H\(_2\)O) had a strong correlation with other alkaline metals, such as Ca (\(r = 0.724\)) and Mg (\(r = 0.669\)), whereas the pH (KCl) had a strong correlation with Al (\(r = 0.732\)). All the pH values measured using KCl were more acidic than the H\(_2\)O values. This decrease in the pH, together with correlations with Ca, Mg and Al, and the correlation between Al and the TOC (\(r = 0.787\)), suggests that the pH buffering is a result of aluminosilicates and not carbonates, due to the fact that these minerals dissolve slower than carbonates and their capacity for neutralisation is much lower [48], the colloids have a negative charge and part of the Al is present as a reactive mineral, such as Al bound to the organic material, largely humic acids [49–52].

The heavy metals and metalloids can be separated into three groups based on their correlation with the main elements, the organic carbon and among themselves. The first
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<td></td>
</tr>
<tr>
<td>pH (H2O)</td>
<td>0.65</td>
<td>0.732</td>
<td>0.681</td>
<td>0.629</td>
<td>0.68</td>
<td>0.682</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>pH (KCl)</td>
<td>0.724</td>
<td>0.669</td>
<td>0.681</td>
<td>0.629</td>
<td>0.68</td>
<td>0.682</td>
<td></td>
<td></td>
<td></td>
<td></td>
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<td></td>
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</tr>
</tbody>
</table>
group comprises Co, Ni and Mn, which exhibit a strong correlation among each other and with Fe and Al. As such, it is possible to conclude that Fe and Al oxides and hydroxides were the main factor affecting the retention and distribution of these metals. The second group comprises Ni, Cr, As, Pb and Zn, which have weak correlations with Al–Fe and the TOC, suggesting that the organic matter and the clay content are not the main factors governing/managing metal loads. Within this group, a significant association between Pb and Zn was detected \( (r = 0.889) \), suggesting that these elements share a similar origin, being introduced in mineral forms, such as complex sulphides, sulphates and oxides unrelated to clays. The third group comprises Cu and Hg. There was a strong correlation between both elements \( (r = 0.852) \), and there were no similar correlations with other elements, suggesting the same mechanism of accumulation in the sediments, since Cu is not present in the Hg ore deposits. In the case of Hg, the element had a strong correlation with the organic carbon \( (r = 0.822) \) and a medium correlation with Al \( (r = 0.627) \). The results indicate that the organic matter is the main form of complexation of Hg. Furthermore, the correlations between the TOC and Hg with Al suggest that aluminosilicates play a significant role in the deposition process, although the detected correlations indicate that this is not the only factor affecting the metal load.

**Contamination degree assessment**

**Enrichment factor (EF)**

In this study, EF values were calculated using the detected background values (point V-0, upstream of the influence mine area), where its major elements’ contents are higher than the continental crust abundance such as Al (8.15%) reported by Rudnick and Gao [53]. The EF range of the heavy metals was as follows: Fe 0.8–1.4 (average 1.2), Cu 0.5–2.0 (average 1.1), Pb 0.8–4.8 (average 2.1), Zn 0.6–5.3 (average 2.1), Ni 0.6–2.6 (average 1.5), Co 1.1–2.2 (average 1.5), Mn 0.7–2.2 (average 1.5), As 0.9–1.9 (average 1.3), Cr 0.8–1.7 (average 1.2), Hg 0.9–107.3 (average 34.2), Sr 0.8–2.4 (average 1.7) (Figure 6).

An EF of approximately 1.5 suggests that a given metal may wholly originate from natural sources, such as crustal materials or natural weathering processes. EF values slightly over 1 may not necessarily result from anthropogenic activities, but may also be caused by the natural variation in the composition of elements between the sediments under study and the reference soils used for calculating the EF. However, an EF over 1.5 suggests that a significant proportion of the metal is originated from anthropogenic processes. In the mining district of Almadén, Pb, Zn and Hg were the most anthropogenically enriched elements in the sediments as a result of mining activities, with an average value above 2. The average EF value for the remaining elements (Cu, Ni, Co, Mn, As and Cr) was under 1.5, indicating that the metals have originated from natural sources, such as the underlying geological material.

In terms of the sampling points, the EF for Hg was above 8 for all of them, except those located upstream from the Las Cuevas and Almadén mines. In the case of Pb–Zn, all the sample points in the Alcudia River can be classified as hotspots, with values above 2 as a result of Pb–Zn mining. The Azogado stream also had a significant level of Pb–Zn, with only two of the seven sample points having an EF value below 2. This shows the significant impact caused by Pb–Zn small-scale mining activities on the stream area. In the Valdeazogues River, the hotspots are located downstream,
originating from the contributions from Alcudia, and Azogado and terrigenous contributions from the small mines located on its left bank. There is an anomalous hotspot in the Tamujar stream, at the sample point near to Almadén (T-1), with an EF value of over 3. As there is no known mining of Pb–Zn in the area, the values may be caused by urban dumping from the Almadén sewage plant.

*Sediments quality index*

This study calculated the SeQI based on seven variables (Cu, Pb, Zn, Ni, As, Cr and Hg). The American National Oceanic and Atmospheric Administration (NOAA) and Interim Sediment Quality Guidelines Probable Effects Levels (ISQG-PEL) were used as reference values [54]. The index was computed for points, streams and the district as a whole. The results are provided in Tables 3 and 4.

The overall results for the district are poor (SeQI = 17.26, average for the whole district). In terms of watercourses, the results showed the same quality pattern in rivers directly affected by Hg mining. The behaviour of the watercourses not directly affected

Table 3. SeQI values by streams.

<table>
<thead>
<tr>
<th>Streams</th>
<th>F1</th>
<th>F2</th>
<th>F3</th>
<th>SeQI</th>
</tr>
</thead>
<tbody>
<tr>
<td>Valdeazogues</td>
<td>71.43</td>
<td>30.77</td>
<td>96.90</td>
<td>28.26</td>
</tr>
<tr>
<td>Gargantiel</td>
<td>57.14</td>
<td>37.50</td>
<td>96.23</td>
<td>31.85</td>
</tr>
<tr>
<td>Tamujar</td>
<td>28.57</td>
<td>28.57</td>
<td>92.05</td>
<td>41.96</td>
</tr>
<tr>
<td>Azogado</td>
<td>57.14</td>
<td>36.73</td>
<td>96.93</td>
<td>31.66</td>
</tr>
<tr>
<td>Alcudia</td>
<td>85.71</td>
<td>57.14</td>
<td>77.49</td>
<td>25.57</td>
</tr>
</tbody>
</table>
by Hg mining (Alcudia and Tamujar) was different in each case, with the Alcudia River having the lowest index and the Tamujar stream having the highest. These results can perhaps be explained by the low number of samples that were taken (three samples); however, in general, the trend of the data measured shows that the Alcudia River being the worst, as a result of the high levels of polymetallic contamination (Pb–Zn mines or other sources), whereas the Tamujar stream only showed a slight anomaly at the point closest to the town as a result of urban waste.

In terms of sample points, the sediment quality at the sites furthest from the mines varied between good and fair, whereas the points closest to the mines varied between marginal and poor. The points downstream from the Almadén mine had the lowest indexes and their values indicate a high level of dispersion of heavy metals in the watercourse. The quality at the other points close to the Las Cuevas and El Entredicho mines was marginal; however, in both cases, it quickly became acceptable downstream

Table 4. SeQI values by sampling points.

<table>
<thead>
<tr>
<th>Sample</th>
<th>F1</th>
<th>F3</th>
<th>SeQI</th>
</tr>
</thead>
<tbody>
<tr>
<td>V-0</td>
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<td>0.38</td>
<td>89.89</td>
</tr>
<tr>
<td>V-1</td>
<td>14.29</td>
<td>3.68</td>
<td>89.57</td>
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<tr>
<td>V-2</td>
<td>28.57</td>
<td>51.50</td>
<td>58.35</td>
</tr>
<tr>
<td>V-3</td>
<td>28.57</td>
<td>48.78</td>
<td>60.02</td>
</tr>
<tr>
<td>V-4</td>
<td>28.57</td>
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<td>V-5</td>
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<td>V-6</td>
<td>42.86</td>
<td>30.27</td>
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<td>V-7</td>
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<td>V-8</td>
<td>28.57</td>
<td>15.61</td>
<td>76.98</td>
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<td>V-9</td>
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<td>68.21</td>
</tr>
<tr>
<td>V-10</td>
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<td>V-11</td>
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<td>60.15</td>
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<td>V-12</td>
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<td>39.43</td>
<td>50.90</td>
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<td>G-0</td>
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<td>0.48</td>
<td>89.89</td>
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<tr>
<td>G-1</td>
<td>57.14</td>
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<td>43.78</td>
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<tr>
<td>G-2</td>
<td>57.14</td>
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<td>47.39</td>
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<tr>
<td>G-3</td>
<td>42.86</td>
<td>36.16</td>
<td>60.34</td>
</tr>
<tr>
<td>G-4</td>
<td>28.57</td>
<td>27.15</td>
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<td>28.57</td>
<td>10.91</td>
<td>78.37</td>
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<tr>
<td>G-7</td>
<td>42.86</td>
<td>7.35</td>
<td>69.25</td>
</tr>
<tr>
<td>T-0</td>
<td>28.57</td>
<td>10.43</td>
<td>78.49</td>
</tr>
<tr>
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<td>T-2</td>
<td>28.57</td>
<td>11.74</td>
<td>78.16</td>
</tr>
<tr>
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<td>79.78</td>
</tr>
<tr>
<td>AZ-1</td>
<td>28.57</td>
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<tr>
<td>AZ-2</td>
<td>28.57</td>
<td>0.81</td>
<td>79.79</td>
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<tr>
<td>AZ-3</td>
<td>42.86</td>
<td>75.23</td>
<td>38.77</td>
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<td>28.57</td>
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<td>57.26</td>
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<td>28.89</td>
<td>63.45</td>
</tr>
<tr>
<td>A-0</td>
<td>42.86</td>
<td>1.34</td>
<td>69.68</td>
</tr>
<tr>
<td>A-1</td>
<td>42.86</td>
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<td>69.67</td>
</tr>
<tr>
<td>A-2</td>
<td>85.71</td>
<td>1.56</td>
<td>39.37</td>
</tr>
</tbody>
</table>
from the sources, suggesting that the introduction of contaminants is lower than the level for the Azogado stream.

Conclusions
The mining district of Almadén has a significant metallic background that has produced a high concentration of metals in sediments. The majority of the heavy metals are of natural origin; however, in the case of Hg, Pb and Zn, anthropogenic activities are the main sources responsible for introducing these elements into sediments. The CCM SeQI, calculated based on the PEL, classifies the district as highly polluted area. In terms of watercourses, Azogado is the most polluted watercourse from the effects of Hg mining as a result of past activity at the Almadén mine and others located in its basin, whereas the Alcudia River is the worst due to strong polymetallic pollution from different sources not determined in this study.

As a final conclusion, Hg is the most significant contaminant in the district. However, as shown in the present study, Pb and Zn also play an important role in the sediment compartment. There remains scope for in-depth research to better understand the processes that occur in this local environment.

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