

# Incidence of the Almadén historical mining district on the hydrochemical characteristics of Valdeazogues Basin (Spain)

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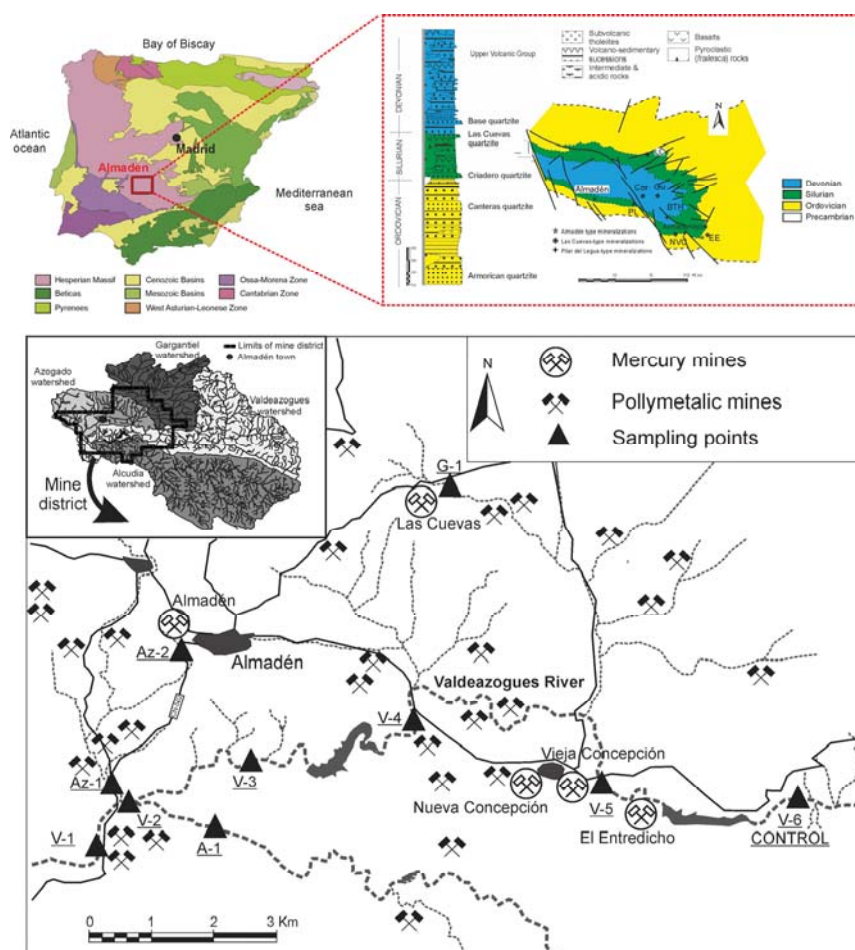
**Abstract.** The distribution of dissolved potentially harmful elements (PHEs), major ions and physico-chemical parameters in the Valdeazogues river basin was studied during 9 surveys, carried out between 2010 and 2013. The observed physico-chemical parameters depend on the season, the major ions depend of the nature of the lithological materials and the PHEs depend of the characteristics of the mine inputs. The Principal Component Analysis performed on the analysed dataset, distinguished the sources of contaminants introduced into waters and that nowadays mine runoffs play a role higher than the played by the natural inputs.

## 1. Introduction

Some metals and metalloids (commonly known as “potentially harmful elements (PHE)”) are an important concern in the environment, due to their persistence, potential toxicity and bioaccumulation capacity by organisms. Among other anthropogenic activities, long periods of extractive works developed in historical mining districts around the world have induced physical and chemical alterations in their waste materials, favouring the mobilizations of PHE to different environmental compartments, involving a significant increase of content of these potential contaminants in the surroundings of mining areas. This fact especially affects the vulnerable aquatic ecosystems, due to its role as a supporter of a great number of organisms and its potential to increase the dispersion of contaminants long distances from the source [1].



The riverine system on which the present study has been focused is the Valdezogues River Basin, in the Almadén historic mining district. This is a large watershed, geologically and physiographically diverse, with a mixture of land cover and land use types, with an intense extractive activity, mainly related to Hg, but also to Pb, Zn and Ag, during two millennia (see Figure 1). As a consequence of this mining activity, the surface aquatic system has been intensely affected by the inputs from active and decommissioned mines scattered in the area [2-3]. In this paper, the results of monitoring of the surface water courses of the basin, during four hydrologic years (2010-2013 period), are presented as a tool for the knowledge of the ecological state of the basin and for the assessment of the potential environmental impact related to the historical mining activities carried out in the area.



**Figure 1.** Study area and sampling network

## 2. Materials and methods

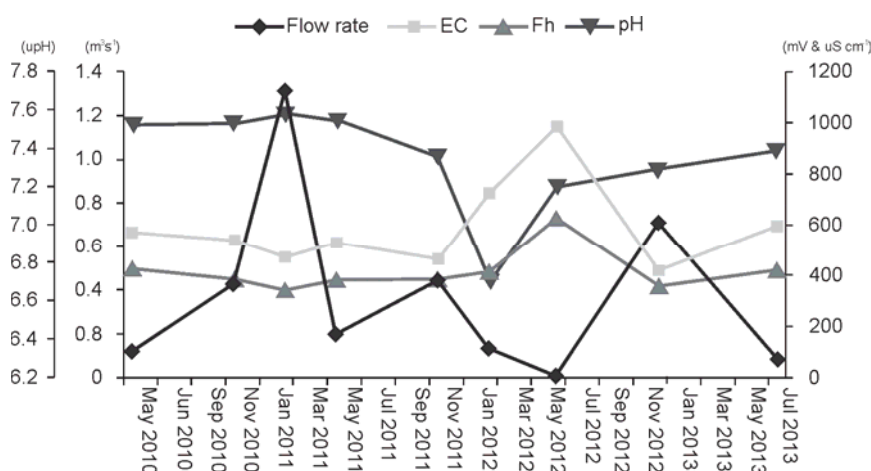
A sampling network consisted of 10 sampling points (see Figure 1) and was designed for the particular characteristics of the area. In the 4-years period (2010-2013), nine sampling campaigns were carried out along the annual hydrological cycles, in order to include different weather periods and hydrological regimens of the streams in the study. Samples for major elements and dissolved PHEs have been collected at each sampling point. Besides that, water's physico-chemical parameters were measured in situ, using a CTD multiprobe YSI 556.

For PHEs analyses, water samples were collected at 15 cm depth by means of disposable syringes. After that, water samples were filtered in situ through 0.45µm Millipore Teflon filters and they were stored in pre-cleaned high-density polyethylene (HDPE) bottles. To stabilize dissolved PHEs in a suspension, all samples were acidified to pH < 2, using ultrapure nitric acid (69% Trace metals analysis HIPERPUR®). Filtered samples were immediately stored for transport in a portable refrigerator at ±4 °C until their analysis in the laboratory. Samples for determination of major ions (Ca<sup>2+</sup>, Mg<sup>2+</sup>, HCO<sub>3</sub><sup>-</sup>, K<sup>+</sup>, Na<sup>+</sup>, Cl<sup>-</sup> and SO<sub>4</sub><sup>2-</sup>) were collected directly in pre-cleaned plastic bottles on the water courses and during their transport to the laboratory samples were stored at ±4 °C without addition of stabilizing agents.

Dissolved PHEs in the water samples were determined using an Inductively Coupled Plasma Mass Spectrometer (ICP-MS) Agilent 7500, following the EPA method 200.8. Major elements were determined using an Ion Chromatography 883 Basic IC METROHM instrument. Samples were analysed in batches, which included a procedural blank and a standard reference material. Each calibration curve was evaluated by quality control standards before, during and after the analyses of a set of samples.

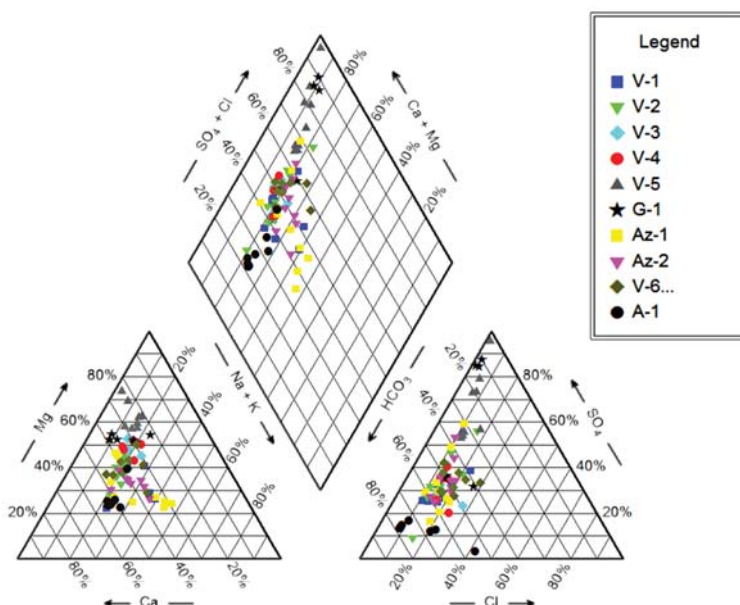
## 3. Results and discussion

Summary of monthly results of water characteristics are presented in Figure 2. During the studied period (2010-2013), flow rates showed a seasonal variation (from null flow to 1.31 m<sup>3</sup> s<sup>-1</sup>), corresponding to an area governed by a Mediterranean climatology. Flow rates trend to null in summer periods as the consequence of the drought phenomena and the absence of important groundwater inputs [4]. In the physicochemical parameters, pH did not show an important variation in its values, ranging from neutral to low alkaline (6.7 to 7.6). In contrast, Electric conductivity (EC) and redox potential (Eh) displayed significant variations, with values ranging from 420.5 to 984.1 µS cm<sup>-1</sup> and from 340.7 to 631.6 mV, respectively. As shown in Fig. 2, variation trends of both parameters (EC and Eh) showed an inverse behaviour in relation to the flow rates, suggesting that during high flow rates the dilution caused by rain contributions is responsible for the thermodynamic buffering reactions, and in consequence, the modification of the redox and electrical conductivity parameters.



**Figure 2.** Summary of physico-chemical parameters during the studied period

Magnesian-bicarbonated facies followed by calcium-bicarbonated facies predominate in the surface waters of the district, as shown in Fig. 3. The large amounts of bicarbonates in water can be considered as a consequence of the abundance of secondary carbonates in soils and lithological materials of the district [5].



**Figure 3.** Major elements - Piper diagram

Cation  $\text{Ca}^{2+}$  in water is related to carbonate materials, but the high presence of  $\text{Mg}^{2+}$ , as compared with  $\text{Ca}^{2+}$ , is attributed to the presence of magnesium-rich rocks related to mafic volcanic processes which occurred in the area [5]. Between anions,  $\text{SO}_4^{2-}$  is not the most abundant, despite the long mining activities, but it presents the highest variability range, with values comprised between 46.9 and 407.3  $\text{mg.l}^{-1}$ . This fact is attributed to the presence of decommissioned mines, which remain nowadays with great amounts of sulphide minerals available for weathering in old, unclaimed, dumps. Biogeochemical processes and weathering of these sulphide minerals-rich residues produces significant amounts of sulphate salts derived from oxidation processes, which are easily leachable by rain and runoff from the liabilities to the aquatic systems.

**Table 1.** Total explained variance and component matrix for dataset (principal component analysis with Varimax rotation; the significance of KMO and Bartlett's sphericity test is  $<0.001$ ).

	PC1	PC2	PC3	PC4	PC5
Al	-0.062	-0.172	0.236	0.057	<b>0.771</b>
As	-0.027	0.250	<b>0.875</b>	-0.083	0.073
Co	<b>0.798</b>	0.099	0.077	0.115	0.212
Cu	0.190	0.538	0.328	-0.053	0.551
Fe	<b>0.952</b>	0.090	-0.023	0.158	0.082
Hg	<b>0.774</b>	0.311	0.214	-0.180	0.421
Mn	<b>0.972</b>	0.081	-0.020	0.132	0.013
Ni	0.340	0.120	0.342	<b>0.724</b>	-0.109
Se	0.368	0.165	-0.171	0.520	0.460
Sr	0.036	<b>0.862</b>	0.102	-0.001	0.044
Zn	-0.030	0.147	<b>0.854</b>	0.147	0.255
$\text{Ca}^{2+}$	<b>0.870</b>	0.351	-0.020	0.119	-0.068
$\text{Cl}^-$	0.053	0.765	0.157	0.316	-0.128
$\text{HCO}_3^-$	0.120	<b>0.932</b>	0.146	0.033	0.016
$\text{K}^+$	0.010	<b>0.904</b>	0.175	0.070	-0.013
$\text{Mg}^{2+}$	<b>0.941</b>	0.035	0.016	0.231	-0.053
$\text{Na}^+$	0.276	<b>0.859</b>	0.098	0.192	-0.061
$\text{SO}_4^{2-}$	<b>0.956</b>	0.056	-0.026	0.189	-0.064
pH	-0.365	-0.235	0.055	<b>-0.750</b>	-0.085
EC	<b>0.814</b>	0.393	0.080	0.132	0.135
Eh	0.248	0.478	-0.098	0.356	0.040
Eigenvalues	6.387	4.508	2.707	1.735	1.482
Cumulative Variance (%)	37.415	51.882	64.774	73.035	80.093

Concentrations of PHEs in the water samples are included within the following ranges: Al: 2.3-78.8  $\mu\text{g l}^{-1}$ , As: <DL-10.3  $\mu\text{g l}^{-1}$ , Co: <DL-4.8  $\mu\text{g l}^{-1}$ , Cu: <DL-4.5  $\mu\text{g l}^{-1}$ , Fe: 10.9-3255.0  $\mu\text{g l}^{-1}$ , Hg: < DL- 0.3  $\mu\text{g l}^{-1}$ , Mn: 10.5-1779.0  $\mu\text{g l}^{-1}$ , Ni:<LD-17.2  $\mu\text{g l}^{-1}$ , Se: 0.2-18.9  $\mu\text{g l}^{-1}$ , Sr: 40.1-365.6  $\mu\text{g l}^{-1}$  and Zn: 0.9-27.2  $\mu\text{g l}^{-1}$ . Among the analysed elements, the highest concentrations correspond to Fe and Mn, whose chemical behaviour is usually very similar in natural waters, commonly being the Fe contents in the district waters higher than Mn contents, as consequence of its enrichment in the district geological materials [4-5].

Moreover, Al concentration is lower than Fe or Mn concentrations, indicating significant water enrichment in Fe and Mn as a result of processes unrelated to natural weathering of rocks. In the case of Sr, which is the third more abundant element, its concentrations can be related to the presence of secondary carbonates. For the rest of the analysed metals and metalloids, their concentrations are always below  $30 \mu\text{g l}^{-1}$ . From this group, Zn shows the highest concentration ( $27.2 \mu\text{g l}^{-1}$ ) related to the presence of leachable Zn minerals such as sphalerite [6].

To characterize variance of the large dataset, and to understand the parameters and the form in which they influence the aquatic ecosystem, a Principal Component Analysis (PCA) was performed with Varimax rotation. Results from the analysis were interpreted according to the Kaiser's criterion, and factor loadings classification followed the methodology of Liu et al. [7]. This statistical analysis allowed to identify the different groups of elements and parameters which can be correlated and thus they can be considered to have a similar or related behaviour and in consequence, a probable common origin.

The first factor (PC1) explained 37.4% of the total variance; it comprised the elements and parameters with high loadings: Co, Fe, Hg, Mn,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{SO}_4^{2-}$  and EC. In the second factor (PC2), the components with higher loadings were: Sr,  $\text{HCO}_3^-$ ,  $\text{K}^+$  and  $\text{Na}^+$  and the factor explained 21.4% of the dataset total variance. The third factor (PC3) explained 12.9% of the total variance, As and Zn being the elements that present higher loadings. The fourth factor includes pH and Ni, and the fifth factor only presents high load for Al. Each one of these last two components explains less than 10% of variance and may be considered insignificant.

In relation to the PC1, the group of elements seemed to be associated with Hg mine sources. The group of metals and  $\text{SO}_4^{2-}$  are a key element of mine waste inputs into the river. Moreover, this fact is supported by the presence of basic cations ( $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$ ) in this group. Their presence can be attributed to hydrochemical processes of acidity buffering of the system, related to the alteration produced in the water hydrochemistry by the input of acid generating elements or compounds from mine waters such as Fe or  $\text{SO}_4^{2-}$ . The PC2 is associated with ions from common Earth's crust materials, related in this case to the soils and the geological formations present in the basin, therefore from a geogenic origin. As a consequence of the elements present with high loading in the PC3, this may be considered another mining-related component. This factor groups the elements As and Zn, related with the other important Pb-Zn-Ag polymetallic ore deposits scattered in the district. The fourth and the fifth factor may be considered as geogenic. This statistical analysis puts in relevance the influence of factors related to mine sources in the total variance of the system, being the amount of the total variance explained by mine factors 50.30%, larger than the variance explained by Earth's crust materials (29.79%). This fact confirms that the decommissioned large-scale mining developed in the district still remains in playing an important role in the hydrochemistry of regional-scale surface waters, and in consequence, runoffs from mine sites govern the quality of this aquatic ecosystem.

#### 4. Conclusions

Although mining stopped in the area more than 10 years ago for the case of mercury, and more than 100 years ago for Pb-Zn, the unrestored environmental liabilities in the area remain as sources of input for large amounts of potential toxic/harmful elements into the environment. The intense extractive activity developed remains, influencing the water quality, allowing to distinguish the sources of contaminants introduced into waters. The runoff from mine sites governs the hydrochemical composition of waters at the watershed scale, being the variance explaining these inputs greater than that explaining natural origin. This fact puts in relevance that mine sites persist as hot environmental spots of contamination in the area and actions aimed at recovery of the environmental quality must be improved in order to decrease anthropogenic inputs to restore a good aquatic hydrochemical quality.

#### Acknowledgment

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