Fate and Transport of Trace Metals under Different Hydrologic Regimes in the World Largest Hg Mining District

Jorge Loredo[1*], Efren Garcia-Ordiales[1], Jose Maria Esbri[2], Miguel Angel Lominchar[3], Rocio Millan[3], Pablo L. Higueras[2]

1 Mining Exploration and Prospecting Department, University of Oviedo, Independecia 13, 33004 Oviedo, Spain, jloredo@uniovi.es; garciaefren@uniovi.es
2 Institute of Applied Geology , Biogeochemistry Laboratory of Heavy Metals, University of Castilla-La Mancha, Plaza Manuel Meca, 13400 Almadén (Ciudad Real) Spain
3 CIEMAT – DMA. Avenida Complutense, 40. E-28040 Madrid, Spain

Abstract The Almadén mercury mining district is located in Ciudad Real (South Central Spain) and it includes the largest Hg mine in the world. The study presented in this paper focuses on the transport and dispersion of Hg and trace metals to the environment in order to evaluate the real impact of the closured mining works in the aquatic environment. Hydrological variables governing temporal and spatial variations in concentrations and state of trace metals in streams affected by mining runoff are considered.

Keywords trace metals, mining runoff, pollutant transport, hydrological effects

Introduction

Heavy metals are introduced into the aquatic systems as results of natural and anthropogenic processes such as volcanoes, fires, agriculture, fossil fuels and mining, which is one of the most important sources of heavy metals to the environment (Bradl 2005, Donkor et al. 2005). Mining operations induce physical and chemical alterations of extracted materials favouring the mobilizations of metals in the different environmental media (Kim et al. 2001) involving a significant increase of their concentrations in the surrounding areas of the mining operations, and this is specially important in the aquatic ecosystems (Donkor et al. 2005, Jordan and D'Alessandro 2004, Jordan et al. 2009, 2011).
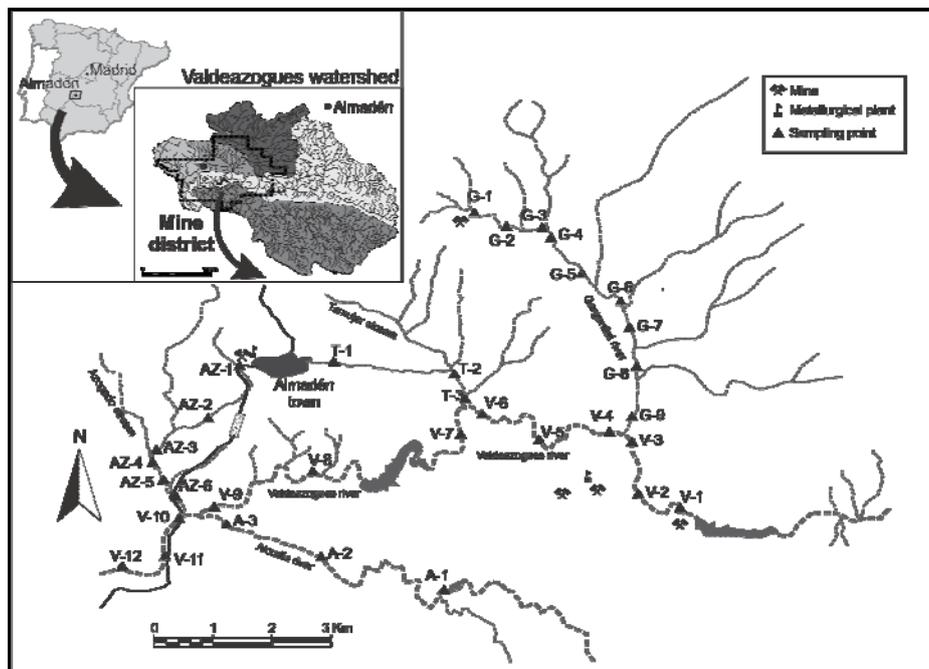
Fig. 1 *Area of study and location of sampling points.*

In the area of Almadén (fig. 1), besides the Hg mines that constitute the most important Hg mining district in the world (Hernández et al. 1999), Pb-Zn-Cu and Fe-Cu mines have also been exploited at an artisanal level. As a results of this intensive mining, there now remains influential mining waste/sediments in the area which can be considered potential sources for dispersion of heavy metals to the aquatic ecosystems. In this context, the study of heavy metal concentrations, their transferences and dispersions highlight a need for a potential risk assessment in the aquatic ecosystem. The study presented in this paper focuses on the mechanisms governing the flow of heavy metals in the water environment, and to study which have been completed in the district during the last four years.

Materials and methods

For the purposes of the study 66 water samples were collected in pre-cleaned plastic bottles. In the field water sample aliquots were filtered (0.45 μm). Collection, storage, and preservation techniques of samples complied with the Method 1631 of US EPA (Louch, 2003). Total and dissolved fractions of trace metals were determined by analysing non-filtered and filtered samples, respectively. Hg concentration in samples were quantified by atomic absorption spectroscopy (AAS) following thermal decomposition of the sample (Costley et al. 2000), using an Advanced Mercury Analyser (LECO AMA-254). Heavy metals and metalloids were quantified by Inductively Coupled Plasma Mass Spectrometry (ICP-MS Agilent 7500 cx) according EPA method 200.8. (Brockhoff et al, 1999) Major ions were determined by ion chromatography (ISO 2007). Also Visual MINTEQ was used to simulate the dissolved trace metals speciation.

To evaluate trace metals variation in the water flow during two different hydrologic conditions, Cl concentration was used to quantify the relative contribution of dilution and precipitation to the variation of metals concentrations because Cl can be conceived as a conservative element (Heim 1985; Bonzongo et al. 2006).

Results and discussion

The geochemical diagram for waters of the district by different hydrological regimes is presented in fig. 2. Results show that the mineralization of the monitored waters is lower in high flow regime (range: 119.8-662.7 mg/L) than in low flow regime (range: 194.2-3052.4 mg/L) and this is a consequence of the dilution processes in the river flow regime. In the geochemical analyses, bicarbonates are the predominant anion in the most part of the samples; on the other side, calcium and magnesium are the predominant cations, and these are related to the lixiviation of primary minerals associated to the basic volcanism con alkaline affinity and the high levels of CO_2 that occur in the district (Sainz de Baranda & Lunar 1989; Higueras et al. 2000a, 2000b, 2013). This important presence of alkaline elements determines that the pH of waters is near to neutral values (between 6.3 and 7.7 pH), where the lowest values are associated with sample points close to the old mining works.

Concentration intervals for metals in waters and in particulate materials for different hydrological regimes are presented in tables 1 and 2. For the different hydrological regimes the main form of transport of metals is the particulate phase, which varies in the rank of 56.2%-99.9% of the whole concentrations for the different analyzed metals. The main element in the particulate material, obtained by difference between total concentration and concentration in waters, is Fe, followed by Al and Mn, which concentrations are in an order of magnitude higher than the others. From these elements the higher concentrations correspond to Zn, Pb and Cu; on the other side, the lowest concentrations in particulate material correspond to As and Hg.
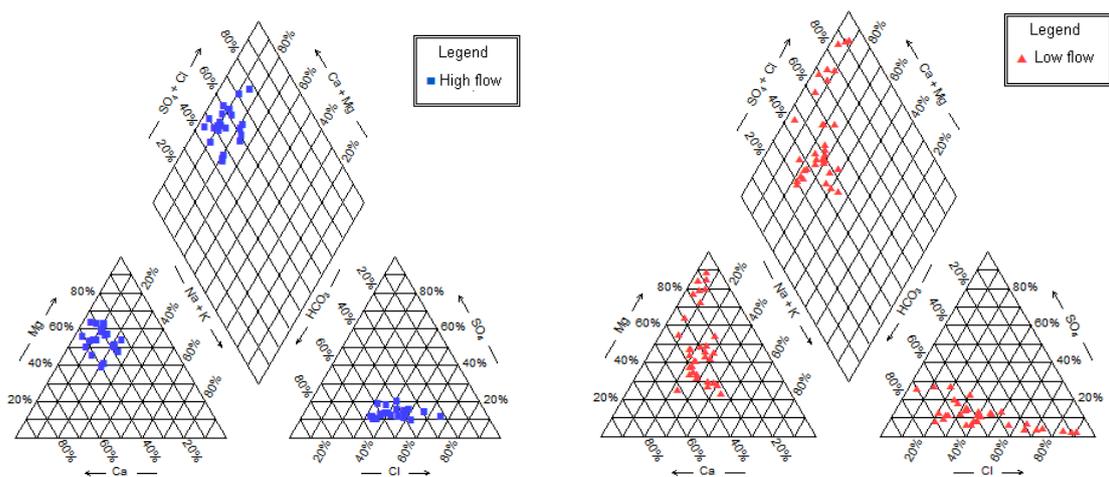
***Fig. 2** Piper diagram for high and low water flow regimen*

The concentration of metals in the solved phase grows with respect to the particulate phase during the low flow regime because of a smaller dilution by low flow in the river. In a similar way to the particulate material the highest concentrations of metals in the solved phase correspond to Fe, Al and Mg.

***Table 1** Particulate matter trace metals concentrations range (µg/l).*

	VALDEAZOGUES		GARGANTIEL		AZOGADO		ALCUDIA		TAMUJAR	
	Max	Min	Max	Min	Max	Min	Max	Min	Max	Min
Hg	0.56	0.11	0.50	0.09	0.87	0.27	0.24	0.11	0.47	0.05
Fe	4736.53	190.87	3272.12	158.44	3297.35	251.45	1844.13	244.85	1083.36	156.93
Mn	2343.28	116.21	1625.22	105.05	1810.05	132.15	906.46	100.06	696.27	54.97
Al	1383.92	57.84	966.92	43.63	1079.38	55.22	580.98	48.24	449.75	29.78
Cu	257.26	15.15	121.41	16.61	306.25	44.01	104.01	20.51	88.22	7.91
Pb	313.84	2.85	198.72	2.30	215.15	2.85	56.47	3.42	28.80	0.71
Zn	402.00	12.81	128.00	17.21	503.96	24.79	156.64	13.60	49.33	5.54
As	209.33	2.09	198.94	3.60	197.92	5.42	99.30	5.91	17.47	1.96

***Table 2** Dissolved trace metals concentrations range (µg/l).*

	VALDEAZOGUES		GARGANTIEL		AZOGADO		ALCUDIA		TAMUJAR	
	Max	Min	Max	Min	Max	Min	Max	Min	Max	Min
Hg	0.32	0.01	0.32	0.01	0.38	0.08	0.10	0.06	0.10	0.01
Fe	554.96	20.72	468.20	12.16	237.80	37.78	94.27	21.80	59.16	11.45
Mn	79.03	10.55	83.40	11.16	105.31	22.48	126.31	18.89	17.50	12.11
Al	37.93	8.98	78.83	2.13	43.10	10.47	56.43	22.47	12.48	2.84
Cu	3.02	0.35	2.15	0.06	7.92	0.01	2.32	0.56	0.91	0.13
Pb	3.22	0.06	0.73	0.02	2.13	0.06	3.04	<DL	0.21	<DL
Zn	22.12	1.05	7.87	0.10	22.56	2.40	9.52	1.28	2.80	0.10
As	6.34	0.58	3.45	0.09	6.19	0.44	5.13	1.30	1.09	0.05

In the physicochemical conditions measured in the field, metals speciation in waters shows that for Fe, Al, Mn, Co, Ni and Zn, the inorganic species are predominant. Fe, Co, Ni and Zn in solved phase, are principally present as monoelemental ions, followed by oxides and hydroxides and in the sampled points located in proximity to the mining works, sulphate species appear sporadically by the influence of leachates flowing from these areas. For Al, the hydroxide ions are the majority because of the basicity of waters which induce the existence of a great quantity of OH^- radicals available in waters; in the same way, in proximity to the mine sites a contribution of sulphates to water and decrease of pH are associated with the appearance of sulphate species that quickly disappear downstream of the sources. From the other elements, the majority of As is found solved as H_3AsO_3 due to the neutral pH of waters (Lee et al, 2005). In the case of Pb, Cu and Hg, the major part of these elements are bound with dissolved organic carbon (DOC), chiefly for Hg which represent over 98% of the total species and may explain the high dissolved concentrations detected as a result of organic ligands inhibit the Hg retention or precipitation (Mierle and Ingram 1991, Watras et al. 1995, Babiarz et al. 1998).

The estimated hydrological effects of decreasing of metals concentration is presented in table 3. Results show that, in general, the most important mechanism in concentration decreasing is the precipitation, where the average for high and low flow is 69% and 59% respectively. For all elements, the precipitation is the predominant mechanism in both regimes, but for Hg, during the low flow the dilution is more important in small riverbeds as the Tamujar stream where the main mechanism for concentration decrease is.

Table 3. Estimated hydrological effects on trace metals concentrations decrease

	Dilution				Precipitation			
	High Flow		Low Flow		High Flow		Low Flow	
	Max	Min	Max	Min	Max	Min	Max	Min
Hg	94.7%	6.0%	95.4%	24.4%	94.0%	5.3%	75.6%	4.6%
Fe	89.0%	12.3%	56.1%	18.9%	87.7%	11.0%	81.1%	43.9%
Mn	51.2%	20.3%	53.3%	26.7%	79.7%	48.8%	73.3%	46.7%
Al	49.0%	13.8%	49.3%	19.7%	86.2%	51.0%	80.3%	50.7%
Cu	51.3%	6.0%	49.6%	23.5%	94.0%	48.7%	76.5%	50.4%
Pb	55.2%	13.2%	50.3%	17.5%	86.8%	44.8%	82.5%	49.7%
Zn	49.7%	5.5%	48.4%	10.6%	94.5%	50.3%	89.4%	51.6%
As	47.1%	9.3%	49.1%	17.0%	90.7%	52.9%	83.0%	50.9%

Conclusions

The results of the study show alkaline waters with near neutral pH. The concentration of total Hg is higher in the high water flow regime than in low water flow regime as a consequence of the terrigenous inputs from spoil heaps; the highest Hg concentrations are measured in water samples collected downstream of mine works, in proximity to them, during the high flow regime and mainly associated with the particulate form, which constitutes the main fraction of the metal in the system; in the low water flow regime the dissolved Hg fraction bound with DOC also represents an important fraction to be considered. In distribution of metallic species in water, inorganic hydroxyl and carbonate complex are predominate in Fe, Al, Mn, Pb and As compounds, whereas organic ligands are more important in Hg, Cu and Zn compounds. Precipitation is the main mechanism for the fast decline of metals in the high flow regime while in the low flow regimes the dilution processes govern the seasonal hydraulic conditions that are key in trace metal transport.

Acknowledgements

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