ARSENIC AND CADMIUM PRESENCE IN AMD-AFFECTED RIVER WATERS

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ABSTRACT:

AMD or acid mine drainage is one of the most important fluvial pollution, for its nature, extension and its trouble of solving. Rivers affects for this type of contamination have special characteristics such as its acidity, high sulphate and heavy metal contents, not only in its water but sediments. In the southwest of Spain, the Iberian Pyrite Belt is one of the biggest sulphide deposits in the world and the rivers in the province of Huelva are historically affected by AMD. This pollution carries out from mining structures as Waste Rock Dumps. These, after rainfall, produce leached discharges characterized by high concentration of sulphates and heavy metals, and a very low pH, near to 2. These acid effluents reach the river beds, changing their chemical properties. The Ría of Huelva is an estuary formed by the junction of the Tinto and Odiel rivers, which are affected by processes of AMD and run together into the Atlantic Ocean.

INTRODUCTION:

The present poster gathers the most relevant methodological aspects and contributions relative to the presence of Arsenic and Cadmium in watercourses undergoing AMD processes in the Iberian Pyrite Belt, from data obtained and processed under two research projects (Characterization of Acid Mine Drainage Processes in the Environment of the Cobica River and Impact on the Andevalo Dam. REN2002-01987/HID. Ministry of Science and Technology; Global Balance and Analysis of Arsenic and Cadmium Routes in AMD-affected Waters in the Iberian Pyrite Belt. P06-RNM-02167. Excellence Project of the Regional Government of Andalusia).
In Andalusia, the main problems of heavy metal presence in river, dam and well waters are associated to Acid Mine Drainage, due to the existence of the Iberian Pyrite Belt in this Autonomous Community (province of Huelva). The intense surface and underground mining activity has left behind in the basins of the rivers in Huelva (mainly the Tinto and Odiel Rivers) a legacy of 150 abandoned mines with their wells, holes and open mines, their uncountable kilometres of tunnels and their 200 million m^3 of scattered waste in 70 mine dumps and 14 mining ponds, all of them being contaminant sources affecting the water and sediments of these rivers and their coastal area of influence (Sáinz *et al.*, 2004). There are numerous scientific publications describing the distribution of heavy metals in this area (Lee *et al.*, 2005; Leblanc *et al.*, 2000; Grande *et al.*, 2000, 2003, 2005 a y b, 2006; Sánchez-España *et al.*, 2005; Sánchez-Rodas *et al.*, 2005).
Among the different elements contaminating these waters, Cadmium and Arsenic are the most toxic ones for humans. Institutions such as the World Health Organization (WHO), the European Union (Directive 98/83) or the Spanish Ministry of Health and Consumption have set up a reduction of the maximum content of Arsenic in drinking water from 50 to 10 ppb (WHO, 1993) and a limit of 5ppb for Cadmium (RD 140/2003)

Photo 1: Zarandas area, exit of Riotinto Mines

OBJECTIVES AND METHODS:

In a first phase, described in this poster, the objective was the characterisation of the potential contaminant sources, with an exhaustive analysis of the medium generating heavy metals in general, and Arsenic and Cadmium, in particular. The methodology applied for the achievement of the first phase of the main objective of this study was the sampling of mine dump leachate from those mines which, due to their historic relevance and mineralogy, are susceptible of throwing important amounts of heavy metals. This was done with the help of existing charts of the topographic map published by the Spanish Ministry of Public Works, where the drainage System affected by AMD contaminant points is drawn and Mines and Dumps affecting Tinto and Odiel Rivers in the Iberian Pyrite Belt are cataloged; also characterizing potencial sources of Arsenic and Cadmium. The sampling was conducted in one single day in October 2006, where a total of 75 samples were collected. In each water sample collected, pH and conductivity were measured 'in situ' and stored appropriately for determining heavy metals and total Arsenic and Cadmium in the lab using Flame Atomic Absorption spectrometry equipment, Graphite Furnace, Flow Injection Hydride Generation Systems, etc.

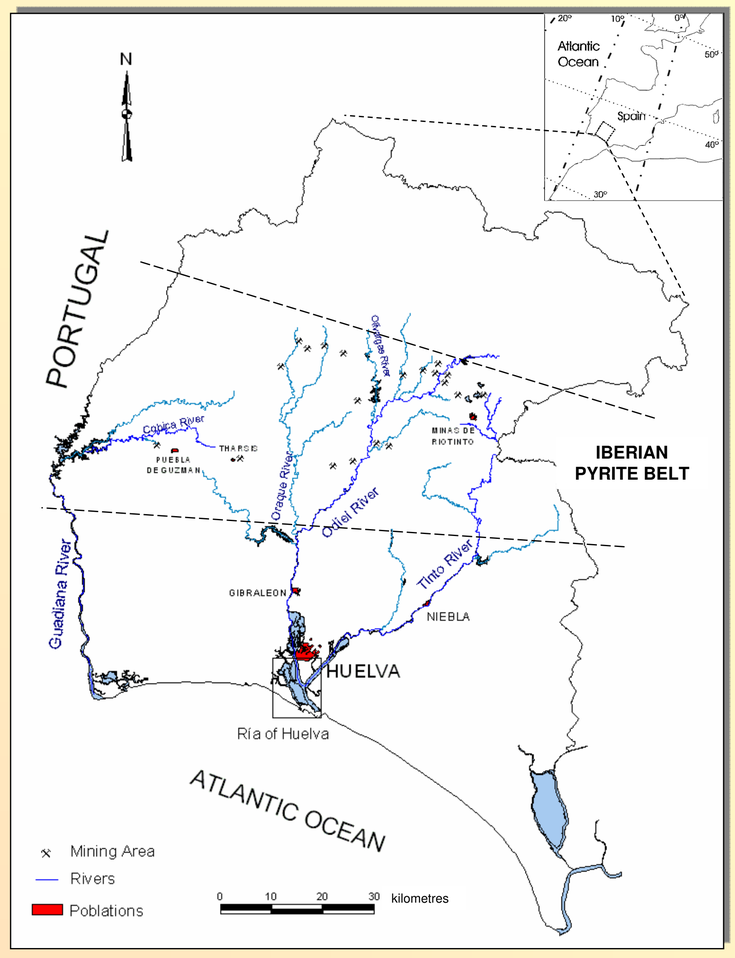

Figure 1. Location map and principal mining waste rock dumps

RESULTS AND DISCUSSIONS:

Once the measurement of all analytical parameters of the 75 samples collected was performed, a total of 1050 data were obtained. After the detailed analysis of the data mass obtained, the following can be observed: in most sampling points pH reaches a value lower than 3, and even lower than 2 at some points, showing a minimum pH of 1.01 in mine dump water North of San Telmo open mine. These extremely low pH values show AMD process phenomena, also proved by the high sulphate concentrations shown at most points (in 16 samples they are over 10000 ppm). As a result of the existing AMD phenomenon, high heavy metal concentrations are also found. Specifically, iron reaches a value higher than 1000 ppm at 38 of the sampling points, and in samples collected at La Zarza, San Telmo, Sotiel, Tharsis and Riotinto mines, it exceeds 10000 ppm. Also Copper and Zinc reach their highest concentrations at San Telmo, La Zarza, Riotinto, Sotiel, San Platón and Aguas Teñidas. Although in lower concentrations, Manganese exceeds 100 ppm at Riotinto, Sotiel, Tharsis, La Zarza, San Telmo and San Platón, being higher than 1000 at Sotiel. Cadmium exceeds 100 ppb at 48 sampling points, reaching values higher than 1000 ppb at some points of Riotinto, Sotiel, La Zarza, San Telmo, San Platón and El Romerito. Arsenic concentration exceeds 100 ppb in 68 of the 75 water samples, reaching even 10000 ppb at certain points of Riotinto, Tharsis, Sotiel, La Zarza, San Telmo and San Miguel.

CONCLUSIONS:

- **The results clearly show the existence of AMD phenomena in the Iberian Pyrite Belt even without existing mining activity 10 years in the last.**
- **It has been proved that Arsenic concentration is 10 times higher than the limit allowed for drinking water, and even 1000 higher at some points of 6 of the studied mines.**
- **Cadmium concentration is 20 times higher than the allowed limit, and 8 samples show 200 times higher concentration.**

Photo 2: Tintillo River, exit of water coming from the dump of the west of Riotinto Mine

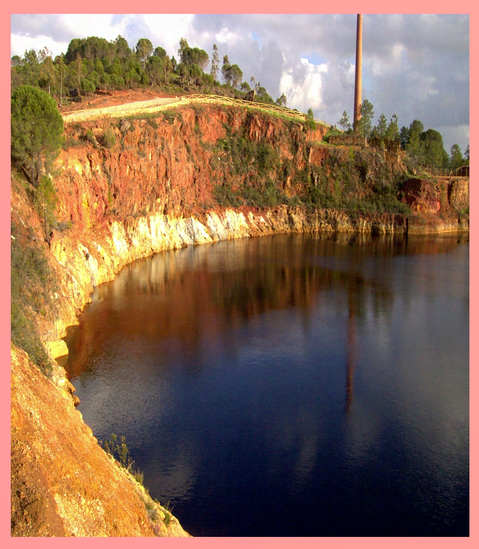

Photo 3: Confesionarios Mine, flooded open pit

MINE	NAME	pH	Conductivity (mS/cm)	Cd (ppb)	As (ppb)
RIOTINTO	ATALAYA OPEN PIT	1,41	21,80	1499,00	44000,00
RIOTINTO	MARISMILLAS	2,47	10,35	2833,00	1466,00
THARSIS	FILON SUR DUMP	2,00	11,79	492,80	21820,00
THARSIS	FILÓN NORTE 1 DUMP	2,40	7,15	480,00	35360,00
THARSIS	FILÓN NORTE 2 DUMP	1,85	10,31	32,31	12370,00
THARSIS	LA TIESA – BEFORE THE GOSSANS	2,50	6,70	348,30	11310,00
SOTIEL	DUMP, ENTRANCE BY CALAÑAS	2,36	8,21	85,14	23230,00
SOTIEL	DUMP, IN THE MIDDLE OF THE TOWN	2,13	11,43	1001,00	22030,00
SOTIEL	DUMPS, IN HILL OF THE TOWN	1,84	18,09	275,20	145900,00
SOTIEL	DUMPS, TRANSPORTING TAPE	2,21	14,56	6601,00	116100,00
LA ZARZA	DUMP	1,12	26,20	1339,00	104500,00
SAN TELMO	DUMP TO THE NORTH OF THE OPEN PIT	1,01	44,50	1088,00	41020,00
SAN MIGUEL	STREAM DUMP	1,84	11,61	229,40	10750,00
SAN PLATÓN	EXIT OF THE DUMPS BY THE HIGH PART	2,46	8,62	2404,00	150,20
ROMERITO	EXIT DUMPS	2,49	5,93	1112,00	1691,00

Table 1. Highest concentration point in October 2006 carried out sampling

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