



## Surface water monitoring in the mercury mining district of Asturias (Spain)

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### ABSTRACT

Systematic monitoring of surface waters in the area of abandoned mine sites constitutes an essential step in the characterisation of pollution from historic mine sites. The analytical data collected throughout a hydrologic period can be used for hydrological modelling and also to select appropriate preventive and/or corrective measures in order to avoid pollution of watercourses. Caudal River drains the main abandoned Hg mine sites (located in Mieres and Pola de Lena districts) in Central Asturias (NW Spain). This paper describes a systematic monitoring of physical and chemical parameters in eighteen selected sampling points within the Caudal River catchment. At each sampling station, water flow, pH, specific conductance, dissolved oxygen, salinity, temperature, redox potential and turbidity were controlled “in situ” and major and trace elements were analysed in the laboratory. In the Hg-mineralised areas, As is present in the form of As-rich pyrite, realgar and occasionally arsenopyrite. Mine drainage and leachates from spoil heaps exhibit in some cases acidic conditions and high As contents, and they are incorporated to Caudal River tributaries. Multivariate statistical analysis aids to the interpretation of the spatial and temporary variations found in the sampled areas, as part of a methodology applicable to different environmental and geological studies.

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### 1. Introduction

The presence of high Hg concentrations in the environment is recognised as an important problem for both humans and ecosystems. Environmental regulation about Hg releases began in the U.S.A. and Canada in the 1970s, partly as a general consequence of the environmental activism which began in the late 1960s, but also as a very specific consequence of scientific studies [1,2] that showed that inorganic Hg could be evolved to a more toxic form (methylmercury) in the environment, leading to significant levels in fish and other high-level predators, and thus posing a human health risk. As a consequence, abandoned Hg mining has a particular interest in relation to the potential environmental pollution associated to it [3].

The most important Spanish Hg mining districts behind Almadén is located in Asturias, NW of the country. Asturias was an important Hg producer on a world scale during the decade 1962–1972, with average annual productions of 15,000 flasks [4]. “La Peña-El Terronal” and “La Soterraña” were the most productive mines, located in Mieres and Pola de Lena districts, respectively,

both in Central Asturias. Other minor mines, such as “Los Ruedos” (Mieres) were intermittently exploited in these areas. As occurred in other Hg mining districts all around the world, the great decline on Hg prices happened on the 1970s gave rise not only to the interruption of some important new mining projects, but to the successive closure of mines between 1973 and 1974 in Asturias. Currently, the legacy of the historical Hg mining activities in this region remains in the form of abandoned underground mines, and remains of metallurgical installations and spoil heaps which constitute potential sources of environmental pollution. Studies about the environmental implications of the abandoned Hg mining operations in Asturias are abundant [5–14] and prove the existence of pollution in soils, surface waters and sediments in areas affected by Hg mining.

From these sources, pollutants can leach into the mine water system and ultimately into the environment when the mine/metallurgical wastes enter in contact with surface runoff or infiltrated water. Polluted mine water and spoil heap leachates release metals and metalloids into the water environment with a variable impact, depending on the quantity and quality of the released effluents. The precipitation of very fine particles and dissolved constituents may result in the contamination of stream sediments by metals and metalloids, which may be found in different chemical forms in various sediment fractions.

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Therefore, the development of a remediation plan for these abandoned mine sites requires an understanding of the pollutants characteristics and their distribution in the mine water environment, as well as the expected release to the surface watercourses. To identify pollutant concentrations and pollution extension, a detailed program of surface water sampling, both upstream and downstream from the three main abandoned Hg mine sites within the Caudal River catchment, was carried out. The hydrochemical information obtained will be used to assess the potential environmental impact and to apply remediation actions in the affected areas.

## 2. Experimental

### 2.1. Characteristics of the studied area

As it is shown in Fig. 1, the three studied Hg mine sites are located within the Caudal River catchment. The Caudal River is a tributary

of Nalón River, which is the main river of the region. La Peña-El Terronal and Los Rueldos sites are located on the right bank of Caudal River, whereas La Soterraña site is placed on the left bank of one of its main tributaries (Lena River). The aim of this study is to assess how the pollution coming from each one of these sites may affect Caudal River water.

An extensive research has been done on the geological, mineralogical and metallogenetical characteristics of Asturian Hg deposits [15–19]. Most important Hg deposits are located in the north-western margin of the Asturian Central Coal Basin, within a zone of intense tectonic deformation under the influence domain of significant fractures. The mined ore deposits of Mieres and Pola de Lena districts are hosted in Carboniferous materials of Westphalian age, and some of the most important deposits are associated with conglomeratic horizons or siliceous breccias, and impregnating fractured lutitic carbonaceous sequences. Hg deposits are generally associated with fractured zones, and the mineralisation is usually irregularly distributed both in veinlets

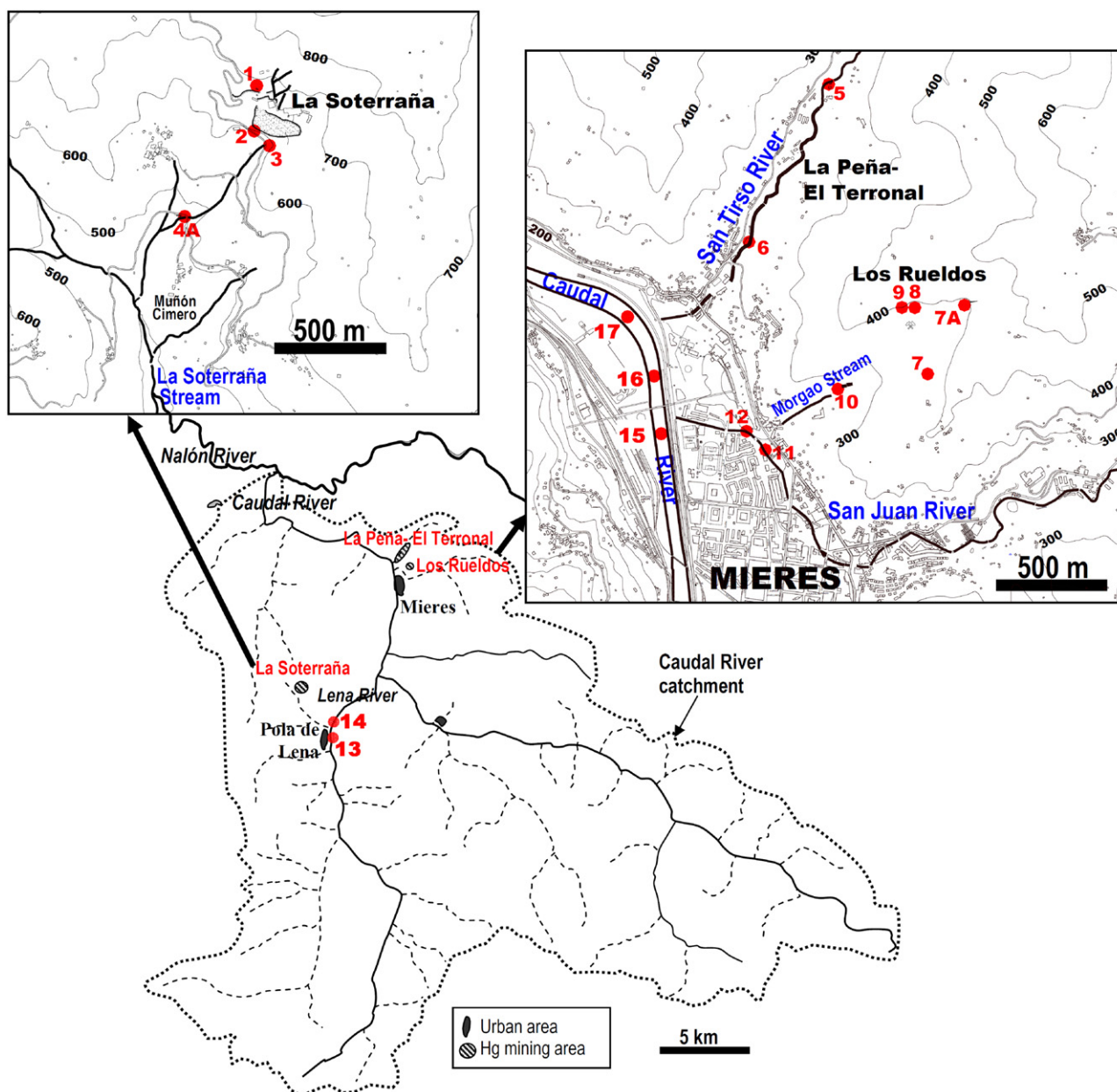


Fig. 1. Location of the abandoned Hg mine sites and water sampling points within Caudal River catchment.

inside conglomeratic-brecciated bodies which show a lenticular morphology or scattered inside the conglomerate matrix. Mineralisation also appears either as irregular massive lenticular stocks in carboniferous limestones, either as irregularly distributed veinlets in fracture planes, and occasionally constituting disseminations in the enclosing limestones and sandstones [15].

Although Hg is present in the form of cinnabar and metacinnabar, native Hg is also occasionally found. The presence of arsenic is very frequent in the form of orpiment, realgar and As-rich pyrite [15,18]. Other primary metallic minerals, which are present in the paragenesis of the ore deposits, are: pyrite, melnikovite, sphalerite, marcasite, chalcopyrite, arsenopyrite, galena, and stibnite. Smithsonite, hemimorphite, cerusite, goethite, malachite, jarosite, melanterite and gypsum are present as secondary minerals. The gangue constituents are quartz, carbonates (calcite, dolomite and ankerite) and argillaceous minerals (kaolinite and dickite). From their geological, mineralogical and metallogenetic characteristics, Asturian Hg ore deposits correspond to a mineralisation of epigenetic type formed by the circulation of low temperature hydrothermal solutions along distensional fractures [17]. Mineralisation generally shows important litologic and tectonic controls, exhibiting a clear spatial relationship between Hg deposits and late-hercynian fractures. Compared to other Hg deposits in the Iberian Peninsula, the presence of As, which is relatively abundant in the above cited mineralogical forms, is diagnostic of these deposits.

The substrate of the mineralised areas is mainly constituted by alternation of limestones, sandstones, shales and some coal beds. From a hydrogeological point of view, they can be considered predominantly impermeable with the exception of thick limestone and sandstone bars which can constitute small aquifers. Water that does not evaporate or flows superficially is infiltrated on these aquifers as well as on the more permeable colluvial materials and weathered shales, giving rise to a number of small springs. In the studied area, springs are scarce and mostly associated with limestone bars, whereas those associated with sandstones have very poor flow.

In contrast to other regions of Spain, Asturias has a humid and temperate climate characterised by abundant rainfall during a great part of the year. The annual average maximum and minimum temperatures of the last twenty years are 17 and 8 °C respectively, and the annual average relative humidity ranges from 74 to 84%. Average yearly rainfall in the same period was 966 mm and annual potential evapotranspiration calculated by Thornthwaite expression is 691 mm year<sup>-1</sup>. In consequence, the average annual effective precipitation is 275 mm year<sup>-1</sup>. The one hundred-year 1 day rainfall is 97.8 mm day<sup>-1</sup>.

Mine wastes are heterogeneous in size and nature, and in consequence, their hydraulic properties vary greatly; waste piles are usually quite permeable and constitute a porous media where wastes are intermittently wetted by meteoric waters and seasonal runoff. Mine wastes exposed to weathering processes and rain water can easily find its way through the waste material. As a result, unstable minerals, such as some sulphides, are oxidised and metals and metalloids are leached and put into solution, with the subsequent formation of secondary weathering minerals. Weathering kinetics of sulphide minerals is dependent on the exposure to the leaching agent. A waste pile, made up predominantly of relatively small broken-up chunks, has an enormous amount of surface area of exposed sulphide mineral susceptible to react when it contacts with water and/or air. The abundance and distribution of acid producing and acid buffering minerals varies extensively on the different parts of the spoil heap, depending on the type of materials stored. Rainfall events provide ideal conditions for the dissolution of secondary weathering products and the transport in solution of leached metals and metalloids to the surface watercourses or to the saturated zone occurs. At the studied abandoned mine sites, the circulation

of surface waters in oxic conditions through the underground mining works and spoil heaps promotes in some cases the formation of acid mine drainage and spoil heap acidic leachates with its typical reddish Fe-oxides precipitates.

The recent European Water Framework Directive (WFD) demands the establishment of adequate water control networks and monitoring programs. In Spain, two national networks (S.S.I.H. and S.A.I.C.A.) provide hydrological and hydrochemical data for surface waters in the main Spanish cathments; however, they are clearly insufficient to meet Directive requirements controlling potential water problems, due to the low number of monitoring stations. In order to manage and to correct mine water discharges at the source, a monitoring program at a local scale would be desirable [20].

## 2.2. Monitoring

As it has been stated, systematic monitoring of surface waters in the area of abandoned mine sites constitutes an essential step in the characterisation of pollution from historic mine sites. To improve effectiveness, a monitoring system must be significantly adapted to the particular characteristics of the site. For example, climate conditions are important factors affecting the quantity and quality of mine waters, as well as the relation between surface and ground-water [21,22]. The analytical data throughout a hydrologic period can be used to create a hydrological model and to select appropriate preventive and/or corrective technologies to avoid the pollution of the surface watercourses [23,24].

In order to protect the quality of water resources in and around mine sites, a preliminary hydrochemical monitoring of surface waters has been carried out in the affected catchment. It consists of the measurement of standardised physicochemical parameters in surface waters over a period of time. Referred to natural baseline conditions, a monitoring campaign looks for the presence of dissolved and/or suspended constituents, as well as significant changes of these constituents with time. A systematic monitoring of 32 physicochemical parameters in 13 selected sampling points (#1–12) located both upstream and downstream of the main mining-metallurgical sites in the Caudal River catchment (Fig. 1), is being undertaken. Besides, other five samples points (#13–17) have been considered in Caudal river, located upstream and downstream of the tributaries which drain the considered sites. Due to economical factors, sampling was restricted to spring and summer in order to assess both high and low flow conditions, respectively. Sampling was also restricted to accessibility to water. These sampling points are described in Table 1.

Water samples were collected, filtered “in situ” and stored in plastic bottles, which were refrigerated at 4 °C until analysis. In order to preserve their chemical characteristics and to keep metals in solution, special precautions, including the previous acidification of samples with HNO<sub>3</sub>, were taken.

Major and minor elements (Al, As, B, Ba, Be, Bi, Ca, Cd, Co, Cr, Cu, Fe, Mg, Mn, Mo, Ni, Pb, Se, Sr, Ti, V and Zn) were determined by inductively coupled plasma atomic emission spectrometry (ICP-AES) using two Jobin Yvon spectrometers (simultaneous JY38+48 and sequential JY38 PLUS), Na and K by flame atomic emission spectrophotometry (FAES) using a Perkin Elmer 2280; finally, Hg was determined by a Milestone direct mercury analyzer (DMA-80). Ultrapure water from a Milli-Q system (Millipore Bedford, MA) was used throughout. All glassware and bottles were cleaned in 0.5 M HNO<sub>3</sub> for 2 days and rinsed three times with water before use. The chemicals used were of analytical-reagent grade. HNO<sub>3</sub> (65%) and stock standard solutions for each element were obtained from Merck (Darmstadt, Germany). Working standard solutions were prepared freshly from individual 1000 mg l<sup>-1</sup> stock standard solutions by sequential dilution with 0.5N HNO<sub>3</sub>. Blanks were analysed

**Table 1**  
Description of the sampling points in the abandoned mine sites (see Fig. 1).

Mine site/River	Monitoring point	Description
La Soterraña	P-1	Surface runoff (upstream of La Soterraña Mine)
	P-2	Air-open channel (downstream of La Soterraña Mine, receiving spoil heap leachates)
	P-3	Brook at the bottom of La Soterraña spoil heap
	P-4A	Stream (downstream of La Soterraña mine site receiving spoil heap leachates)
La Peña-El Terronal	P-5	San Tirso River (upstream of La Peña-El Terronal mine site)
	P-6	San Tirso River (downstream of La Peña-El Terronal mine site)
Los Ruedos	P-7A	Spring upstream of Los Ruedos mine site
	P-7	Surface runoff upstream of Los Ruedos mine site
	P-8	Los Ruedos mine drainage (water pond at the entrance of the gallery)
	P-9	Los Ruedos mine drainage (water inside the gallery)
	P-10	Morgao stream (downstream of Los Ruedos mine site)
	P-11	San Juan River (upstream of Los Ruedos mine site)
Caudal River	P-12	San Juan River (downstream of Los Ruedos mine site)
	P-13	Caudal River tributary (Lena River) upstream of La Soterraña mine site
	P-14	Caudal River tributary (Lena River) downstream of La Soterraña mine site
	P-15	Caudal River upstream of San Juan River mouth
	P-16	Caudal River downstream of San Juan River mouth and upstream of San Tirso River mouth
	P-17	Caudal River downstream of San Tirso River mouth

together with the samples, giving values always lower than detection limits for all the considered elements. Samples were stored under refrigeration and analysed not later of fifteen days after sampling date, verifying their stability during this period. For each analysed sample, the final concentration results from the average of three measurements. Several certified reference materials (Fresh water CRM 398 and CRM 399 from BCR, Simulated Fresh Water IAEA/W-4, and Waste Water SPS-WW-1 from Spectrapure Standards AS) were selected for this study in order to assess the accuracy of the results. The errors in the analysis of these reference materials were found to be always less than 3%. Quantification limits were  $0.5 \mu\text{g l}^{-1}$  for Hg,  $0.20 \text{ mg l}^{-1}$  for Bi and Se,  $0.05 \text{ mg l}^{-1}$  for Al, B, Ba, Ca, Co, Cr, Cu, Mg, Pb, Sr, Ti, V and Zn,  $0.03 \text{ mg l}^{-1}$  for As, Be, Cd, Fe, Mn, Mo and Ni and  $5 \text{ mg l}^{-1}$  for K and Na. Flow measurements were made with a current meter (Global Water flow probe), at every sampling point, when it was possible. Parameters such as pH, specific conductance, dissolved oxygen, salinity, temperature, redox potential and turbidity were measured by means of a portable multiparameter probe (Turo-graph 611).

### 3. Results and discussion

#### 3.1. La Soterraña mine site

It is located in the northern slope of a deep valley that is crossed by a small stream whose flow ranges from  $0.02$  to  $0.09 \text{ l s}^{-1}$ . This stream collects surface runoff, spoil heap leachates and effluents from a local industry devoted to the manufacture of ceramics, increasing its flow to  $0.15$ – $0.80 \text{ l s}^{-1}$ . This stream enters into Lena River, a tributary of Caudal River. The area occupied by the abandoned mining and metallurgical installations, including the spoil heap, is estimated at  $72,000 \text{ m}^2$ . About 85% of this area is permeable, leading to infiltration. Taking into account the climate data and considering an infiltration coefficient of 0.7 for the spoil heap, infiltrated rainwater with possibility to enter in contact with mine waste materials is about  $11,781 \text{ m}^3 \text{ year}^{-1}$ . This water transports pollutants in solution to groundwater and/or to the surface watercourses. The impact of La Soterraña Mine into the water environment is mainly evidenced by the presence of high levels of As downstream of the mine operations. Physicochemical data corresponding to the five sampling points selected in this area during a four months period are presented in Table 2.

Compared to that measured in point P-1 (upstream of the mine site), specific conductance increases in sampling points P-2, P-3 and P-4A, located downstream of it. In point P-3 specific conductance is

usually high, ranging from  $882$  to  $1753 \mu\text{S cm}^{-1}$ , particularly in dry periods. Arsenic concentrations also increase from not detectable values (upstream of the mine site) to  $57 \text{ mg l}^{-1}$  (downstream of it), as a consequence of the weathering of As-rich wastes stored in the spoil heap. Enrichment in alkaline and earth alkaline elements was also observed in water samples collected downstream of the mine site. Dissolved Hg concentration was always below  $0.5 \mu\text{g l}^{-1}$ .

#### 3.2. La Peña-El Terronal mine site

This mine is located in the valley of San Tirso River, tributary of Caudal River, and whose flow ranged from  $3$  to  $140 \text{ l s}^{-1}$  during the monitoring period. There are not significant differences in water quality when comparing samples collected upstream (P-5) and downstream (P-6) of the mine site, excepting As concentration, which increases up to  $6.7 \text{ mg l}^{-1}$  downstream of the mine works. Hg concentration was always below  $0.5 \mu\text{g l}^{-1}$ . Physicochemical parameters monitored for a fourth months period in the area, are presented in Table 3.

#### 3.3. Los Ruedos mine site

This mine is crossed by Morgao stream, which has a low flow upstream of the mine works, being canalised underground, downstream of the mine site. Mine drainage and spoil heap leachates reach Morgao stream when it reappears on surface. The flow of Morgao stream, at the end of the canalisation, ranges from  $1$  to  $5 \text{ l s}^{-1}$ . Specific conductance is low ( $200 \mu\text{S cm}^{-1}$ ) upstream of the mine site (P-7 and P-7A sampling points), but it increases downstream of the site (P-10 and P-12), with values around  $1200 \mu\text{S cm}^{-1}$ . This is due to the influence of mine leachates generated in the mine site (P-8 and P-9), with values around  $6000 \mu\text{S cm}^{-1}$ , that finally enter into Morgao stream. Mine water and spoil heap leachates have very low pH, around 2.5 units. Fe and As concentrations are significantly high in acid mine drainage and spoil heap leachates (around  $760 \text{ mg l}^{-1}$  Fe and  $8 \text{ mg l}^{-1}$  As), and they remain also quite high in Morgao stream, downstream of the site ( $5.5 \text{ mg l}^{-1}$  Fe and  $0.4 \text{ mg l}^{-1}$  As, as average values). Total concentration of elements such as Al, B, Co, Cu, Ni and Zn are high in mine drainage and spoil heap leachates, but they decrease remarkably after polluted waters reaches Morgao stream. Ca and Mg concentrations increase downstream of the site. Due to the low solubility of its compounds, Hg concentration in waters was always below  $0.5 \mu\text{g l}^{-1}$ . Physicochemical parameters measured in the sampling points in the area are presented in Table 4.

**Table 2**  
Results of selected parameters in samples taken at La Soterraña site in 2005.

Sample point	Date (MM-DD)	S. Conductance ( $\mu\text{S cm}^{-1}$ )	pH	Al ( $\text{mg l}^{-1}$ )	As ( $\text{mg l}^{-1}$ )	Ca ( $\text{mg l}^{-1}$ )	Fe ( $\text{mg l}^{-1}$ )	K ( $\text{mg l}^{-1}$ )	Mg ( $\text{mg l}^{-1}$ )	Na ( $\text{mg l}^{-1}$ )
P-1	04-27	415	7.88	0.06	<0.03	71	0.05	0.72	15	<5
	05-10	422	7.13	0.07	0.10	68	0.36	0.51	16	<5
	05-26	397	7.99	<0.05	0.06	56	<0.03	0.4	15	<5
	06-08	421	6.25	<0.05	0.04	59	0.07	0.43	15	<5
	06-23	432	6.63	<0.05	<0.03	59	<0.03	0.52	16	<5
	07-04	441	6.55	<0.05	0.07	61	<0.03	0.54	16	<5
	07-28	289	6.72	0.06	<0.03	63	<0.03	0.55	17	<5
P-2	04-12	832	7.31	0.07	26	170	0.09	14	29	32
	04-27	698	7.85	0.07	26	130	<0.03	6.5	23	23
	05-10	955	7.50	0.09	6.5	152	4.7	55	17	30
	05-26	705	8.41	0.05	25	117	0.04	3.9	22	18
	06-08	865	7.81	0.06	29	142	0.07	5.2	27	29
P-3	04-12	1029	7.31	0.16	26	220	0.10	6.4	46	16
	04-27	809	8.20	0.06	0.54	85	0.05	1.1	13	7.8
	05-10	1052	8.02	0.23	24	176	0.11	7	39	13
	05-26	882	8.16	0.22	29	149	0.2	7.9	36	14
	06-08	1484	6.47	0.14	39	219	<0.03	9.6	47	15
	06-23	1397	7.70	0.18	41	252	0.13	13	60	18
	07-04	1486	7.72	0.15	48	234	<0.03	14	68	19
	07-28	1753	7.75	0.22	44	341	0.18	16	80	22
P-4A	05-10	1029	8.17	0.10	48	228	0.07	11	39	17
	05-26	951	8.26	0.09	43	183	0.04	9.1	32	15
	06-08	1115	7.96	0.07	57	215	0.04	10	38	17
	06-23	1185	8.03	0.10	52	232	0.05	11	42	19
	07-04	1299	7.94	0.14	46	254	0.04	12	47	20
	07-28	1278	7.98	0.12	46	256	<0.03	11	46	23

### 3.4. Statistical analysis of data from Los Ruedos site

A selection of results obtained from this mine site has been included in Table 4, but many other parameters were measured. Due to the high number of parameters monitored in this study, it was difficult to establish associations. Physicochemical analyses together with chemometry are essential disciplines to tackle these studies [25,26]. For this reason, Supervised Pattern Recognition and Cluster Analysis were performed with the physicochemical results classified by their sampling points. A statistical processing of the data was carried out by using SPSS software, version 11.5 and STATGRAPHICS Plus version 5.0 for Windows®. Cluster analysis was carried out to establish groups of samples with similar characteristics. Supervised Pattern Recognition was applied by Discriminant Analysis. It was used for hard classification purposes, trying to establish possible connections among groups of samples and variables [26–28]. This procedure generates a small number of functions of quantitative measurements which are lin-

ear combinations of the standardised pattern variables with weight coefficients. These functions are called “Canonical Discriminant Functions” and help to discriminate among groups of samples. The procedure assumes that the variables are drawn from a population with multivariate normal distributions and that variables have equal variances.

A Supervised Patterns Recognition study was applied to all parameter results obtained for the 41 samples collected in Los Ruedos mining area. Linear Discriminant Function Analysis was designed to develop a set of discriminating functions which can help to classify samples and extract all those samples with significant differences in physicochemical composition. 41 cases were applied to this study and 27 predictor variables were entered: 8 physicochemical parameters taken in situ during sampling step (water flow, specific conductance, salinity, pH, redox potential, dissolved oxygen, turbidity and temperature) and 18 major and trace elements (Al, As, B, Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Na, Ni, Se, Sr, V and Zn). Those variables whose concentrations were below the

**Table 3**  
Results of selected parameters analysed in samples taken at La Peña-El Terronal site in 2005.

Sample point	Date (MM-DD)	S. Conductance ( $\mu\text{S cm}^{-1}$ )	pH	Al ( $\text{mg l}^{-1}$ )	As ( $\text{mg l}^{-1}$ )	Ca ( $\text{mg l}^{-1}$ )	Fe ( $\text{mg l}^{-1}$ )	K ( $\text{mg l}^{-1}$ )	Mg ( $\text{mg l}^{-1}$ )	Na ( $\text{mg l}^{-1}$ )
P-5	04-27	684	8.48	0.06	<0.03	96	0.05	5.2	55	9.8
	05-10	837	8.46	0.08	0.08	119	0.07	6.1	69	12
	05-26	775	8.45	0.07	0.03	94	0.10	5.8	63	10
	06-08	984	8.19	<0.05	0.04	127	0.05	6.8	80	14
	06-23	1093	8.20	<0.05	<0.03	141	<0.03	7.7	94	16
	07-04	1019	8.20	0.07	0.05	134	<0.03	7.7	91	14
	07-28	1200	8.09	<0.05	<0.03	153	<0.03	9.3	99	23
P-6	04-12	731	7.33	0.06	4.0	107	0.08	5.3	61	12
	04-27	647	8.46	<0.05	3.5	95	0.06	4.9	49	9.5
	05-10	760	8.60	0.10	4.0	107	0.06	5.7	58	11
	05-26	716	8.45	0.06	3.3	95	0.06	5.3	55	9.5
	06-08	898	8.49	0.05	4.6	109	0.07	6.2	70	12
	06-23	974	8.62	<0.05	5.7	126	0.05	7.1	77	14
	07-04	934	8.39	0.21	4.8	128	0.08	7.0	79	12
	07-28	1085	8.46	0.08	6.7	125	0.04	8.2	88	18

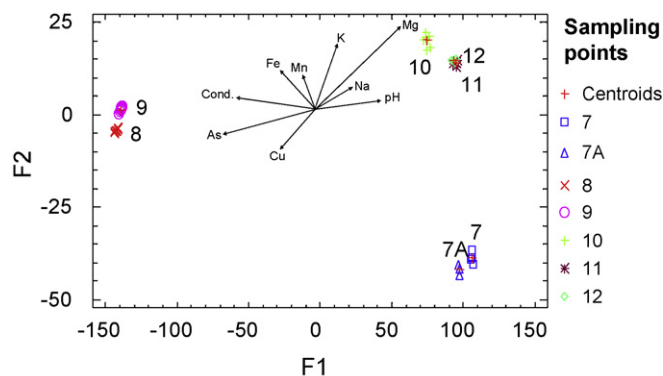
**Table 4**  
Results of selected parameters in samples taken at Los Rueldos site in 2005.

Sample point	Date (MM-DD)	S. Conductance ( $\mu\text{S cm}^{-1}$ )	pH	Al ( $\text{mg l}^{-1}$ )	As ( $\text{mg l}^{-1}$ )	Ca ( $\text{mg l}^{-1}$ )	Fe ( $\text{mg l}^{-1}$ )	K ( $\text{mg l}^{-1}$ )	Mg ( $\text{mg l}^{-1}$ )	Na ( $\text{mg l}^{-1}$ )
P-7	04-27	129	4.46	0.44	<0.03	12	<0.03	1.0	4.5	<5
	05-10	134	5.09	0.45	0.07	10	<0.03	1.0	4.4	<5
	05-26	135	4.90	0.38	<0.03	11	<0.03	0.95	4.2	<5
	06-08	408	6.74	<0.05	0.07	54	0.11	1.0	14	<5
P-7A	05-10	194	6.34	0.08	0.08	33	0.07	0.48	8.7	5.1
	05-26	168	6.11	<0.05	<0.03	22	0.13	0.48	5.9	5.1
	06-08	226	5.44	0.05	0.06	26	0.12	0.46	8.6	<5
P-8	04-12	5320	2.28	175	11	135	879	2.5	69	<5
	04-27	6100	2.53	144	6.5	112	725	2.1	52	<5
	05-10	5459	2.52	153	8.0	115	770	2.5	60	<5
	05-26	5450	2.50	144	8.5	98	725	2	59	<5
	06-08	5736	2.28	167	9.2	120	827	2.3	68	<5
	06-23	5560	2.40	155	8.3	124	744	2.2	70	<5
	07-04	5505	2.48	168	8.9	127	718	3	73	<5
	07-28	5865	2.50	164	5.9	154	736	3.4	67	9
	P-9	04-12	–	–	186	12	141	927	5	74
04-27		4543	2.49	183	8.5	131	927	3.1	63	<5
05-10		5862	2.55	152	6.3	119	757	2.8	59	<5
05-26		6355	2.55	140	9.1	118	705	2.4	61	<5
06-08		6455	2.45	149	7.9	104	728	2.9	63	<5
06-23		6115	2.50	143	8.4	110	695	2.6	70	<5
07-04		6260	2.54	165	8.5	135	684	2.6	73	<5
07-28		5065	2.28	160	6.0	121	718	2.1	67	<5
P-10		04-12	1149	7.34	1.3	0.43	153	5.4	4.6	85
	04-27	1008	8.60	1.6	0.34	126	4.3	4.1	66	60
	05-10	1116	7.77	1.3	0.37	130	4.3	4.6	68	72
	05-26	1080	7.41	1.6	0.44	121	5.1	4.4	64	68
	06-08	1190	8.03	1.3	0.43	121	5.8	4.7	73	85
	06-23	1256	6.45	0.94	0.52	117	7.1	5.5	78	87
	07-04	1250	7.80	0.84	0.43	129	5.0	5.4	81	90
	07-28	1200	7.50	0.83	0.61	102	6.7	5.7	72	92
	P-11	04-27	933	8.72	<0.05	<0.03	131	0.07	4.2	63
05-26		1030	8.26	0.07	<0.03	123	0.19	4.6	61	54
06-08		1169	8.12	0.11	0.07	126	0.29	5.4	66	85
06-23		1684	8.16	1.1	<0.03	147	0.35	12	83	244
07-04		–	–	3.8	0.08	185	1.5	6	62	31
07-28		989	7.96	0.46	<0.03	170	0.97	5.8	62	39
P-12	04-27	954	8.72	0.10	<0.03	131	0.23	4.2	61	42
	05-10	1015	8.66	0.08	0.09	134	<0.03	4.9	58	49
	05-26	1036	8.46	0.09	0.05	126	0.18	4.5	61	55
	06-08	1196	8.36	0.17	0.07	127	0.34	5.4	69	85

detection limits (Ba, Be, Bi, Hg, Mo, Pb and Ti) were not considered in this study, since the analysis did not overcome the tolerance test (0.001).

A graphical representation of the samples as a function of the two canonical discriminant functions is presented in Fig. 2, where F1 represents 96.5% of the variance and F2 represents 3.0%. These functions with P-values less than 0.05 are statistically significant at 95% confidence levels. The projection of the significant variables is also represented in the figure. Sampling point was used as grouping variable, where each category corresponds to the samples taken in the same point. Each sampling point is characterised by a centroid (marked as +), which is the average for each category (unique value in the classification factor field). Three different groups were selected according to the samples location (samples taken in P-8 and P-9, samples taken in points P-7 and P-7A, and samples taken in P-10, P-11 and P-12). The graph shows that samples of a same sampling point are closely grouped and there are not aberrant patterns (or outliers). Samples collected in P-7 and P-7A (upstream of Los Rueldos mine) show a similar composition which means that they are not influenced by the mine, so they are considered as natural (non anthropogenically affected) waters. On the contrary, samples taken in P-8 and P-9 (mine drainage collected at the entrance and inside the mine gallery, respectively) form a group in the left area

of the graph. These samples are taken as stagnant water and characterised by a low pH (about 2.5), high conductivity, salinity and turbidity values, high redox potential and dissolved oxygen and, as a consequence, high Al, As, Fe, Mn and Zn contents. Both categories (P-8 and P-9) have a similar behaviour due to their similar



**Fig. 2.** Linear discriminant analysis of physicochemical data corresponding to samples from Los Rueldos mine site.



**Table 5**  
Average results of different physicochemical parameters in sampling points in the surroundings of mine sites.

Sampling point	La Soterraña			El Terronal			Los Ruedos						
	P-1 (upstream)	P-2 (downstream)	P-3 (downstream)	P-4A (downstream)	P-5 (upstream)	P-6 (downstream)	P-7A (upstream)	P-7 (upstream)	P-11 (upstream)	P-8 (downstream)	P-9 (downstream)	P-10 (downstream)	P-12 (downstream)
Flow (l s <sup>-1</sup> )	0.05 ± 0.03	0.013 ± 0.007	0.09 ± 0.10	0.32 ± 0.25	53 ± 45	53 ± 42	0.02 ± 0.03	0.02 ± 0.01	308 ± 239	<0.01	<0.01	2.5 ± 1.6	373 ± 148
S. Conductance (μS cm <sup>-1</sup> )	402 ± 52	811 ± 110	1236 ± 338	930 ± 470	942 ± 184	844 ± 150	196 ± 29	201 ± 138	1161 ± 305	5624 ± 257	5807 ± 727	1156 ± 85	1050 ± 103
Salinity (ppt)	0.20 ± 0.03	0.38 ± 0.06	0.63 ± 0.18	0.57 ± 0.07	0.45 ± 0.09	0.42 ± 0.07	0.10 ± 0.01	0.10 ± 0.08	0.57 ± 0.15	3.1 ± 0.2	3.1 ± 0.4	0.57 ± 0.05	0.52 ± 0.06
pH	7.0 ± 0.7	7.8 ± 0.4	7.6 ± 0.6	8.0 ± 0.2	8.3 ± 0.2	8.3 ± 0.4	6.0 ± 0.5	5.2 ± 1.0	8.2 ± 0.3	2.4 ± 0.1	2.5 ± 0.1	7.6 ± 0.6	8.6 ± 0.2
Turbidity (NTU)	13 ± 7	27 ± 38	57 ± 44	12 ± 6	18 ± 9	19 ± 10	66 ± 38	18 ± 20	154 ± 184	310 ± 215	160 ± 202	40 ± 17	22 ± 17
Temperature (°C)	16 ± 3	14 ± 3	13 ± 2	13 ± 1	15 ± 2	16 ± 2	13 ± 2	12 ± 1	19 ± 2	15 ± 3	15 ± 5	14 ± 1	17 ± 2
Al (mg l <sup>-1</sup> )	0.06 ± 0.01 <sup>a</sup>	0.07 ± 0.01	0.17 ± 0.06	0.10 ± 0.02	0.06 ± 0.01 <sup>a</sup>	0.08 ± 0.05 <sup>a</sup>	0.06 ± 0.02 <sup>a</sup>	0.33 ± 0.19 <sup>a</sup>	0.09 ± 1.5 <sup>a</sup>	158 ± 12	160 ± 17	1.2 ± 0.3	0.11 ± 0.04
As (mg l <sup>-1</sup> )	0.05 ± 0.03 <sup>a</sup>	23 ± 9	31 ± 15	49 ± 5	0.04 ± 0.02	4.6 ± 1.1	0.05 ± 0.02 <sup>a</sup>	0.05 ± 0.02 <sup>a</sup>	0.04 ± 0.02 <sup>a</sup>	8.3 ± 1.6	8.3 ± 1.8	0.45 ± 0.08	0.06 ± 0.03 <sup>a</sup>
Ca (mg l <sup>-1</sup> )	62 ± 5	142 ± 20	209 ± 77	228 ± 27	123 ± 22	111 ± 13	27 ± 5.6	22 ± 22	147 ± 25	123 ± 17	122 ± 17	124 ± 14	129 ± 4
Fe (mg l <sup>-1</sup> )	0.09 ± 0.11 <sup>a</sup>	0.99 ± 2.08 <sup>a</sup>	0.10 ± 0.07 <sup>a</sup>	0.05 ± 0.02 <sup>a</sup>	0.05 ± 0.01 <sup>a</sup>	0.06 ± 0.01	0.11 ± 0.03	0.05 ± 0.04 <sup>a</sup>	0.56 ± 0.56	765 ± 58	767 ± 101	5.5 ± 1.0	0.20 ± 0.13 <sup>a</sup>
K (mg l <sup>-1</sup> )	0.52 ± 0.10	17 ± 22	9.4 ± 4.8	11 ± 1	6.9 ± 1.4	6.2 ± 1.1	0.47 ± 0.01	0.99 ± 0.03	6.3 ± 2.9	2.5 ± 0.5	2.9 ± 0.9	4.9 ± 0.6	4.7 ± 0.5
Mg (mg l <sup>-1</sup> )	16 ± 1	24 ± 5	49 ± 21	41 ± 6	79 ± 17	67 ± 14	7.7 ± 1.6	6.8 ± 4.8	66 ± 8	65 ± 7	66 ± 6	73 ± 7	62 ± 5
Na (mg l <sup>-1</sup> )	<5	26 ± 6	16 ± 4	19 ± 3	14 ± 4	12 ± 3	5.1 ± 0.1	5.0 ± 0.2	83 ± 81	5.5 ± 1.4	5.0 ± 0.1	81 ± 12	58 ± 19
Cl <sup>-</sup> (mg l <sup>-1</sup> )	7.3 ± 0.5	12 ± 6	17 ± 9	16 ± 8	14 ± 2	13 ± 1	12 ± 1	12 ± 1	12 ± 1	10 ± 4	9.1 ± 1.2	14 ± 1	12 ± 1
CO <sub>3</sub> <sup>2-</sup> (mg l <sup>-1</sup> )	19 ± 5	15 ± 4	18 ± 5	15 ± 5	20 ± 7	18 ± 4	16 ± 1	15 ± 1	21 ± 8	15 ± 1	15 ± 1	19 ± 5	23 ± 8
HCO <sub>3</sub> <sup>-</sup> (mg l <sup>-1</sup> )	225 ± 47	15 ± 20	128 ± 2	231 ± 8	277 ± 114	238 ± 73	19 ± 4	15 ± 6	289 ± 35	15 ± 1	15 ± 2	301 ± 77	263 ± 115
NO <sub>3</sub> <sup>-</sup> (mg l <sup>-1</sup> )	0.54 ± 0.28	180 ± 40	0.28 ± 0.07	1.6 ± 0.2	1.3 ± 1.0	1.4 ± 1.4	0.40 ± 0.10	0.26 ± 0.09	7.6 ± 4.8	0.10 ± 0.06	0.10 ± 0.08	2.8 ± 0.4	3.7 ± 0.9
SO <sub>4</sub> <sup>2-</sup> (mg l <sup>-1</sup> )	40 ± 1	283 ± 250	58 ± 80	585 ± 420	321 ± 141	299 ± 131	46 ± 10	48 ± 54	316 ± 16	8.4 ± 5.1	9.1 ± 4.0	395 ± 32	325 ± 152

<sup>a</sup> One or more values are below detection limit.

major ions. Cl<sup>-</sup> and Na<sup>+</sup> are low in all cases. Ca<sup>2+</sup>, Mg<sup>2+</sup> and SO<sub>4</sub><sup>2-</sup> are higher downstream the mine sites. In particular, water sampled downstream of La Soterraña (P-4A) contains the highest calcium and sulphate contents, due to the presence of limestone bars in the first case, and a large amount of mine wastes exposed to oxidation, in the second one.

It can be noted that water samples collected in point P-11 (Los Ruedos) are really different when compared to those collected in sampling points P-7 and P-7A. Point P-11 is only comparable to point P-12 (both belonging to San Juan River, before and after the contribution of the Morgao stream). Water samples collected in points P-8 and P-9 have high pollution levels, whereas samples taken in P-10 and P-12 are considered cleaner waters. At Los Ruedos mine site, the water environment is mainly affected by an important decrease of pH and, consequently, an increase of dissolution phenomena of ecotoxic elements (including As, Fe, etc.), present in wastes, soils and sediments. Nevertheless, the impact is limited to the site and only affects the closest area to the mine drainage occurrence, which experiments a dilution when reaches Morgao stream, and moreover when reaching San Juan River, where the pollution is not detected.

Another Supervised Pattern Recognition study was applied to the physicochemical results at the three mine sites classified by their sampling points (Fig. 4). In this study, Discriminant Analysis was applied to 83 samples, considering the following parameters as variables: water flow, specific conductance, salinity, pH, redox potential, dissolved oxygen, turbidity, temperature, Al, As, B, Ba, Be, Bi, Ca, Cd, Co, Cr, Cu, Fe, Hg, K, Mg, Mn, Mo, Na, Ni, Pb, Se, Sr, Ti, V and Zn. Samples were previously classified in six groups: those taken upstream and downstream of each mine site. In the figure, arrows represent the alteration of natural waters in relation to abandoned mine works and spoil heaps. This study reveals significant differences between samples taken upstream and downstream of La Soterraña mine site, mainly as a consequence of their enrichment in As, leached from the mineralised area and spoil heaps. On the other hand, samples from Los Ruedos mine site show a remarkable decrease of pH from 8.2 (P-11) to 2.4 (P-8), together with an increase of the level of Al, Fe and their associated elements. In this case, an enrichment in As was also noticed, but to a lower extent. As it has been mentioned, at La Peña-El Terronal site, only minor differences between waters collected upstream and downstream were detected, except for As concentration, that increases from 0.04 (P-11) to 8.3 mg l<sup>-1</sup> (P-8 and P-9). This statistical study helps to visualize the environmental impact of each mine, to associate the pollution with their source, and also to compare the different situations of each mine. All these studies compile a suitable methodology for the treatment of a large number of data coming from different analytical techniques helped by several statistical tools. This methodology could be analogously applied to different topics in chemical and geological fields.

### 3.6. Influence of Hg mines in the arsenic concentration in Caudal River

Arsenic concentrations in samples taken in Caudal River (sampling points P-13 to P-17) showed values below the detection limit (0.03 mg l<sup>-1</sup>), except for sampling point P-14, located downstream of La Soterraña mine, which reached a concentration of 0.09 mg l<sup>-1</sup>, below the Spanish standard.

In order to compare the impact of the three sites on their surrounding surface waters, the mass loads that they carry have been estimated. Mass loadings of As have been calculated considering the flow and the concentrations both upstream and downstream the mines. These contents were always <0.10 mg l<sup>-1</sup> upstream of the three sites, whereas average concentrations of 49 (P-4A), 4.6 (P-6) and 0.4 mg l<sup>-1</sup> (P-10) were found downstream of La Soterraña



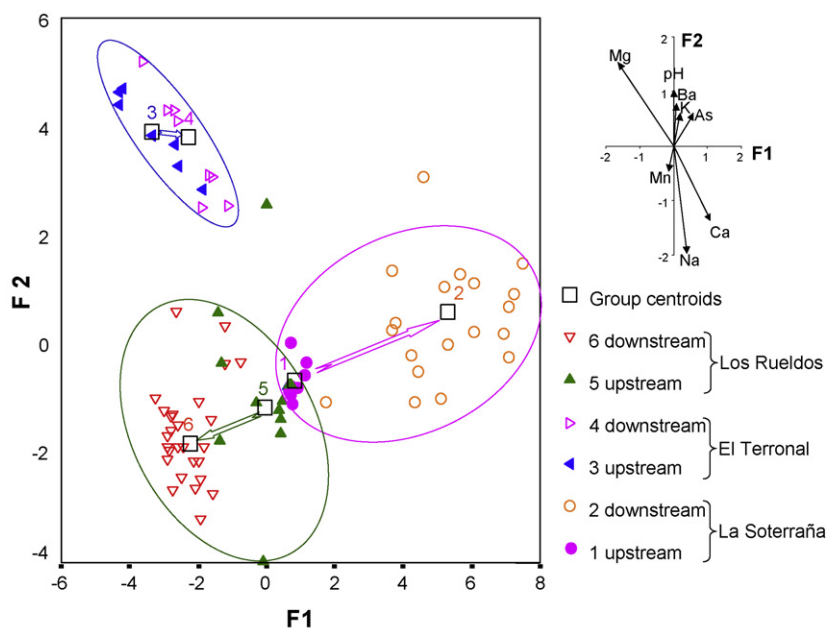


Fig. 4. Linear discriminant analysis of physicochemical data from La Peña-El Terronal, Los Rueldos and La Soterraña mine sites.

(La Soterraña Stream), El Terronal (San Tirso River) and Los Rueldos (Morgao Stream), respectively. Average flows of the watercourses downstream the sites were 0.32, 53 and  $2.51\text{s}^{-1}$ , respectively. Therefore, the calculated As loads that these streams carry are 40, 600 and  $1.3\text{ kg month}^{-1}$ , respectively, as an average over the monitoring period. This constitutes a constant input to Caudal River catchment, even when As is undetectable in its water, due to its high flow, although presumably part of this As is retained in the bed sediments. As the studied drainage basins of La Soterraña, La Peña-El Terronal and Los Rueldos sites only account for 0.25%, 1.8% and 0.16% of the total Caudal River catchment, respectively, it is not surprising that their As input is undetectable in Caudal River waters. It should be noted that the main As input comes from El Terronal site.

Dams used for drinking water supply in Caudal River are located upstream of the mining works. However, there are catchment points that collect water from the alluvium aquifer of Nalón River, downstream of the mining district (Fig. 1), that are used for drinking purposes. Groundwater sampled in wells near the mine sites, used for irrigation and as drinking supply for animals, show As contents ranging from  $1.2$  to  $15\text{ }\mu\text{g l}^{-1}$  [30].

Although it is out of the scope of the present study, the authors believe that some remediation actions should be undertaken in the studied sites. These actions are nonetheless complicated to take on and they depend on the characteristics of each site. Paradoxically, the site with the current highest input to the Caudal River catchment (La Peña-El Terronal), is the only one in which a remediation plan consisting of the encapsulation of the main spoil heap, has been carried out. This could be explained by a number of reasons, including: (i) this site housed the most significant Hg mine and metallurgical plant in the region, (ii) San Tirso River runs right through the site, (iii) most of the wastes were isolated in an in situ security landfill in 2002, but no maintenance of the deposit was taken on since, (iv) there are wastes in nearby areas that have not been isolated, (iv) the spoils of the mining and metallurgical installations still remain on site, (v) the existence of very polluted soils in the surroundings has been proved in previous studies, so rainfall infiltrating these soils can leach As that finally ends in the river, (vi) the As retained in the river sediments during the past 40 years can be redissolved to the water. During the isolation in

2002, the As concentration in the river increased due to the mobilisation of the wastes to decrease again some months later to values similar to those found before the remediation action. The impact of the other two sites is less significant and since the watercourses draining them have much less flow, some classical preventive measurements for mine water, such as passive systems with iron oxides where the As would be trapped, as well as waste disposal, could be undertaken.

#### 4. Conclusions

The monitoring accomplished in surface watercourses flowing through the area of the abandoned Hg mines in Caudal River catchment (Asturias, Spain) makes evident the presence of anthropogenic hydrochemical anomalies, attributed to the circulation of mine water drainage and spoil heap leachates. Waste materials from mining and metallurgical operations spread in the sites are considered important sources of pollution as potential generators of acidic leachates that can mobilize As and heavy metals from the mined areas to surface watercourses. Mine drainage and spoil heap leachates show occasionally very acidic conditions, e.g. in Los Rueldos mine site, although these conditions are easily neutralised when polluted waters reach streams or rivers with enough water flow to dilute pollutants concentration.

Some of these hydrochemical anomalies represent a significant environmental impact, reflected mainly by high concentrations of total As. Although in some particular areas the local As hydrochemical background is naturally high by weathering of mineralised rocks, the enrichment in this element is clearly exacerbated by the presence of abandoned mines and spoil heaps, where the increase in secondary porosity favours the capability of sulphide minerals in ore and/or mineralised rocks to be unstabilised. Weathering of As-bearing minerals in mines and spoil heaps results in the transport of dissolved As to superficial watercourses.

The three abandoned mine sites included in the study show an environmental impact in accordance with the source of pollution and the hydrological, geological and chemical characteristics of the area. At La Soterraña site, total As concentration increases from average values lower than  $0.08\text{ mg l}^{-1}$ , upstream of the mine works, to values up to  $57\text{ mg l}^{-1}$  at the bottom of the spoil heap. Although

As concentrations in San Tirso River, downstream of La Peña-El Terronal site, are lower than those found in a brook downstream of La Soterraña, the mass loading is higher in the first case, where the water flow is 160 times higher. At Los Ruedos mine site, heavy metals and As are dissolved in acidic mine drainages and incorporated to Morgao stream. These values are highly dependent on the water flow and thus on the seasonal variations. These As-enriched waters are eventually discharged to watercourses that are incorporated to important rivers at regional level. As an average over the monitoring period, it has been calculated that Caudal River receives more than 600 kg month<sup>-1</sup> of As. However, since the drainage areas of the studied sites are almost negligible compared to the total Caudal River catchment, the As input is undetectable in its waters.

Mercury concentrations in surface waters both upstream and downstream of the mining sites were always below 0.5 µg l<sup>-1</sup>, in agreement with its reduced solubility. These results indicate that in spite of the past large mining activities and the weathering of mine wastes, local stream waters are not significantly polluted by Hg.

Remediation actions are difficult tasks to undertake in these sites, as a detailed and complete characterisation of the sources in each case is necessary. Disposal or isolation of wastes and passive treatments of mine water are some of the common measurements to define, but after a detailed cost-benefit analysis.

In order to achieve the objective of water quality demanded on the E.U. Water Framework Directive, it is necessary a progressive reduction of pollution from anthropogenic sources, including abandoned mines and spoil heaps among the anthropogenic sources. Then, for an effective water pollution control in abandoned mine sites, adequate and dense monitoring networks and water quality control programs are necessary. This network must be designed at the scale of the local subcatchment of the mine site, where the pollution source is located, and before the dilution of mine waters into superficial watercourses takes place. The preliminary monitoring studies presented in this paper can serve as a starting point for the design of an effective monitoring network in abandoned mine sites.

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