

## Arsenic contamination and speciation in surrounding waters of three old cinnabar mines

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The impact of arsenic pollution in waters from the surroundings of three abandoned Hg mines in Northern Spain, as well as reaching the Caudal River, was evaluated. For assessing the factors controlling arsenic release, an extensive study based on the physicochemical characterization and multivariate statistical analysis of waters upstream and downstream each mine site was performed. Waters downstream of the La Soterraña mine present the highest arsenic concentrations, up to 38.8 mg L<sup>-1</sup>, coming mainly from the solubilisation of calcium, magnesium and strontium arsenates at a pH close to neutral. Although arsenic concentrations downstream of La Peña are markedly lower, these values remain too high, indicating that the encapsulation carried out in this spoil heap is insufficient. In addition, the high water flow in this point involves an extremely high input of arsenic to the surroundings (0.3 g s<sup>-1</sup>). Waters close to tailings from Los Ruedos suffer from acid mine drainage, provoking an important solubilisation of arsenic and heavy metals, a situation which is rapidly softened with distance. The study of arsenic speciation reveals the omnipresence of As(v) in waters from the three mines, whereas in La Peña low amounts of As(III) were also detected. Different preservation methods for As speciation were compared, such as the addition of HCl, EDTA and the storage of samples without any additive, and no alteration of samples in any case up to nine months after the collection was observed. A study of seasonal variations of As and the main parameters affecting its concentration and speciation was completed throughout a year, showing no remarkable dependency with rainfall for any studied variable.

### 1. Introduction

Arsenic (As) is an element naturally present in the environment. Long before man's activities had any effect on the balance of nature, As was distributed ubiquitously throughout earth's crust, soil, sediments, water, air and living organisms.<sup>1</sup> The major

occurrence of As is due to the mineralogical and geological characteristics of the areas and most environmental As problems are the result of mobilization under natural conditions. However, anthropogenic activities such as mining works, ore processing, combustion of fossil fuels, the use of arsenical pesticides, herbicides and other uses of As have involved an important additional impact.<sup>2,3</sup>

As is recognized as one of the most serious inorganic contaminants in drinking water on a worldwide basis. Its toxicity depends on the chemical species that it presents.<sup>4</sup> It has been well established that organic As compounds are less toxic than the inorganic forms, and among them, As(III) is considered 10 times

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#### Environmental impact

Several studies have tackled the problem of arsenic contamination in soils, sediments, surface waters and plants of three different old cinnabar mine areas with spoil heaps and tailings, and extremely high arsenic concentrations have been found in these matrices. However, no studies have been performed for identifying the different arsenic species occurring in surrounding waters of these mining sites. Since arsenic toxicity depends on the chemical form in which it occurs, knowing arsenic speciation is essential. Hence, a study of arsenic speciation in waters from the surroundings of these mining areas has been carried out. Moreover, for completing the evaluation of the impact of mining in this environment, an assessment of factors controlling arsenic release in every mine was performed, as well as a study of arsenic pollution reaching the Caudal River, one of the most important rivers in the region.

more toxic than As(v), due to its higher mobility.<sup>5–8</sup> In natural waters, As is mostly found in inorganic forms, although certain amounts of monomethylarsonic acid (MMA) and dimethylarsonic acid (DMA) can be present as a result of microbial activity.<sup>9</sup> Inorganic As species dominate in sulphide oxidation environments.<sup>10</sup> Water is the main route of exposure of humans to As, so regulation of maximum allowed values is needed. Whereas the WHO guideline<sup>11</sup> value for As in drinking water is 10  $\mu\text{g L}^{-1}$ , the Spanish legislation limits total As content to 500  $\mu\text{g L}^{-1}$  for mining and industrial effluents and 10  $\mu\text{g L}^{-1}$  for drinking water.<sup>†</sup>

As mobility is directly related to As speciation, and it is highly dependent on the physicochemical conditions of the site. It has been widely studied that redox potential (Eh) and pH are the most important factors controlling As speciation.<sup>9,12</sup> The hazardous potential of As relies on its relative mobility over a wide range of redox conditions, which make As different and unique among the metalloids and oxyanion forming elements. In general, the occurrence of the different forms of As depends on the aerobic and anaerobic conditions: arsenite [As(III)] is normally the predominant species in groundwater under anaerobic conditions, whereas arsenate [As(V)] is mainly present in surface waters under aerobic conditions. It is well known that arsenate is usually adsorbed onto mineral phases to a greater extent than arsenite, and this adsorption highly depends on pH. Roussel *et al.*<sup>13</sup> and Daus *et al.*<sup>14</sup> postulated that As speciation is controlled by the pH-affected speciation and solubility of iron. In acid mine drainage (AMD) with pH lower than 3.5, the Eh–pH relation shows that Fe(II) is strongly susceptible to oxidation to Fe(III), which then precipitates as oxyhydroxide or oxyhydroxysulphate. In oxidizing environments, the main attenuation mechanism of As migration is its adsorption onto Fe(III) precipitates; however, As(V) is less soluble and it is adsorbed more efficiently than As(III) under acidic conditions.<sup>15</sup> Hence in acid mine waters, dissolved As is quickly removed as the iron is oxidized and precipitated and the As is scavenged through adsorption.<sup>9</sup>

Abandoned mines have left behind toxic pits and acid mine drainage. Naturally occurring minerals were disturbed, crushed during ore treatment and left in massive tailing piles. As a consequence, potentially toxic materials containing As and heavy metals can be found in dangerously high levels throughout historic mining regions. Natural weathering can lead the mobilization of As into the environment and solubilisation into the surrounding waters. As often occurs as As-bearing sulphides, predominantly pyrite. During periods of excess oxygenation pyrite is dissolved, allowing As to enter the aquifers.<sup>16,17</sup> Oxidation of pyrite ore is a major cause of AMD.<sup>16,18,19</sup> The production of Fe(III) and hydrogen ions can catalytically dissolve secondary minerals, thereby increasing the metal load to the drainage.<sup>19</sup> In addition, the generally low pH (~1–4) of AMD systems also contribute to the solubilisation of heavy metals.<sup>20</sup> Therefore, although at a world scale typical concentrations for As in non-polluted stream waters have been estimated at 4  $\mu\text{g L}^{-1}$ ,<sup>21</sup> in the case of waters affected by mining activities these values can

increase greatly. As concentrations up to 556  $\mu\text{g L}^{-1}$  were found in streams adjacent to tailings deposits in British Columbia.<sup>22</sup> Williams *et al.*<sup>23</sup> and Smedley *et al.*<sup>24</sup> noted around 200–300  $\mu\text{g L}^{-1}$  of As in surface waters affected by Sn in the Nakhon Si Thammarat Province<sup>23</sup> and because of Au mining activities in the area of Ghana.<sup>24</sup> In waters affected by AMD, extreme As concentrations have been reported. Plumlee *et al.*<sup>25</sup> found up to 340 000  $\mu\text{g L}^{-1}$  in Various, USA.<sup>25</sup> Sarmiento *et al.*<sup>26</sup> reported As concentrations of 1975  $\mu\text{g L}^{-1}$  and 441  $\mu\text{g L}^{-1}$  for the Tinto river and the Odiel river, respectively, in Spain.<sup>26</sup> Higher As concentrations, up to 850 000  $\mu\text{g L}^{-1}$  were found by Nordstrom and Alpers<sup>27</sup> in surrounding waters of the Richmond Mine of the Iron Mountain copper deposit.<sup>27</sup>

Asturias in northwestern Spain is a historical mercury mining district, where mining activity was developed in different periods from the Roman period (first and second centuries) until the 1970s, when the mining activity was definitively abandoned. Deposits are located in Precambrian to Carboniferous formations and although the most frequent hosted rocks are limestones, some of the richest deposits are located in conglomeratic horizons or siliceous breccias in sandstones. Ore deposits appear as irregular veins, granular aggregates or impregnations in rocks, commonly associated to fractured rocks with high porosity. The paragenesis of cinnabar ore includes the presence of arsenic sulphide minerals, mainly arsenian pyrite, realgar and orpiment. From a hydrogeological point of view, the substrate of the mine areas is mainly constituted by alternation of limestone, sandstone and shale. Whereas the shale can be considered impermeable, limestone and sandstone are permeable formations and constitute small aquifers. Mines have been exploited by underground mining, usually by the chamber and pillars method, and at the La Peña-El Terronal site the underground mine works reach more than 500 meters depth. Smelting operations were accomplished at the most important mine sites for decades, with the ore processed on site in large rotary furnaces. More than 20 abandoned mercury mine sites are scattered throughout the region, but the most important ones are located in central Asturias, in the Caudal River basin. Because of the great decline of Hg prices in the 1970s, most mines were closed between 1973 and 1974, but sometimes any preventive measure was carried out after the closures. Thus mine facilities and metallurgical installations remain abandoned, as well as their corresponding spoil heaps. It poses an evident risk, since natural weathering or variations in physicochemical parameters at the disposal site can alter the stability of waste materials, including the As-rich ores, and lead to the release of Hg, As and associated heavy metals into underlying aquifers and superficial waters, which eventually discharge to streams and rivers. Studies of the environmental impact of Asturian abandoned Hg mines are abundant<sup>28–34</sup> and prove the existence of pollution in soils, surface waters, sediments and even in plants of the surroundings.<sup>35,36</sup> However, no studies exist about the As species occurring in surrounding waters of these mining areas.

Hence, the objectives of this work are: i) evaluation of the impact of As pollution and assessment of factors controlling As release based on physicochemical characterisation and statistical studies of waters upstream and downstream of each mine site; ii) study of the As speciation in waters from three abandoned Hg mining areas; iii) study of alteration of As species with different

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preservation procedures just after the sampling collection and over time; iv) investigation of seasonal variations in As contents and other associated parameters.

## 2. Experimental

### 2.1 Studied area description and sampling points

The studied areas correspond to three Hg mine sites of Asturias: La Soterraña, located in the vicinity of the village of Pola de Lena, and La Peña-El Terronal and Los Rueldos, located close to Mieres. As it is shown in Fig. 1, runoff from spoil heaps of the three mines discharge in the Caudal River catchment. The Caudal River is a tributary of the Nalón River, the main river of the region.

The presence of As is very frequent in the form of orpiment, realgar and As-rich pyrite.<sup>37,38</sup> 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. From an environmental point of view, the presence of As minerals in the ore deposit paragenesis is especially significant, as high As concentrations have been found in pyrites and iron oxides.<sup>31</sup>

In contrast to other regions of Spain, Asturias has a humid and temperate climate characterized 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 Thorntwaite 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>.<sup>32</sup> These climatic conditions contribute to the spread of the contaminants throughout the area.<sup>39</sup>

Sampling points are showed in Fig. 1 and described in Table 1. When possible, surface water samples were collected upstream and downstream the spoil heap of each mine.

La Soterraña mine is located in the northern slope of a deep valley crossed by a small stream, sometimes dry, but whose flow at other times can reach up to 0.125 L s<sup>-1</sup>. This stream collects surface runoff, spoil heap leachates and effluents from a local industry devoted to the manufacture of ceramics, increasing its flow to an average value of 0.166 L s<sup>-1</sup> or 0.750 L s<sup>-1</sup> maximum. 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 m<sup>2</sup>. The substrate of the mineralized area is mainly composed of

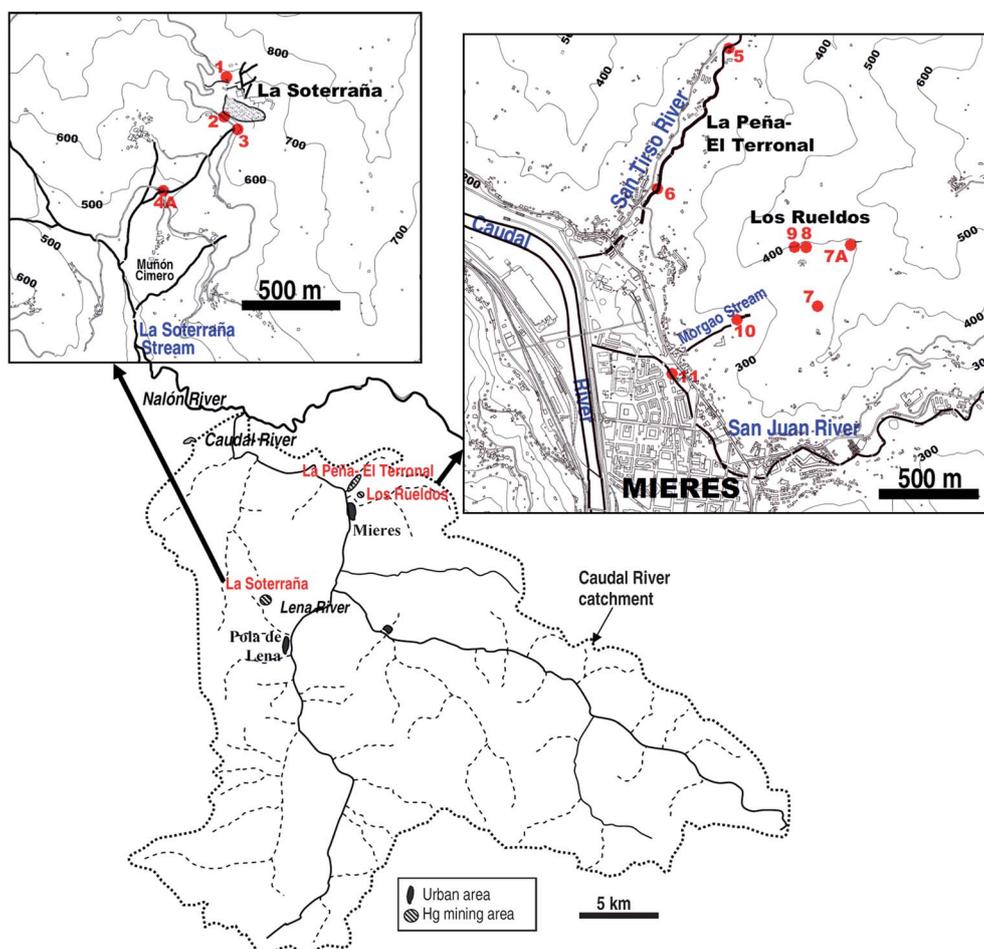


Fig. 1 Map with the three mines and sampling points.

**Table 1** Description of sampling points

Mine site	Sampling point	Description
La Soterraña	P1	Surface runoff (upstream of La Soterraña Mine)
	P2	Air-open channel (downstream of La Soterraña Mine, receiving spoil heap leachates)
	P3	Brook at the bottom of La Soterraña spoil heap
	P4A	Stream (downstream of La Soterraña mine site receiving spoil heap leachates)
La Peña- El Terronal	P5	San Tirso River (upstream of La Peña-El Terronal mine site)
	P6	San Tirso River (downstream of La Peña-El Terronal mine site)
Los Ruedos	P7A	Spring upstream of Los Ruedos mine site
	P7	Surface runoff upstream of Los Ruedos mine site
	P8	Los Ruedos mine drainage (water pond at the entrance of the gallery)
	P9	Los Ruedos mine drainage (water inside the gallery)
	P10	Morgao stream (downstream of Los Ruedos mine site)
	P11	San Juan River (downstream of Los Ruedos mine site)

materials of the “Llanón–Tendeyón” unit, constituted by an alternation of limestones, sandstones and lutites (dominant), which can be considered impermeable except for some limestone and sandstone bars which constitute small aquifers.<sup>31</sup> Taking into account the climate data and considering an infiltration coefficient of 0.7 for the spoil heap, infiltrated rainwater with the possibility to come into contact with mine waste materials is about 11 781 m<sup>3</sup> year<sup>-1</sup>. This water transports pollutants in solution to groundwater and/or to the surface watercourses.<sup>32</sup>

La Peña-El Terronal mine is located in the valley of San Tirso River, a tributary of Caudal River, and whose flow ranged from 76 to 310 L s<sup>-1</sup> during the monitored period. The mineralization is included in the Westphalian stratigraphic level, which consists of a thick series of shales with intercalations of sandstones, conglomerates, limestones and coal beds usually less than 50 cm thick. The carboniferous sediments are overlain discordantly by Upper Stephanian–Lower Permian materials of the San Tirso formation, comprising calcareous conglomerates, clay lutites, and tuffaceous materials.<sup>40</sup> Contrary to the other two mines, where any restoration program was implemented after the closure of the mines, a remediation plan consisting of the encapsulation of the main spoil heap was carried out in this mine in 2002, when 300 000 tons of spoil heap waste (consisting of tailings and granulated materials of various sizes) were isolated in an on-site secure landfill.<sup>39</sup>

Los Ruedos mine is crossed by the Morgao stream, which is canalized underground, downstream of the mine site. Mine drainage and spoil heap leachates reach the Morgao stream when it reappears on surface. Upstream water flow levels are usually low and even absent during summer months. At the end of the canalization (P10), water flow ranges from 0.075 to 2.1 L s<sup>-1</sup>, whereas in P11 (San Tirso River), it remains very low.<sup>32</sup> From a hydrogeological point of view, the substrate of the catchment (alternance of sandstones, shales and some coal beds) can be considered as an impermeable substrate. In these conditions, the water does not evaporate nor flow superficially; instead it is infiltrated on the more permeable colluvial materials and weathered shales, giving rise to a number of small springs. In this case, downstream of the Hg mining works there is a spoil heap constituted by low-permeability wastes from coal washery, and they behave as a pseudokarstic aquifer with the capacity to store a great volume of water.<sup>34</sup>

## 2.2 Water characterization

Water samples were collected, filtered on-site and stored in plastic bottles. Some physicochemical parameters such as pH, specific conductance, dissolved oxygen, salinity, temperature, redox potential and turbidity were measured in the field by means of a portable multiparameter probe (Turo-graph 611). Water flow was measured when it was possible with a current meter (Global Water flow probe). Then, samples were refrigerated at 4 °C until analysis.

Total As contents, as well as concentrations of major and minor elements (Al, As, Ca, Cd, Co, Cr, Cu, Fe, Mg, Mn, Ni, Pb and Zn) were determined by inductively coupled plasma atomic emission spectrometry (ICP-AES) using a VARIAN 735-ES instrument with radial configuration following the EPA/200.7 method.<sup>41,42</sup> Quantification limits, calculated as ten times the standard deviation of a blank injected 10 times divided by the sensitivity (slope of the calibration curve), were 0.05 mg L<sup>-1</sup> for Al, Ca, Co, Cr, Cu, Mg, Pb, and Zn, and 0.03 mg L<sup>-1</sup> for As, Cd, Fe, Mn and Ni.

Na and K were determined by flame atomic emission spectrophotometry (FAES) using a Perkin Elmer 2280 following the EPA/273.1 and EPA/258.1 methods, respectively.<sup>43</sup> Detection limits were 0.1 mg L<sup>-1</sup> for both elements.

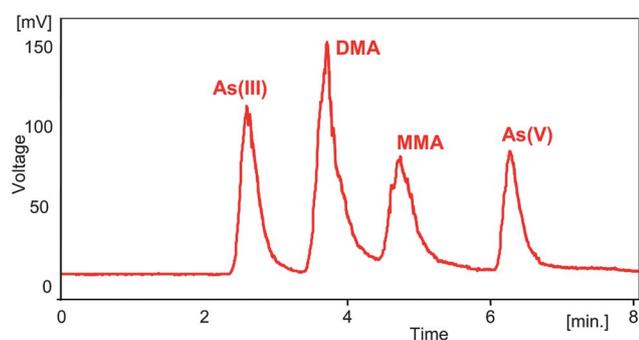
Cl<sup>-</sup>, NO<sub>2</sub><sup>-</sup>, NO<sub>3</sub><sup>-</sup> and SO<sub>4</sub><sup>-</sup> were analysed by means of ionic chromatography following the EPA/9056a method.<sup>44</sup> The used instrument was a Dionex Serie DX-500, equipped with a suppressor device (Dionex CSRS-ULTRA 4 mm). The column used in the separation of the anions was a Dionex IonPac AS14 (4 × 250 mm) and its corresponding guard column, Dionex IonPac AG14 (4 × 50 mm). The mobile phase consisted of two solutions: 3.5 M Na<sub>2</sub>CO<sub>3</sub> and 1 M NaHCO<sub>3</sub>. Detection limits were 0.510, 0.055, 0.501 and 0.514 mg L<sup>-1</sup> for Cl<sup>-</sup>, NO<sub>2</sub><sup>-</sup>, NO<sub>3</sub><sup>-</sup> and SO<sub>4</sub><sup>-</sup> respectively.

Alkalinity, expressed as carbonate and bicarbonate was analyzed by potentiometric titration with 0.02 M HCl by means of the automatic titroprocessor 796 of Metrohm following the EPA/310.1 method.<sup>43</sup> The detection limits for both of them are 12 mg L<sup>-1</sup>. Total organic carbon was determined as NPOC (Non Purgeable Organic Carbon) with an analyzer TOC (Shimadzu–VCHS) by means of oxidative combustion and determination with a non-dispersive infrared sensor (NDIR).

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 deionized water before use. All chemicals used were of analytical-reagent grade (Merck, Darmstadt, Germany). Working standard solutions for ICP-AES and FAES were prepared freshly from individual 1000 mg L<sup>-1</sup> stock standard solutions by sequential dilution with 0.5 M HNO<sub>3</sub>. Stock standard solutions of As species (1000 mg L<sup>-1</sup>, as As) were prepared from As trioxide (Panreac, Barcelona, Spain), sodium arsenate (Merck, Darmstadt, Germany), sodium monomethylarsinate (MMA) (Carlo Erba, Milan, Italy) and dimethylarsinic acid (DMA) (Sigma, St. Louis, MO) in distilled water. These solutions were stored in the dark at 4 °C and their stability frequently checked. As(III) standard solution was kept for 1 month to prevent eventual transformation into As(V) species. The others solutions can be considered stable for several months. Intermediate standard solutions (As = 10 mg L<sup>-1</sup>) were prepared daily and used directly for the preparation of appropriate working standard solutions which were tested every day in the quality control of the analytical procedure.

### 2.3 Arsenic speciation

As speciation studies were carried out by coupled high performance liquid chromatography–hydride generation–atomic fluorescence spectrometry (HPLC-HG-AFS). The HPLC system consisted of a Varian Prostar ternary solvent delivery module model 230 equipped with a Rheodyne injector model 7725 and a 200 µL loop for sample introduction. The instrument used in the combination of vapour generation and atomic fluorescence spectrometry was a PSA 10.055 Millennium Excalibur from PS Analytical equipped with an As hollow cathode lamp and a Perma pure drying membrane (Perma Pure Products, Farmingdale, NJ, USA) for drying the generated hydride. The chromatographic separation of As(III), DMA, MMA and As(V) was achieved in this order in 7 min using a Hamilton PRP-X100 anion-exchange column (250 × 4.1 mm id, 10 µm) (Fig. 2). Chromatographic conditions reported by Gómez-Ariza *et al.*<sup>45</sup> were chosen as starting point for the optimization of our chromatographic method. 10 mM and 100 mM phosphate solutions (eluent A and B), buffered at pH 6.2, were used as eluents. Both solutions were freshly prepared, degassed and filtered at 0.45 µm before analysis. The gradient programme was performed as



**Fig. 2** Chromatogram of the four As species (100 µg L<sup>-1</sup> of each species).

follows: from 0 to 2.0 min, 100% A; from 2.1 to 3.1 min, change to 100% B; from 3.1 to 6.0 min, 100% B; from 6.0 to 7.0 min, change to 100% A. The injected volume of sample (previously filtered at 0.22 µm) was 200 µL and the flow rate of the mobile phase was 1.0 mL min<sup>-1</sup>. The separated As species were subjected to hydride generation with HCl (12.5% v/v, 2 mL min<sup>-1</sup>) and NaBH<sub>4</sub> (1.4% w/v in 0.1 M NaOH, 2 mL min<sup>-1</sup>) in a PEEK mixing cross to generate hydrogen and volatile arsines. The gas–liquid mixture was delivered to a gas–liquid separator, and gas compounds were swept from the mixture with a flow of argon (200 mL min<sup>-1</sup>). Arsines entering the atomic fluorescence spectrometer were dried in a Perma-Pure mini-dryer using argon as drying gas at 100 mL min<sup>-1</sup>. Finally, arsines were atomized in a hydrogen flame aligned in the lightpath of a boosted As hollow cathode lamp and fluorescence emission was detected at 193.7 nm. Detection limits, calculated as three times the standard deviation of a blank injected ten times divided by the sensitivity, were 0.1 µg L<sup>-1</sup> for As(III) and DMA, and 0.2 µg L<sup>-1</sup> for MMA and As(V).

### 2.4 Preservation studies for arsenic speciation

Different preservation strategies were tested in order to check the possible alteration of the original speciation of samples with time.

All samples were firstly filtered at 0.45 µm *in situ*, and then three aliquots were stored in polypropylene bottles of 125 mL. The first aliquot was stored without any stabilization additive; the second one with a few drops of concentrated HCl, to about pH 2; and the third one with a 5% (v/v) of a 0.25 mol L<sup>-1</sup> EDTA solution. Finally, all samples were stored at 4 °C in the dark.

The study of As speciation was carried out as soon as it was possible after the sample collection in the field. Time stability of inorganic As species in samples was also checked by speciation studies in all aliquots every three months over one year.

## 3. Results and discussion

### 3.1 Total arsenic contents and associated parameters

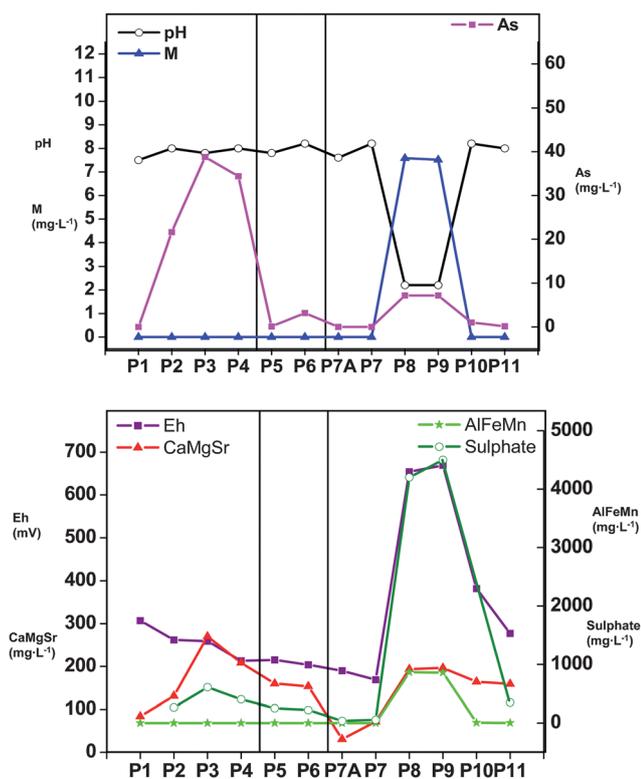
Water characterization parameters, as well as total contents of the studied elements for all samples are summarised in Table 2. Fig. 3 shows the parameters most influenced by the environmental impact of each mine, and stresses the differences among the three studied mine sites.

As concentrations in points situated upstream of La Soterraña mine were non detectable. However, the impact of the mine is evidenced by the extremely high levels of As found in waters downstream of the mine operations (up to 38.8 mg L<sup>-1</sup> in P3). This clearly indicates that water flowing nearby the spoil heap can mobilize a great amount of As. Data show that these points are not affected by AMD (acid mine drainage), since pH values are weakly alkaline (7.5–8.0) with slightly oxidants values of redox potential (213–307 mV). Consequently, dissolution of heavy metals does not occur and conductance (1366 µS cm<sup>-1</sup> as the maximum value after the mine) and salinity (0.68 ppt as the maximum after the mine) were not remarkable. The appreciable Ca, Mg and Sr concentrations observed in these samples, especially in points located after the mine (up to 255, 41.7 and 3.09 mg L<sup>-1</sup> respectively in P3) suggest the solubilisation of Ca,

**Table 2** Water characterization for all tested points in each mine. Blanks were analysed together with the samples, and values always remained lower than detection limits for all the considered elements. For each analysed sample, the final concentration results from the average of three measurements. Carbonate contents do not appear in the table because they were always below the detection limit. n.d. means not detectable, since concentrations were below the detection limit

Sampling point	La Soterraña					El Terronal					Los Ruedos				
	P1 (upstream)	P2 (downstream)	P3 (downstream)	P4A (downstream)	P5 (upstream)	P6 (downstream)	P7A (upstream)	P7 (upstream)	P8 (downstream)	P9 (downstream)	P10 (downstream)	P11 (downstream)			
Flow (L s <sup>-1</sup> )	0.077	0.129	0.173	0.196	99	110	0	0.021	0	0	0.643	0.033			
Specific conductance (μS cm <sup>-1</sup> )	462	762	1366	1133	1105	886	211	406	5248	5523	1228	1107			
Salinity (ppt)	0.21	0.36	0.68	0.54	0.54	0.42	0.98	0.89	39.3	29.7	0.57	0.53			
Turbidity (NTU)	34.5	75.9	43.4	57.0	38.4	33.4	47.0	39.4	119	22.8	49.8	51.3			
Temperature (°C)	13.7	11.1	12.2	11.4	12.5	13.9	14.5	18.5	14.0	12.4	13.7	13.2			
pH	7.5	8.0	7.8	8.0	7.8	8.2	7.6	8.2	2.2	2.2	8.2	8.0			
Eh (mV)	307	262	259	213	215	204	190	169	654	669	382	277			
Dissolved oxygen (mg L <sup>-1</sup> )	6.55	9.63	7.25	6.84	8.24	6.82	7.87	6.95	8.36	7.12	11.7	7.37			
TOC (mg C L <sup>-1</sup> )	<sup>a</sup>	7.40	4.30	4.07	20.3	17.9	6.85	16.7	5.60	4.73	<sup>a</sup>	2.53			
Cl <sup>-</sup> (mg L <sup>-1</sup> )	<sup>a</sup>	13.0	18.4	16.8	13.6	13.2	10.2	10.1	6.9	7.0	<sup>a</sup>	14.6			
HCO <sub>3</sub> <sup>-</sup> (mg L <sup>-1</sup> )	<sup>a</sup>	198	171	189	252	224	58	166	n.d.	n.d.	<sup>a</sup>	278			
NO <sub>3</sub> <sup>-</sup> (mg L <sup>-1</sup> )	<sup>a</sup>	n.d.	0.18	n.d.	0.19	0.34	n.d.	n.d.	n.d.	n.d.	<sup>a</sup>	0.14			
NO <sub>4</sub> <sup>-</sup> (mg L <sup>-1</sup> )	<sup>a</sup>	1.40	0.86	2.62	2.80	3.12	0.82	1.10	0.70	0.23	<sup>a</sup>	3.20			
SO <sub>4</sub> <sup>2-</sup> (mg L <sup>-1</sup> )	<sup>a</sup>	267	613	405	255	222	37	55	4200	4500	<sup>a</sup>	351			
Al (mg L <sup>-1</sup> )	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.18	150	145	0.87	0.50			
As (mg L <sup>-1</sup> )	n.d.	21.6	38.8	34.4	0.12	3.16	n.d.	n.d.	7.2	7.2	1.00	0.13			
Ca (mg L <sup>-1</sup> )	69.0	112	225	177	103	101	25.3	56.7	134	136	111	105			
Cd (mg L <sup>-1</sup> )	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.01	0.01	n.d.	n.d.			
Co (mg L <sup>-1</sup> )	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.15	0.12	n.d.	n.d.			
Cr (mg L <sup>-1</sup> )	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.12	0.12	n.d.	n.d.			
Cu (mg L <sup>-1</sup> )	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.35	0.35	n.d.	n.d.			
Fe (mg L <sup>-1</sup> )	0.05	0.11	0.05	0.04	0.05	0.20	0.49	0.96	716	716	4.0	2.1			
K (mg L <sup>-1</sup> )	2.44	4.00	12.2	11.1	6.03	5.89	1.05	2.86	2.66	2.95	5.01	4.60			
Mg (mg L <sup>-1</sup> )	14.8	18.6	41.7	29.5	56.6	52.3	5.53	14.8	59.6	60.3	52.6	53.6			
Mn (mg L <sup>-1</sup> )	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	1.68	1.66	0.26	0.07			
Na (mg L <sup>-1</sup> )	4.54	12.6	15.8	16.2	10.7	14.9	5.43	8.00	7.39	4.54	50.7	54.3			
Ni (mg L <sup>-1</sup> )	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.70	0.67	n.d.	n.d.			
Pb (mg L <sup>-1</sup> )	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.034	0.033	n.d.	n.d.			
Sr (mg L <sup>-1</sup> )	0.17	0.66	0.66	1.83	0.34	0.37	0.08	0.28	0.27	0.28	0.58	0.62			
Zn (mg L <sup>-1</sup> )	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	6.22	6.21	n.d.	n.d.			

<sup>a</sup> There are no values for these variables in these samples.



**Fig. 3** Differences in the main parameters affecting As release in the sampling points. “M” is the sum of Cd, Co, Cr, Cu, Ni, Pb and Zn concentrations (in  $\text{mg L}^{-1}$ ). “AlFeMn” is the sum of dissolved Al, Fe and Mn concentrations (in  $\text{mg L}^{-1}$ ). “CaMgSr” is the sum of Ca, Mg and Sr concentrations (in  $\text{mg L}^{-1}$ ).

Mg and Sr arsenates, since it has been reported that at a pH between 6.90 and 8.35, Ca, Mg and Sr arsenates are moderately soluble.<sup>46,47</sup> In addition, the higher sulphate contents downstream compared with those found in P1 indicate that As may be also partially leached because of the oxidation of sulphur minerals. Particularly worrying it is the fact that As concentration does not decrease with the distance to the spoil heap, since P3 and P4A have similar As contents. These As-enriched waters are eventually discharged to streams that are incorporated into important rivers at regional level. As concentrations in these waters (up to  $34.4 \text{ mg L}^{-1}$  in P4A, corresponding to a stream) are comparable to those extreme values reported by Plumlee *et al.*<sup>25</sup> in waters affected by AMD in Various, USA and are clearly higher than those found in other Spanish mining areas affected by AMD. Sarmiento *et al.*<sup>26</sup> reported As concentrations of  $1.97 \text{ mg L}^{-1}$  and  $0.44 \text{ mg L}^{-1}$  for the Tinto and Odiel rivers, respectively. Higher As concentrations up to  $850 \text{ mg L}^{-1}$  were found by Nordstrom *et al.*<sup>27</sup> in surrounding waters of the Richmond Mine of the Iron Mountain copper deposit.

Waters upstream and downstream of La Peña-El Terronal mine seem not to be so different, except for the higher As concentration in P6. The point collected upstream of the tailings (P5) presented the highest As concentration among all points collected upstream of the studied mines ( $0.12 \text{ mg L}^{-1}$ ). That means that in this site the presence of As in surrounding waters may be in part due to the mineralogy of the area. In contrast, P6 was the sample presenting the lowest As content of the points

collected immediately after all mines ( $3.16 \text{ mg L}^{-1}$ ). However, this concentration still remains very high, which means that although the preventive measure carried out in this mine results in a marked decrease of As release, it is not enough. In addition, the water flow in this point ( $110 \text{ L s}^{-1}$  as mean value) is significantly higher than the rest of the points. In consequence, the input of As to the surrounding waters is extremely high and very striking. No AMD occurred in this mine, as indicates pH (7.80–8.2) and Eh values (204–215 mV). Hence, the solubilisation of heavy metals did not occur and conductivity values ( $886$ – $1105 \text{ }\mu\text{S cm}^{-1}$ ) and salinity (0.42–0.54 ppt) remained unelevated.

In Los Ruedos mining site the influence of AMD is evident. At points collected upstream of the spoil heap As concentrations are non detectable, waters are weakly alkaline (pH = 7.9–8.6), moderately oxidant (Eh = 169–190 mV) and do not present detectable heavy metals concentrations in solution. However the situation in P8 and P9, close to the spoil heap, changes drastically. The mineralogy of the area, with abundance of pyrites, together with a very strong oxidant redox potential (654–669 mV), cause the oxidation of sulphurs to sulphates ( $4200$ – $4500 \text{ mg L}^{-1}$ ), resulting in an important decrease in pH (2.2). This led to the solubilisation of heavy metals (the sum of the concentrations of Cd, Co, Cr, Cu, Ni, Pb, Zn ranges from non detectable upstream to  $7.5 \text{ mg L}^{-1}$  in points downstream of the spoil heap), as well as the As contained in sulphur minerals, which reach values of  $7.2 \text{ mg L}^{-1}$ . The same occurs with Al, Mn and Fe, whose concentration as sum of the three elements increased from 0.49 and  $1.14 \text{ mg L}^{-1}$  in P7 and P7A to  $862$  and  $868 \text{ mg L}^{-1}$  in P8 and P9, respectively. As is usually adsorbed onto the surfaces of Al, Mn and Fe minerals.<sup>48,49</sup> Therefore, the dissolution of these minerals provokes the release of As to waters. The higher calcium and magnesium concentrations in waters that have passed through the tailings indicate that the solubilisation of calcium and magnesium arsenates is also responsible for the leaching of As, although to a lesser extent. Conductance (up to  $5523 \text{ }\mu\text{S cm}^{-1}$ ) and salinity (up to 39.3 ppt) are the highest values for all the tested points, due to the great concentration of ions in solution.

For points P10 and P11, downstream of the mine, it seems that the tested parameters tend to reach the values found upstream, indicating that the grade of pollution in waters decreases with the distance to the focus. However, As concentrations at these two points ( $1.00$  and  $0.13 \text{ mg L}^{-1}$ , respectively) still remain at elevated levels according to the Spanish law, which establishes the limits at  $500 \text{ }\mu\text{g L}^{-1}$  for mining and industrial effluents and  $10 \text{ }\mu\text{g L}^{-1}$  for waters destined for consumption.†

Fig. 3 highlights the differences in the main parameters affecting As release at all sampling points. The similar behaviour of some variables can be noticed. Eh increases from upstream (P7 and P7A) to points close to the spoil heap (P8 and P9) and then becomes lower again downstream (P10 and P11). The same tendency follows in the amount of dissolved As, metal concentration in solution (M, as the sum of Cd, Co, Cr, Cu, Ni, Pb, Zn concentrations), the sum of dissolved (Al + Fe + Mn), the sulphate concentration, and to a lesser extent the amounts of (Ca + Mg + Sr). Just the opposite happens with pH, which decreases from upstream (P7 and P7A) to points close to the spoil heap (P8 and P9) and then becomes higher again (P10 and P11). This justifies that the release of As into

waters from Los Ruedos is the combination of the previously mentioned factors: the oxidation of sulphur minerals containing As, the dissolution of Al, Mn and Fe minerals where As was adsorbed, and to a lesser extent, the solubilisation of calcium and magnesium arsenates.

### 3.2 Statistical analysis

Due to the high number of parameters monitored in this study, it was difficult to establish relations between them. In this sense, statistical analyses together with chemometry are essential disciplines to tackle these studies.<sup>50,51</sup> Statistical processing of the data was carried out by using SPSS software (version 11.5) and STATGRAPHICS Plus (version 5.0 for Windows®). Supervised pattern recognition was applied to the physicochemical results at the three mine sites classified by their sampling points. Discriminant analysis was performed with the 167 samples collected from the 12 sampling points and Al, As, Ca, Fe, K, Mg, Na, Sr, Zn, electrical conductivity, Eh and pH results were considered as variables. This procedure generates a small number of functions of quantitative measurements which are linear combinations of the standardized 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 similar variances. A graphical representation of the samples as a function of the two canonical discriminant functions is presented in Fig. 4, where F1 represents 88% of the variance and F2 represents 8.0%, both of them representing 96% of the total variance. 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 characterized by a centroid (marked as a +) which is the average for each category (unique value in the classification factor field). The graph shows that samples from the same sampling point are closely grouped and there are no anomalous patterns (or outliers). Since similar water composition was found for some points, samples from points 2, 3 & 4 are grouped together, as well as points 7 & 7A, points 8 & 9, and points 10 & 11. Finally, samples were classified in six groups: those taken upstream and downstream of each mine site. In the

figure, arrows represent the alteration of natural waters related 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 its high enrichment in As, leached from the mineralized area and spoil heaps. Waters from La Soterraña have a noticeably different behaviour from the other mine sites. Ca, As, K, Na, Mg, Sr and pH values increased from sample point P1 to P2 and especially to P3 & P4 points, as a consequence of the presence of spoil heaps.

La Peña-El Terronal mine site does not cause a great influence due to the encapsulation of the area (both groups are located in the graph in the same zone with a large common area).

The influence of the Los Ruedos mine was very strong in waters collected at points 8 & 9, characterized by low pH, high concentrations of heavy metals and high electrical conductivity, but when these waters are incorporated to streams (10 & 11 points), this AMD typical behaviour changes quickly and it is neutralized. These statistical results corroborate the conclusions previously obtained.

Correlations among As and other variables were established. The most remarkable correlations are summarized in Table 3.

The high correlation coefficient existing among As and Al concentrations in P1 ( $r = 0.996$ ) seems to indicate that both elements are strongly associated in La Soterraña mine site. However, the lack of correlation of these elements in points downstream of the mine points out that the leaching of As does not occur due to the solubilisation of Al minerals where As could be superficially adsorbed. This does not happen either in the La Peña mine. The correlation in the group of points P8 & P9 ( $r = 0.314$ ) reveals that the presence of As in these points could be in part due to the previously mentioned phenomenon. A certain similarity exists with Mn. Despite the high correlation between As and Mn contents in P1 ( $r = 0.985$ ), indicating the association of these elements in La Soterraña, the inexistant correlation downstream of the mine suggest that the solubilisation of arsenates bound to manganese oxyhydroxides is not very important, neither in La Peña and Los Ruedos mines. Ca, Mg and Sr showed noticeable positive correlations for points downstream of La Soterraña mine and La Peña mine, meaning that the release of As in these two mines is important due to the solubilisation of Ca, Mg and Sr arsenates. In the case of Los Ruedos only As–Sr correlation was significant, indicating that release of As is partially owed to the dissolution of Sr arsenates. An opposite

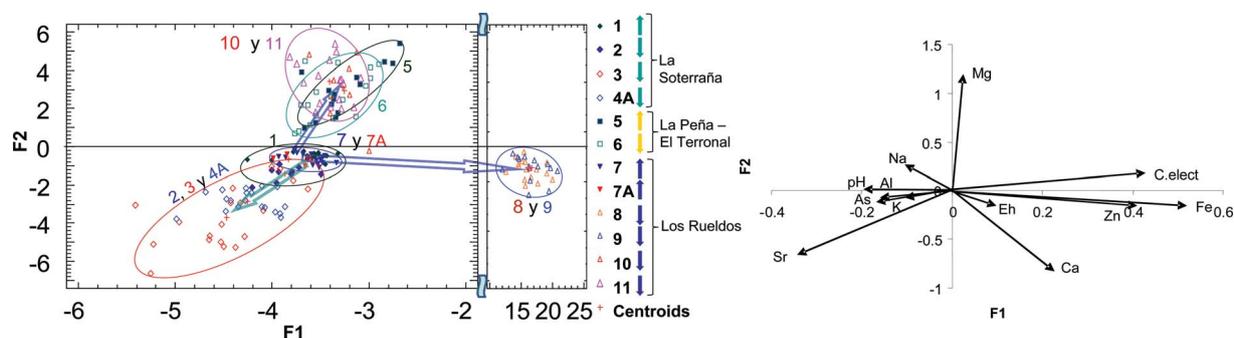


Fig. 4 Linear discriminant analysis of physicochemical data from La Soterraña, La Peña-El Terronal, and Los Ruedos mine sites.

**Table 3** Pearson correlation coefficients among As and some selected variables ( $n = 171$ )

Variables	P1	P2, P3 & P4A	P5	P6	P7 & P7A	P8 & P9	P10 & P11
Al	0.996 <sup>a</sup>	-0.015	-0.239	-0.412	0.057	0.314	-0.152
Ca	-0.030	0.619 <sup>a</sup>	0.099	0.774 <sup>a</sup>	0.122	-0.375 <sup>b</sup>	0.241
Fe	0.492	-0.082	0.192	-0.372	0.059	0.621 <sup>a</sup>	-0.107
Mg	-0.518	0.441 <sup>a</sup>	0.165	0.677 <sup>a</sup>	0.075	-0.335	0.246
Mn	0.985 <sup>a</sup>	-0.094	0.388	-0.349	-0.110	-0.173	-0.094
Sr	-0.275	0.425 <sup>a</sup>	0.197	0.404	0.055	0.656 <sup>a</sup>	-0.229
Bicarbonate		-0.207	0.320	0.845	-0.483	0.658	-0.214
Sulphate		0.643	0.279	0.937 <sup>b</sup>	0.446	0.687	-0.424

<sup>a</sup> Statistically significant correlation at the 95% confidence level (two-tailed). <sup>b</sup> Statistically significant correlation at the 99% confidence level (two-tailed).

behaviour occurs with iron. While the correlation among As and Fe concentrations is significant in points affected by AMD from Los Ruedos ( $r = 0.621$ ), the rest of the tested points showed no significant As–Fe correlation. Therefore, the release of the arsenates bound to the surfaces of iron oxyhydroxides is only important in points close to Los Ruedos spoil heap. Surprising is the significant correlation found between As and sulphate concentrations downstream of all mines, with  $r$  values of 0.643, 0.937 and 0.687 for La Soterraña, La Peña and (P8 & P9) from Los Ruedos, respectively. This means that oxidation of sulphur minerals containing As occurs in all mines. Nevertheless, the extent of this phenomenon is much higher in Los Ruedos, because of the most favourable conditions in this mine, such as higher Eh, and evidenced by the greater amounts of sulphate generated in P8 and P9 (Table 3). Another interesting correlation was found among As and bicarbonate concentrations in P6 ( $r = 0.845$ ) and P8 & P9 ( $r = 0.658$ ) suggesting that leaching of As must somehow occur together with carbonate solubilisation in La Peña and Los Ruedos. Although natural carbonates usually do not contain significant amounts of As, it has been demonstrated that As may be trapped also by natural calcite.<sup>52</sup>

### 3.3 Arsenic speciation studies

**3.3.1 Preservation of arsenic speciation.** The preservation of As species in water samples is an indispensable method to avoid changes during storage. It has been established that As preservation is dependent on the sample matrix.<sup>53</sup> The distribution of As(III) and As(V) species depends greatly on the abundance of redox-active solids, especially organic carbon, the activity of micro-organisms, and the extent of diffusion of O<sub>2</sub> from the atmosphere. According to recommendations from literature,<sup>54–58,12,59–61</sup> samples were filtered through 0.45 μm and HCl acid and EDTA were assayed as preservatives of samples; additionally, the samples were kept in the dark until analysis.

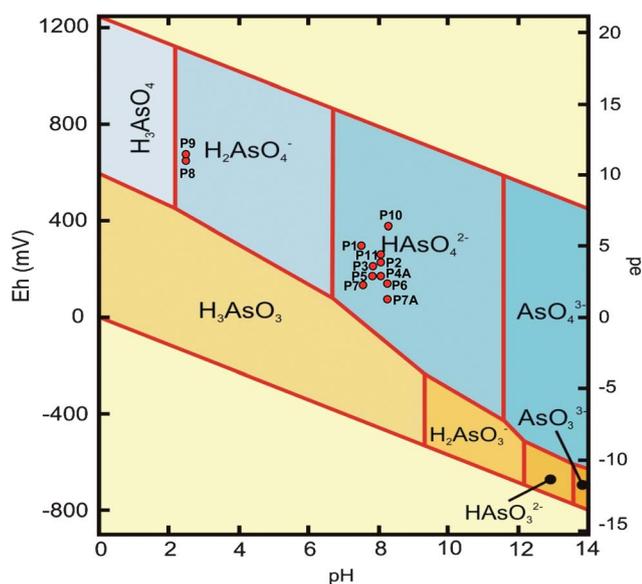
The results of As speciation carried out after the sample collection for the three different aliquots (without any additive, with HCl and with EDTA) show no significant differences between them. Results from the temporal study confirm that no alteration of the original As distribution occurred up to nine months after the collection in any of the assayed media. These results are in agreement with those reported by some authors,<sup>62,63</sup> who found that HCl acidification and storage in the dark successfully preserved As redox species, and also with the ability of preservation of EDTA.<sup>12</sup>

In relation to preservation of total dissolved As with time, reduction of any species was not observed for any of the three aliquots during the considered time. This can be due to the fact that the main components responsible for adsorbing As and therefore lowering its concentration in solution are Mn and Fe, and their contents in the studied samples were very low, with the exception of P8 and P9 from Los Ruedos, whose contents rise up to more than 700 mg L<sup>-1</sup> for Fe and 1.68 mg L<sup>-1</sup> for Mn. However, no decrease in dissolved As occurred in these samples, even in the aliquot without preservation. The reason could be the nature itself of these samples, since their acid pH (mean value of 2.2) would avoid the precipitation of Mn or Fe compounds and the subsequent adsorption of As into them.

**3.3.2. Arsenic speciation.** The results of As speciation showed that only inorganic species were detected (Table 4). The absence of organic As species reflects the origin of contamination by weathering of mine wastes containing As minerals. Moreover, speciation results indicate that As occurs exclusively as As(V) in most samples, which is in agreement with the theoretical Eh–pH diagram of species (Fig. 5). It has been described that the presence of high As(V) concentrations can be explained by the promotion of desorption of arsenates bound to iron oxyhydroxides at neutral–alkaline conditions,<sup>64</sup> as well as dissolution of thermodynamically unstable Fe and Ca-arsenates minerals.<sup>65,66</sup> Taking into account the low Fe concentrations present in the La Soterraña samples and their relatively high Ca and Mg concentrations, it seems that dissolution of Ca and Mg

**Table 4** As species, pH and Eh upstream and downstream of the three mine sites

Sampling point	As(V) (μg L <sup>-1</sup> )	As(III) (μg L <sup>-1</sup> )	pH	Eh (mV)
La Soterraña	P1	56	7.5	307
	P2	24 000	8.0	262
	P3	37 250	7.8	259
	P4A	37 500	8.0	213
La Peña	P5	182	7.8	215
	P6	2475	7.7	204
Los Ruedos	P7A	13	7.6	190
	P7	9.8	8.2	169
	P8	7125	2.2	654
	P9	7350	2.2	669
	P10	176	8.2	382
	P11	65	8.0	277

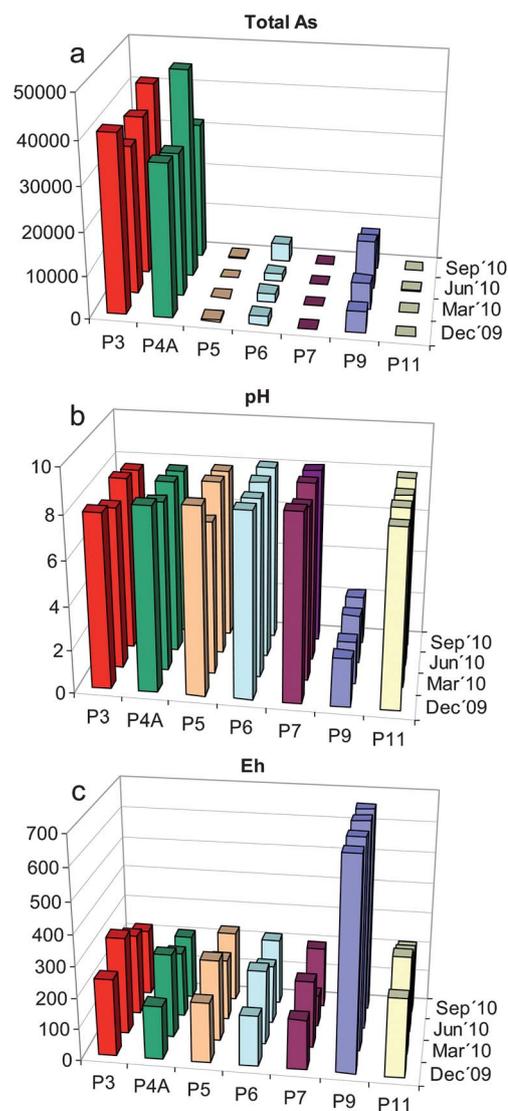


**Fig. 5** pH–Eh diagram for As speciation with the location of studied points.

arsenates must be the most important process controlling As(v) release into waters in this area. In the case of samples P8 and P9 from Los Ruedos, affected by AMD, the high Fe concentrations suggest that dissolution of adsorbed arsenates onto iron oxyhydroxides is the predominant process, together with dissolution of Ca and Mg arsenates to a lesser extent. In contrast to samples from La Soterraña and Los Ruedos, low concentrations of As(III) were detected in samples from La Peña, with proportions of As(III) around 3%. Contrary to samples from La Soterraña and most from Los Ruedos, samples P5 and P6 showed high dissolved organic contents (20.3 and 17.9 mg L<sup>-1</sup> respectively). The potential of dissolved organic matter (DOM) to chemically reduce arsenates to arsenite has been studied by other authors.<sup>67</sup> The redox properties of natural DOM are not accurately known but the experiences with model compounds suggest that DOM can cover a wide spectrum of redox potentials. In addition, thermodynamic calculations suggest that reduction of arsenate with DOM is an energetically favoured process.<sup>67</sup> The rate of arsenite appearance was comparable to that obtained by Bauer and Blodau<sup>68</sup> in the aqueous phase of soil samples.

### 3.4 Seasonal variations of total arsenic and some associated parameters

A seasonal variation study was carried out for selected samples collected every three months for a complete year in each mine site. Although it would be desirable to have sampled waters before and after the spoil heap in each mine, it was not possible in the case of La Soterraña, as no water flow was found in P1 during the whole studied year. Hence, for La Soterraña only the downstream points (P3 and P4A) were selected for this study. The relationship between As concentration in the studied waters and period of the year was intended to be studied. The other studied parameters were pH and redox potential, which are the main variables influencing As mobility and speciation. These



**Fig. 6** Seasonal variations in As contents ( $\mu\text{g L}^{-1}$ ), pH and Eh (mV) upstream and downstream of each mine site.

variations are presented in Fig. 6 a, b and c, whereas water flow values are summarized in Table 5.

For La Peña and Los Ruedos mining areas, the highest values of As concentration coincided with the lowest values of water flow in the sampling points (Fig. 6a). It is noticeable that point P6, downstream of La Peña, showed an average As concentration of 2.6 mg L<sup>-1</sup> with an average water flow of 122 L s<sup>-1</sup>. This

**Table 5** Water flow in the studied points every sampling campaign.<sup>a</sup>

Period	Water flow (L s <sup>-1</sup> )					
	P3	P4A	P5	P6	P7	P11
Dec '09	0.010	0.300	87.2	99.8	0.010	0.005
Mar '10	0.025	0.041	155.3	162.9	0.008	0.001
Jun '10	0.040	0.052	121.9	130.4	0.005	0.001
Sep '10	0.020	0.025	84.6	95.4	0.015	0.000

<sup>a</sup> Note: Water course is often dried in P1 and it is stagnant in P9.

means an average input of total As of  $0.3 \text{ g s}^{-1}$  to San Tirso River, with its greatest contribution during late summer ( $0.4 \text{ g s}^{-1}$ ). Among the studied areas, points from La Peña presented the highest water flow values since they are collected from a river close to the spoil heap. This As input to waters is relatively high compared with other studies developed in other mining sites. Hewlett *et al.*<sup>69</sup> reported As inputs below  $2 \text{ mg s}^{-1}$  in river waters from adjacent coal and gold mines. However, these As inputs are lower than those reported by Masson *et al.*<sup>70</sup> who found As discharges above  $3 \text{ g s}^{-1}$  into the Gironde estuary receiving water from historic mining areas in France. De Gieter *et al.*<sup>71</sup> reported As discharges of  $0.2\text{--}1.1 \text{ g s}^{-1}$  in the Scheldt estuary from drains of both industrial and domestic wastes.

pH values remained approximately constant for all tested sampling points during the observation period (Fig. 6b). For most points the lowest values corresponded to samples collected during March. The decrease of alkalinity can be attributed to the dilution effect due to the rainfall between December and March. On the contrary, effect of rainfall resulted in no significance for point P9. This is consistent with results obtained by other authors for natural waters affected by AMD.<sup>26</sup>

Related to Eh (Fig. 6c), the highest values were found in samples collected during early spring (March) for all mine sites. This behaviour is expected since the increasing of water flow occurs together with an increase of dissolved oxygen.

Nevertheless, no remarkable seasonal variations could be established for any of the studied variables in the three mines, contrary to what occur with other rivers.<sup>26</sup>

#### 4. Conclusions

Results from this study confirmed the high degree of As pollution in waters from the studied mining areas. It is evident that mine tailings act as a continuous source of As mobilization into water. However, the environmental impact of mining is different for the three studied mine sites, and in accordance with the mineralogy, the geological and the physicochemical characteristics of each area. The highest total As concentrations were found in waters from La Soterraña mining area (up to  $38.8 \text{ mg L}^{-1}$ ). It may be explained by the massive solubilisation of calcium and magnesium arsenates, and to a lesser extent by the solubilisation of strontium arsenates and the oxidation of sulphur minerals containing As.

In La Peña-El Terronal, where encapsulation of the main spoil heap was carried out, a lower impact in waters is expected. However, the high As concentrations found downstream reveal that the preventive measure is not enough to avoid As release into waters. In fact, the high water flow at this point implies the greatest input of As to surroundings, an average of  $0.3 \text{ g s}^{-1}$  of As reach San Tirso River, which means that the As spread in this mine site is the most important among the studied mines. As leaching in this mine is due to the solubilisation of calcium, magnesium and strontium arsenates, as well as because of the oxidation of sulphur minerals containing As and somehow it occurs together with carbonate solubilisation.

Waters close to Los Ruedos spoil heaps are strongly affected by AMD. This entails an important solubilisation of As and heavy metals. In this case the release of As may be attributed to different sources: the oxidation of sulphur minerals containing

As, the dissolution of Al, Mn and Fe minerals where As was superficially adsorbed, and to a lesser extent, the solubilisation of calcium, magnesium and strontium arsenates. Despite the high concentrations of As and heavy metals, quality of waters notably improves with distance to the focus. However, As concentrations exceed Spanish limits of  $500 \mu\text{g L}^{-1}$  of As for mining and industrial effluents in most of tested points downstream of the mines.

The presence of As in the studied waters only occurs in the form of inorganic species, and almost exclusively as As(v), with the exception of a low amount of As(III) found in waters from La Peña-El Terronal.

Regarding the preservation of samples, no alteration of As speciation was found up to nine months after collection for samples stored without any preservative, or for those preserved with HCl or EDTA acids.

In contrast to other rivers, no important seasonal variations in the main physicochemical parameters controlling As concentrations and speciation were observed in the three studied mining areas, which means that As release remains approximately constant throughout the year and the dependency of rainfall is not very remarkable.

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