

Implications of several physicochemical parameters in the arsenic speciation in mine waters from Asturias mercury mining district (Spain)

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Abstract The present study is focused in the establishment of the arsenic species present in waters close to three abandoned mercury mines located in the mercury metallogenetic province of Asturias, Northern Spain (La Soterraña, La Peña-El Terronal and Los Rueldos, within the Caudal River catchment) and the understanding of the factors that control arsenic speciation in their waters. Several parameters, such as pH, Eh, dissolved oxygen, dissolved organic carbon, sulphate, Fe, Mn, Al, Ca and dissolved heavy metals concentrations were determined and their influence was estimated for each mine site. Results showed that arsenate is the dominant species in all collected samples.

Key Words arsenic, mine waters, speciation, arsenate solubilisation

Introduction

Arsenic is an element widely distributed in the environment not only due to natural sources but also by anthropogenic contributions. Arsenic can occur in the environment in several oxidation states (-3, 0, +3 and +5). Inorganic arsenate As(V) and arsenite As(III) are the most toxic forms while methylated compounds are moderately toxic. In natural waters it is mostly found in inorganic form as oxyanions of trivalent arsenite (As(III)) or pentavalent arsenate (As(V)). Organic arsenic forms may be produced by biological activity, mostly in surface waters, but are scarcely important. Arsenic is perhaps unique among the heavy metalloids and oxyanion-forming elements (e.g. arsenic, selenium, antimony, molybdenum, vana-

dium, chromium, uranium, rhenium) in its sensitivity to mobilization at the pH values typically found in surface and groundwaters (pH 6.5–8.5) and under both oxidizing and reducing conditions (Baeyens *et al.* 2007). Compared to other oxyanion-forming elements, arsenic is one of the most troublesome in the environment because of its relative mobility over a wide range of redox conditions. Arsenic can be found at higher concentrations than all other oxyanion-forming metals such as Se, Cr, Mo, V (Smedley and Kinniburgh 2002). Redox potential (Eh) and pH are the most important factors controlling arsenic speciation (Figure 1). Under oxidizing conditions, H_2AsO_4^- is dominant at low pH (less than about pH 6.9), whilst at higher pH, HAsO_4^{2-} becomes dominant

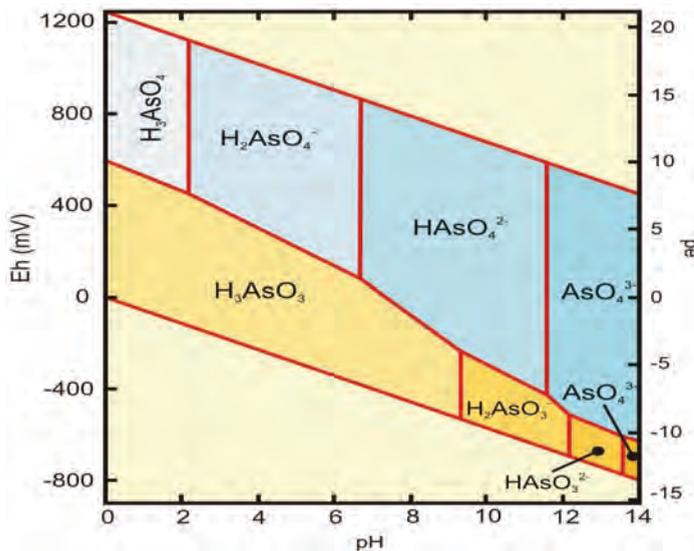


Figure 1 Eh-pH diagram for arsenic species.

(H_3AsO_4 and AsO_4^{3-} may be present in extremely acidic and alkaline conditions respectively). Under reducing conditions at pH less than about pH 9.2, the uncharged arsenite species H_3AsO_3 will predominate (Yan *et al.* 2000). As(V) is generally the dominant species in lake and river waters (e.g. Seyler and Martin 1990; Pettine *et al.* 1992), although the relative proportions of As(V) and As(III) may vary according to changes in input sources, redox conditions and biological activity.

Abandoned mines have left behind toxic pits and acid mine drainage. Naturally occurring minerals were disturbed, crushed during ore treatment and left in sometimes massive tailing piles. As a consequence, potentially toxic materials containing arsenic and heavy metals can be found in dangerous high levels throughout historic mining regions. Natural weathering can lead the mobilization of arsenic to the environment and its solubilisation into the surrounding waters. Arsenic usually occurs as arsenic-bearing sulphides, predominantly pyrite. During periods of excess oxygenation pyrite is dissolved allowing arsenic to enter the aquifers (Gault *et al.* 2001; Williams 2001). Oxidation of pyritic ores is a major cause of acidic mine drainage (AMD) (Wildeman *et al.* 1974; Black and Craw 2001; Gault *et al.* 2001). The production of Fe(III) and hydrogen ions can catalytically dissolve secondary minerals, thereby increasing the metal load to the drainage (Wildeman *et al.* 1974). In addition, the generally low pH ($\approx 1-4$) of AMD systems, also contributes to the solubilisation of heavy metals (Welch *et al.* 2000). Ca and Mg arsenates may be present in alkaline Ca-Mg-rich soils and sediments (Matschullat 2000).

In Asturias (Northern Spain) mercury mining has been an important activity during decades. Because of the great decline on Hg prices on the 1970s, most mines were closed between 1973 and 1974, but often none preventive measure was carried out after the closures. Therefore, mine facilities and metallurgical installations remain currently 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 Hg and As-rich ores, and lead to the release of mercury, arsenic and associated heavy metals into underlying aquifers and surface waters. Studies about the environmental impact of Asturian abandoned Hg mines are abundant (Loredo *et al.* 2010; Fernández-Martínez *et al.* 2005; Loredo 2000) and prove the existence of pollution in soils, surface waters, sediments and even in plants of the surroundings. However, no studies exist about the arsenic species occurring in surrounding waters of these mining areas.

Methods

Sampling

The locations of sampling points are shown in figure 2. Surface water was collected at 4 points in La Soterraña mine site, 2 points in La Peña-El Terrenal and 6 points in Los Ruedos. Four sampling campaigns were performed between September 2009 and June 2010. All samples were firstly filtered by $0.45 \mu\text{m}$ in situ, stored in polypropylene bottles of 125 ml and one or two drops of concentrated HCl were added in order to preserve arsenic speciation. Finally, all samples were stored at 4°C in dark, and analyzed within 1 week of sampling.

Analytical determinations

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). Total arsenic 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. Na and K were determined by flame atomic emission spectrophotometry (FAES) using a Perkin Elmer 2280. Cl^- , NO_2^- , NO_3^- and SO_4^{2-} were analysed by means of ion chromatography with a Dionex Serie DX-500 equipped with a suppressor device (Dionex CSRS-ULTRA 4 mm).

Arsenic speciation studies were carried out by coupling high performance liquid chromatography-hydride generation-atomic fluorescence spectrometry (HPLC-HG-AFS). The HPLC system consisted of a Varian Prostar ternary solvent delivery module 230 and a Hamilton PRP-X100 anion-exchange column. The chromatographic separation of As(III), DMA, MMA and As(V) was achieved following the method described by Gómez-Ariza *et al.* (1998). Detection and quantification of arsenic species were performed by Hydride Generation - Atomic Fluorescence by means of a PSA Excalibur instrument (Orpington, UK).

Results

Arsenic speciation is shown in table 1. Only inorganic species of arsenic were detected. The absence of organic arsenic species reflects the origin of contamination by weathering of mine wastes containing arsenic minerals. Moreover, speciation results indicate that arsenic occurs exclusively as As(V) in most samples, which is in agreement with the theoretical Eh-pH diagram of species (Fig. 1). 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 (Pierce

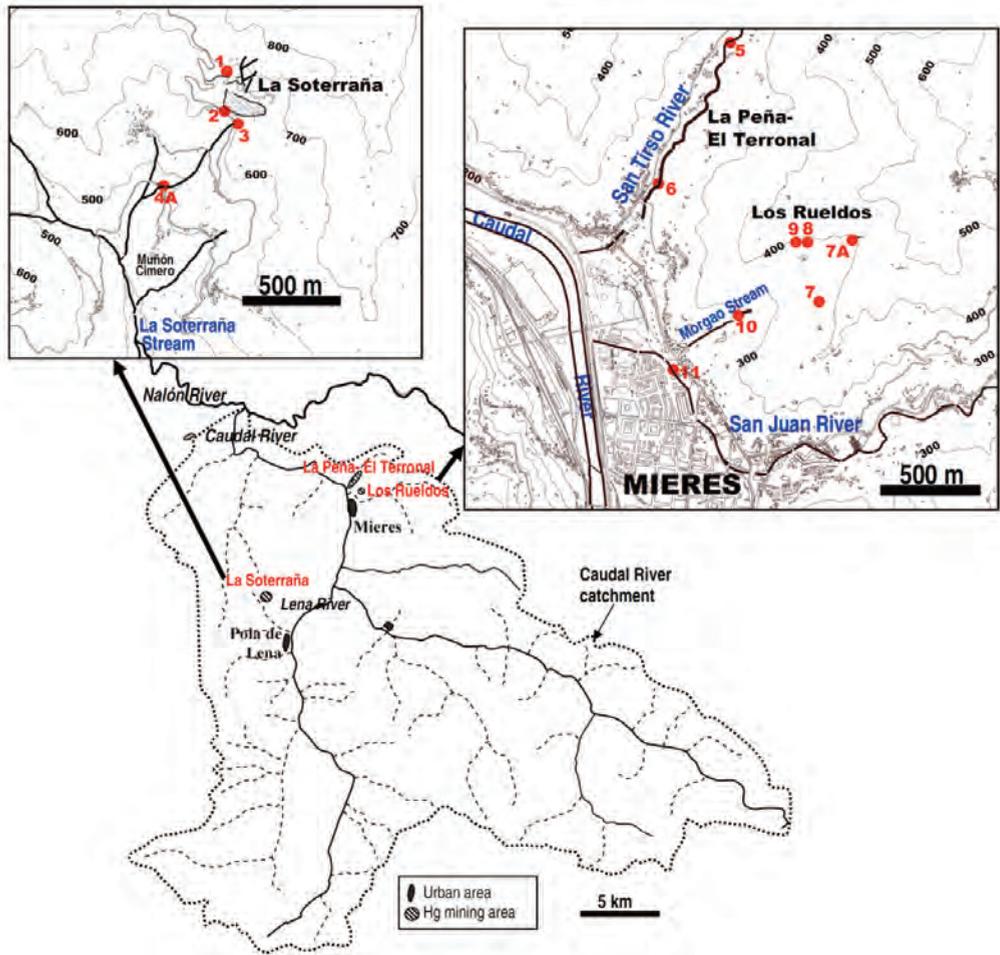


Figure 2 La Soterraña, La Peña-El Terronal and Los Rueldos mercury mine sites, indicating main streams and sampling points, within the Caudal River catchment.

and Moore 1982) as well as dissolution of thermodynamically unstable Fe and Ca-arsenates minerals (Dove and Rimstidt 1985; Paktunc *et al.* 2004). Extremely high As(V) concentrations were detected in samples collected downstream in La Soterraña mine with an average concentration of $37917 \mu\text{g.L}^{-1}$. Taken into account the low Fe concentrations found in water sampled in La Soterraña and its relatively high Ca and Mg concentrations, it seems that dissolution of Ca and Mg arsenates must be the most important process controlling As(V) releasing into waters in this area. In the case of samples P8 and P9 from Los Rueldos, the high Fe concentrations shown in figure 3a suggest that the elevated As(V) concentrations (average value of $7238 \mu\text{g.L}^{-1}$) are related to the AMD. In this area, dissolution of adsorbed arsenates onto iron oxyhydroxides may take place together with dissolu-

tion of Ca and Mg arsenates. In addition, the dilution effect is remarkable, since As(V) concentration markedly decrease with the distance to the spoil heap (points P10 and P11). In contrast to samples from La Soterraña and Los Rueldos, low concentrations of As(III) could be detected in samples from La Peña-El Terronal where the proportion of As(III) was around 3%. Samples P5 and P6 show high total organic carbon contents (56.7 and 48.6 mg.L^{-1} respectively; Fig. 3b). The potential of dissolved organic matter (DOM) to reduce chemically arsenates to arsenite has been studied by other authors. 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

Table 1 Arsenic speciation in waters from Asturian mines.

Sampling point	As(V) ($\mu\text{g L}^{-1}$)	As(III) ($\mu\text{g L}^{-1}$)	pH	Eh (mV)	
La Soterraña	P1	56 ^a	n.d.	7.5	307
	P2	24000	n.d.	8.0	262
	P3	37250	n.d.	7.8	259
	P4A	37500	n.d.	8.0	213
La Peña-El Terronal	P5	182	5	7.8	215
	P6	2475	77	8.2	204
Los Ruedos	P7A	13	n.d.	7.6	190
	P7	9.8	n.d.	8.2	169
	P8	7125	n.d.	2.2	654
	P9	7350	n.d.	2.2	669
	P10	176	n.d.	8.2	382
	P11	65	n.d.	8.0	277

^a n=3; n.d.: non detectable

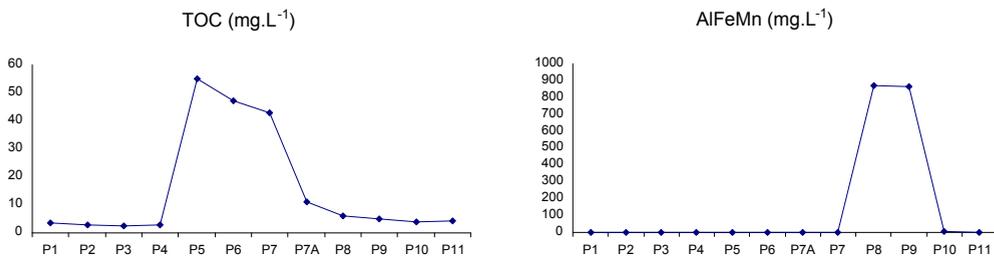


Figure 3 a: Sum of Al, Fe and Mn concentrations in water samples; b: Total Organic Carbon in water samples.

favoured process (Redman *et al.* 2002). The rate of arsenite appearance was comparable to that obtained by Bauer and Blodau in aqueous phase of soil samples (2006).

Conclusions

Results from this study confirmed a high degree of As impact in waters from the studied mine areas. It is evident that mine tailings act as a continuous source for arsenic mobilisation into water. However, mobilization of arsenic is different for the three studied sites. In La Soterraña, arsenic speciation can be related mainly to the solubilisation of Ca and Mg arsenates at neutral-alkaline pH. A similar arsenic releasing pattern is observed in La Peña-El Terronal mine site. However the presence of significant TOC concentrations in this site promotes the partial reduction of arsenate to arsenite. On the other hand, samples collected in Los Ruedos, close to the mine, are highly affected by AMD showing pH<3. In these points oxidative dissolution of arsenopyrite and other arsenic sulphide minerals causes arsenic releasing of arsenate bound to Al, Mn and Fe oxyhydroxides.

These data increase considerably the knowledge on surface water pollution by mine waters

on the Caudal River catchment and this information is of great interest in order to achieve the objectives of water quality demanded by the E.U. Water Framework Directive.

Acknowledgements

Authors thank the Miguel Sanchez group for the assistance in the anion determinations. This work was financially supported by the Spanish Ministry of Education and Science through CGL2006-08192 project.

References

Baeyens W, de Brauwere A, Brion N, De Gieter M, Leermakers M (2007) Arsenic speciation in the River Zenne, Belgium. *Sci Total Environ* 384: 409–419
 Bauer M, Blodau C (2006) Mobilization of arsenic by dissolved organic matter from iron oxides, soils and sediments. *Sci Total Environ* 354: 179–190
 Dove PM, Rimstidt JD (1985) The solubility and stability of scorodite, FeAsO₄·2H₂O *Am Mineral* 70: 838–844
 Fernandez-Martinez R, Loredó J, Ordoñez A, Rucandio MI (2005) Distribution and mobility of mercury in soils from an old mining area in Mieres, Asturias (Spain). *Sci Total Environ* 346: 200–212
 Gault AG, Polya DA, Lythgoe PR (2001) Hyphenated

- IC-ICP-MS for the determination of arsenic speciation in acid mine drainage. Cambridge, UK. 267: 387–400
- Gómez-Ariza JL, Sánchez-Rodas D, Giráldez I (1998) Selective extraction of iron oxide associated arsenic species from sediments for speciation with coupled HPLC-HG-AAS. *J Anal At Spectrom* 13: 1375–1379
- Loredo J, Petit-Domínguez MD, Ordóñez A, Galán MP, Fernández-Martínez R, Álvarez R, Rucandio MI (2010) Surface water monitoring in the mercury mining district of Asturias (Spain). *J Hazard Mater* 176: 323–332
- Loredo J (2000). Historic unreclaimed mercury mines in Asturias (Northwestern Spain): Environmental approaches. *Assessing and Managing Mercury form Historic and Current Mining Activities*. San Francisco, USA, U.S. Environmental Protection Agency, 175–180
- Matschullat J (2000) Arsenic in the geosphere - a review. *Sci Total Environ* 249:297–312
- Paktunc D, Foster A, Heald S, Laflamme G (2004) Speciation and characterization of arsenic in gold ores and cyanidation tailings using X-ray absorption spectroscopy. *Geochim Cosmochim Acta* 68: 969–983
- Pettine M, Camusso M, Martinotti W (1992) Dissolved and particulate transport of arsenic and chromium in the Po river Italy. *Sci Total Environ* 119:253–280
- Pierce, M, Moore C (1982) Adsorption of Arsenite and Arsenate on Amorphous Iron hydroxide. *Wat Res* 16: 1247–1253
- Redman AD, Macalady DL, Ahmann D (2002) Natural organic matter affects arsenic speciation and sorption onto hematite. *Environ Sci Technol* 36:2889–2896
- Seyler P, Martin JM (1990) Distribution of arsenite and total dissolved arsenic in major French estuaries: dependence on biogeochemical processes and anthropogenic inputs. *Mar Chem* 29:277–294
- Smedley PL, Kinniburgh DG (2002) A review of the source behaviour and distribution of arsenic in natural waters. *Appl Geochem* 17:517–568
- Welch AH, Westjohn DB, Helsel DR, Wanty RB (2000) Arsenic in groundwater of the United States: occurrence and geochemistry. *Groundwater* 38: 589–604
- Wildeman TRD, Cain D, Ramiriz AJ (1974) The relation between water chemistry and mineral zonation in the Central City Mining District, Colorado. *Water Resources. Problems Related to Mining, Proc. 18. Minneapolis, American Water Resources Association: 219–229*
- Williams M (2001) Arsenic in mine waters: an international study. *Environ Geol* 40(3): 267–278
- Black A, Craw D (2001) Arsenic, copper and zinc occurrence at the Wangaloa coal mine, southeast Otago, New Zealand. *Int J Coal Geol* 45: 181–193
- Yan XP, Kerrich R, Hendry MJ (2000) Distribution of arsenic(III), arsenic(V) and total inorganic arsenic in porewaters from a thick till and clay-rich aquitard sequence Saskatchewan Canada. *Geochim Cosmochim Acta* 64:2637–2648

