Environmental impact of past Hg mine activities in tributaries of Caudal River in Mieres district (Northern Spain)

Loredo. Jorge, Ordóñez. Almudena, Álvarez. Rodrigo, Bros. Teresa

Dpto. de Explotación y Prospección de Minas. Universidad de Oviedo. E.T.S. Ingenieros de Minas. Independencia, 13. 33004. Oviedo. España.
E-mail: jloredo@uniovi.es
Keywords: Mercury, Arsenic, Abandoned mining, Hidrogeochemistry, Spain.

ABSTRACT
Asturias has numerous derelict Hg mine sites as a legacy of a intensive historic mine activity, and the most important mines are located in the Caudal River catchment, in Mieres district. San Juan and San Tirso Rivers, both are tributaries of Caudal River and they receive polluted waters from La Peña – El Terronal and Los Rueldos mines, which have been abandoned without remediation. The instability of As-rich sulphides and sulphoarsenides subjected to the action of a humid environment, gives to the production of acid and metal rich leachates that are incorporated to the surface water or infiltrated through land reaching the groundwater. Acidic mine waters reaching up to 2,900 mg/l SO_4 and 17.7 mg/l As are drained from abandoned mine sites to tributaries of Caudal River where suffer important dilutions. Stream sediments collected in the surface watercourses of the catchment, downstream mine operations, show important anomalies in As and Hg, reaching .

INTRODUCTION
Asturias, in north-western Spain, has a long mercury mining tradition that was an important industry in the region until the beginning of the 1970s, when mercury prices began to decline due to falling demand as consequence of emerging toxicological problems by Hg use and production. This Hg word-scale crisis in Asturias gave rise not only the cessation of some important mining projects, but the successive closure between 1973 and 1974 of all up till then Hg mines in activity. The potential environmental risk of Hg mines exploited in Asturias was enhanced by the presence of As in the mined ore.
Although mercury extraction in Asturias is known to date back to the Roman period (centuries I and II B.C.), it was in the 19th and 20th centuries when mercury mining constituted an important and prosperous industry (Dory, 1894; Aramburu and Zuloaga, 1899; Gutiérrez Claverol and Luque, 1993). The most productive mines were located in the Caudal River catchment. One of the more conspicuous and environmentally important legacies of the historical mining activities remains in the form of abandoned underground mine works, metallurgical installations and significant quantities of mine/metallurgical wastes which remain stored on land. The instability of some toxic metal rich residues from the abandoned mercury mines, which lay in a humid environment and are affected by surface waters, has led to the production of metal rich leachates causing an obvious impact on the environment. Environmental problems related to Asturian Hg mining operations have been previously object of research (Loredo, 2000; Loredo et al., 1999, 2002, 2003a, 2003b, 2004a, 2004b, 2004c).
Among the elements abundantly present in the mine water and spoil leachates draining from abandoned mercury mines located in the catchment of the Caudal River in Mieres district, the most important, for its toxic effects both to humans and ecosystems, is arsenic. The notoriety of this element as a toxicant is best exemplified by the fact that for centuries it has been the poison “par excellence”. The toxicity of arsenic varies depending upon its chemical state: in general, inorganic forms are more toxic than organic complexes, and soluble forms more than insoluble. The area has a natural high mercury and arsenic concentration (local background levels), related to the presence of mercury mineralizations and outcropping Hg-enriched rocks. The current Spanish legislation about mining / industrial effluents limits the total As content to 0.50 $mg \cdot l^{-1}$ and 0.05 $mg \cdot l^{-1}$ for superficial waters destined for the production of drinking water.

GEOLOGY, HYDROGEOLOGY AND MINING HISTORY
In the Caudal River catchment, in Mieres district, some mercury mines have been intermittently exploited from centuries. The most important of them has been La Peña – El Terronal, but others such as Los Rueldos or El Rucio have had too small periods of activity.
In contrast to other areas of Spain, Asturias has a humid climate characterised by abundant precipitation during much of the year. In the area of study the annual average maximum and minimum temperatures are in the order of 17ºC and 8ºC respectively, with an annual average of 13ºC over the last twenty years. Average yearly relative humidity is about 78 % and the average yearly rainfall is 971 mm Maximum daily precipitations are 82.1 mm, 95.6 mm, 99.8 mm and 103.8 mm for return periods of 10, 25, 50 and 100 years, respectively.
Mercury mineralizations are located in the north-western margin of the Asturian Central Coal Basin, in a zone of intense tectonic deformation. The structural geology is constituted by a complex anticline structure with a N-S trend, in an area influenced by two important fractures of NW-SE trend: La Peña overthrust fault and La Carrera fault. Materials represented in this area shales with intercalation of sandstones, conglomerates and limestones, and they belong to “La Justa - Aramil” unit of Carboniferous age (Westphalian). Coal beds, which usually have thicknesses less than 50 cm, are intercalated in these unit. The Carboniferous sediments are overlain discordantly by Upper Stephanian – Lower Permian materials of the San Tirso formation, constituted from bottom

to top by calcareous conglomerates, clay lutites, and tuffaceous and cineritic materials. Mineralisations have a tectonic and stratigraphic control and they are irregularly distributed both in veinlets inside conglomeratic-brecciated bodies which show a lenticular morphology, or scattered inside the matrix of the conglomerate (Luque, 1985).

Mercury is most commonly present in the form of cinnabar, though metacinnabar and native mercury are also occasionally found. Other primary metallic minerals which are present in the paragenesis are pyrite, melnikovite, sphalerite, marcasite, chalcopyrite, galena, and stibnite. The arsenic is quite abundant in the form of sulphides (As-rich pyrite), sulphoarsenides (arsenopyrite, realgar and orpiment), and supergenic minerals (scorodite). Smithsonite, hemimorphite, cerusite, goethite, malachite, jarosite, melanterite and gypsum are present as secondary minerals. The gangue constituents are quartz, carbonates (ankerite, calcite and dolomite) and argillaceous minerals (kaolinite and dickite). These mineralizations have an epigenetic origin and they are associated to La Carrera Fault (Luque, 1992; Luque et al., 1991). Geothermometrical data corresponding to primary fluid inclusions in different minerals of the paragenetic sequence of these deposits showed they have been formed by the circulation of low temperature hydrothermal solutions along distensional fractures in reactive enclosing rocks (Loredo et al., 1988).

The hydraulic characteristics of the different materials constituting the substrate of the catchment (alternation of sandstones, shales and some coal beds) can be considered as an impermeable substrate from a hydrogeological point of view. In these conditions, the water that does not evaporate nor flows superficially is infiltrated on the more permeable colluvial materials and weathered shales, giving rise to small springs. Where the thickness of the weathered materials and weathered shales is great enough, water infiltration is favoured. Variations of the water table are closely correlated with infiltration from rainfall, following its seasonal changes. At Los Rueldos mine site, downstream 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 capacity to stock a great volume of water.

INFLUENCE OF ABANDONED MERCURY MINING IN THE CAUDAL RIVER CATCHMENT

Two tributaries of Caudal River in the district of Mieres, San Tirso and San Juan Rivers receive the polluted effluents of abandoned mercury mines and leachates from abandoned spoil heaps.

In the subcatchment of San Juan River, in the valley of the Morgao stream, lies Los Rueldos mine. This abandoned mine site is located 2 km north-east of the village of Mieres (30,000 inhabitants) and 20 km south-east of Oviedo, the capital city of Asturias (Figure 1). Mine works of small importance have been developed at this site, on the slope of a mountain whose altitude does not exceed 500 m above sea level. The mine was operated during a short period of time up to 1972 when the mineralised bodies exploited were found not to have continuity and mine works were abandoned. Mine operations were accomplished by drift mining and two drift portals, at different elevations on the mountain slope, are known. Through the lower of the two existing drifts, mine drainage is discharged and after accumulation in a small pond out of the gallery, mine water is drained to the basin of the Morgao stream, which has a short way and is soon incorporated to the San Juan River. The Morgao stream is a perennial watercourse with average flow between 5 and 10 $l.s^{-1}$.On the other hand, San Juan River has a flow ranging from 200 $l.s^{-1}$ in summer periods to more than 500 $l.s^{-1}$ in rainy periods. In this subcatchment, mine wastes from Los Rueldos mine were accumulated at the site of the mine, forming a small spoil heap totalling some 3000 m^3 (Baldo, 2000) and with an average inclination of 35º. At the bottom of the spoil heap, which is constituted by enclosing rocks and low-grade ore, a small drainage channel has been excavated to drain any mine water and spoil heap leachates towards Morgao stream. Los Rueldos wastes are lying on the mountain side, downhill from the mine entrances, without any preventative measures to impede leaching. Consequently, land adjacent to this site is contaminated by mining activities, either directly as a result of the spoil heap that is subjected to the washing effects of rainfall and subsequent chemical and mechanical dispersion, or indirectly through airborne dispersion. The steep slope of the spoil heap promotes vigorous mechanical and chemical dispersion of pollutants. Mercury and arsenic geochemical anomalies have been detected in urban soils and particulate materials in Mieres village (Loredo *et al*., 1999; 2003b).

In the subcatchment of the San Tirso River, the most important mine was La Peña – El Terronal, exploited by two different companies by underground works at two sites: La Peña and El Terronal. Other small mine works in the area, as the developed at the site of El Rucio, must be considered in terms of pollutants dispersion. Main spoil heap constituted by 150,000 m^3 of wastes from the metallurgical operations has been restored in 2002 in an on site security landfill. Currently, in spite of the restoration of this spoil heap, San Tirso River follows receiving pollution from the abandoned metallurgical and mine works of La Peña – El Terronal, including polluted soils and small deposits of wastes abandoned at the site. San Tirso River drains a catchment of 6,524,946 m^2, and has a flow ranging from 10 $l.s^{-1}$ in summer periods to more than 200 $l.s^{-1}$ in rainy periods. The circulation of surface water in oxidizing conditions through the underground mining works and spoil heaps promotes in some cases the formation of acid drainage, which in a great part reaches directly the Caudal River course.

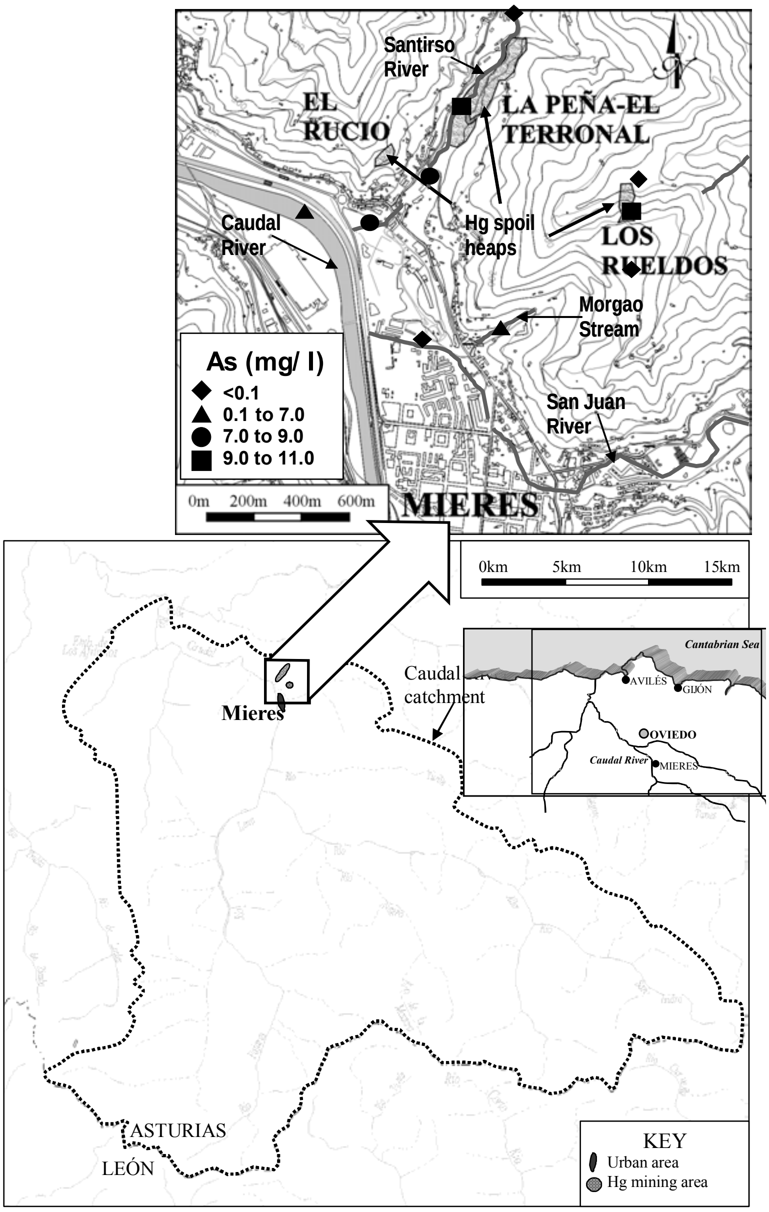


Figure 1: Location of Caudal River catchment and range of As concentrations found in surface waters in the area of the old Hg mining sites in Mieres.

MATERIALS AND METHODS

The present study has been made on the basis of different environmental prospecting campaigns accomplished in the areas where main mine and metallurgical operations in the Caudal River catchment, in Mieres district, were developed. Representative samples of waste materials from mine and metallurgical operations, stream sediments and surface water have been collected both upstream and downstream abandoned mine operations. At the abandoned mine sites, when possible, mine drainage and spoil heap leachates have been sampled in different points and for different periods of the hydrologic year. Groundwater has also been sampled in springs in the area. In-situ measurements of pH, Eh, electrical conductivity, salinity, dissolved oxygen, and turbidity, have been made by use of a portable multiparametric probe.

Representative samples of wastes were study by optical and electronic microscopy in order to determine mineralogy and textures. For chemical characterization waste materials were dried in laboratory for 48 h. in an oven at temperature lower than 35ºC to minimise loss of mercury due to volatility. After drying materials were desegregated and ground with a pestle and mortar and sieved through a 150 μm aperture stainless-steel sieve. They were homogenised and each sample was quartered by means of an aluminium rifler (which was cleaned between samples using a jet of compressed air), to provide a representative subsample for analysis. Chemical characterization was performed by analysis of the soluble fraction resulting from a strong acid attack of the sample with HCl-HNO_3-H_2O at 95ºC to put elements in solution. Concentrations of major and trace elements analysis (Mo, Cu, Pb, Zn, Ag, Ni, Co, Mn, Fe, As, U, Au, Th, Sr, Cd, Sb, Bi, V, Ca, P, La, Cr, Mg, Ba, Ti, B, Al, Na, K, W, Tl) were determined by ICP and Hg by FAA at ACME Analytical Laboratories in Vancouver (Canada). For the

purposes of the study, however, arsenic and heavy metals results in the aqua regia extraction are considered as total concentrations, due to the fact that hot aqua regia totally decomposes sulphides, which are the major sources of these elements. Quality control was achieved by routine analyses of certified reference standards and field and analytical duplicates.
Water samples were filtered in the field and placed in plastic bottles where acidification with HNO_3 to keep metals in solution has been made. Then they were maintained refrigerated until analysis in order to conserve their chemical characteristics. Water samples were analysed for Mo, Cu, Pb, Zn, Ag, Ni, Co, Mn, Fe, As, U, Au, Th, Sr, Cd, Sb, Bi, V, Ca, P, La, Cr, Mg, Ba, Ti, B, Al, Na, K, W and Tl by the ICP-MS/ICP-AES technique in the laboratories of ACME Analytical Laboratories in Vancouver (Canada).

RESULTS AND DISCUSSION
As consequence of mineralogical and chemical characteristics of exploited ore, operations related to historic Hg mining has a big influence in soils, sediments and surface waters in the catchment of rivers draining the mined area. The microscopical study of samples from spoil heaps shows that iron sulphides (pyrite, marcasite and pyrrhotite) are very abundant, and are typically in an advanced oxidation state, presenting hematite and amorphous iron hydroxide coatings. Jamesonite replacing sulphides is also frequent. Some cinnabar, arsenopyrite and sphalerite have also been detected. Electronic microprobe analyses of minerals show different generations of pyrite, where one of them shows high content in arsenic reaching up to 5.73 % As content (Loredo et al., 2003a).
The influence of mining on the environment can be observed in table 1, where a summary of As concentrations found in representative samples of mine/metallurgical wastes, stream sediments and surface water, at the mine sites, is represented.

Mining area	Type of sample	No. of samples	Min.	Max.	Mean
Los Rueldos (San Juan River subcatchment)	Mine wastes	9	4746	62196	33842
	Stream sediments	10	6809	41366	18991
	Surface water	22	1.4	17.7	9.8
La Peña-El Terronal (San Tirso River subcatchment)	Metallurgical wastes	12	13118	72153	35420
	Stream sediments	9	652	806	780
	Surface water	44	0.8	13.8	5.6

Table 1: Total As concentrations for representative samples of waste materials from mining and metallurgical operations ($mg.kg^{-1}$), stream sediments ($mg.kg^{-1}$), and surface water ($mg.l^{-1}$) collected at the mine sites.

In particular, at Los Rueldos´ spoil heap, where sterile rocks and low-grade ore are stored, in addition to arsenic, very high concentrations of Hg, Fe and S have been found, reaching up to 323 $mg{\cdot}kg^{-1}$, 12.4 % and 3.74 % respectively. At this spoil heap, average concentrations of Pb, Zn, and Sb are 3680 $mg.kg^{-1}$, 45 $mg.kg^{-1}$, and 2,391 $mg.kg^{-1}$ respectively. Concentrations of arsenic and heavy metals in wastes tends to decrease significantly with depth, according to data from samples collected in a trench excavated at the bottom of Los Rueldos´s spoil heap. In this trench, total As ranges from 41,939 $mg{\cdot}kg^{-1}$ at 0.20 m deep to 4,190 $mg{\cdot}kg^{-1}$ at 0.80 m deep. At the site of La Peña-El Terronal, the main spoil heap constituted basically by fine materials from metallurgical operations has been encapsulated in 2002 in a security landfill, but some small stocks of these materials and small spoil heaps constituted by enclosing rocks and low-grade ore remain on the site.
Stream sediments collected in streams and rivers tributaries of Caudal River show important anomalies in As and Hg. The As background level in sediments of streams of the Caudal River catchment (deduced from analysis of samples collected in different areas upstream of mining works) is 186 $mg{\cdot}kg^{-1}$. In contrast, the concentrations of total As in sediments range from 6,809 to 41,366 $mg{\cdot}kg^{-1}$ in the perimetrical channel constructed at the bottom of Los Rueldos´spoil heap to receive mine drainage and leachates. Very high concentrations of Hg (323 $mg{\cdot}kg^{-1}$), Fe (12.4 %), and S (3.74 %) have been also found. Concentrations of total As in sediments of San Tirso River, downstream mine works, range from 652 to 1,728 $mg{\cdot}kg^{-1}$ (729 mg kg^{-1}, average value), whereas total Fe concentration was 3.01 % (average value).
In the Caudal River catchment, samples of surface waters collected upstream of the mining works show pH values comprised between 7.96 and 8.72 in San Juan River and between 8.09 and 8.48 in San Tirso River. The baseline concentrations of As in surface water of this catchment, upstream mine operations, are in the range of 9 μgl^{-1}, excepting particular mineralised areas when the local hydrochemical background of As is naturally high because of the presence of As-rich iron sulphides associated to Hg mineralisations in the local rocks. In general, an As enrichment occurred in superficial waters and this enrichment is exacerbated by the presence of Hg mines in state of abandonment, where the increase in secondary porosity associated to mine voids and storage of wastes

in surface is favourable to a bigger destabilization of As-rich minerals. The estimated mean of total As in stream waters at a world scale is 0.004 mg l^{-1} (Reimann & Caritat 1998).
Total mercury concentrations are always below 1 µg.l^{-1} (detection limit of the analytical equipment). Range of characteristic physicochemical parameters of waters from San Juan and San Tirso Rivers upstream mining and metallurgical operations, measured in 2005 in different periods of the hydrological cycle, are indicated in table 2.

Parameter	San Juan River		San Tirso River	
Electrical conductivity (µS.cm^{-1})	933 – 1684 N = 5	(1161)	684 – 1200 N = 7	(942)
Salinity (ppt)	0.44 – 0.83 N = 5	(0.57)	0.32 – 0.57 N = 7	(0.45)
pH (units)	7.96 – 8.72 N = 5	(8.24)	8.09 – 8.48 N = 7	(8.30)
Eh (mV)	289 – 643 N = 5	(521)	193 – 339 N = 7	(268)
Dissolved oxygen (mg.l^{-1})	2.1 – 5.3 N = 5	(3.56)	1.2 – 7.6 N = 7	(3.5)
Turbidity (NTU)	6.5 – 360.9 N = 5	(154)	5.0 – 30.4 N = 7	(18)
Total As (mg.l^{-1})	< 0.2 N = 6	(< 0.2)	< 0.2 N = 7	(< 0.2)

Table 2. Range and average values of characteristic physico-chemical parameters of water from San Juan and San Tirso Rivers, upstream mine operations (N = number of samples considered).
In contrast, total As concentrations in surface waters at the site of the mine works and before they reach the Morgao stream (which is incorporated to San Juan River), show important anomalies, reaching values up to 17.7 mg·l^{-1} in samples of leachates collected at the bottom of Los Rueldos´ spoil heap. Total As concentrations in groundwater reach up to 6.05 mg·l^{-1} downstream mine works. A summary of the average characteristics of effluents from Los Rueldos mine is included in table 3 that shows the range of values for the parameters analysed in surface water upstream Los Rueldos mines, as well as mine drainage and spoil heap leachates.

	Upstream mine works	*Mine drainage*	*Spoil heap lechates*
pH	5-7	2.1 - 3.5	2.1 - 2.6
Elec. Cond. (µS/cm)	190-230	4500 - 6500	5300 - 6100
Nitrates (mg/l)	-	748	528 - 880
Phosphates (mg/l)	36-42	-	2.2
Sulphates (mg/l)	30-40	5000	2900 - 4600
As (mg/l)	<0.2	6.0 -12.0	1.4 - 17.7
Ca (mg/l)	33-58	115 - 120	64 - 140
Fe (mg/l)	0.07	757 - 1085	770 - 1048
Fe II (mg/l)	-	836	734
Fe III (mg/l)	-	249	314
Hg (µg/l)	<0.001	<0.001 - 3.7	<0.001 - 14
K (mg/l)	-	-	1.91
Mg (mg/l)	9 - 78	58 - 60	50 - 220
Mn (mg/l)	<0.03 - 0.18	1.4 - 2.5	1.6 - 2.7
Na (mg/l)	<5	<5	<5 - 5.2
Pb (mg/l)	<0.05	<0.05 - 0.33	<0.05 - 0.48
Zn (mg/l)	<0.05	<0.05 - 4.7	0.7 - 7.2

Table 3. Typical chemical characteristics of surface waters upstream and downstream Los Rueldos mercury mine's spoil heap.
Physicochemical parameters of mine drainage from the lowest gallery of Los Rueldos Mine, and the correspondent to Morgao stream, before and after to reach mine drainage and leachates from Los Rueldos mine are systematised in table 4 according to measurements made in 2005.

Parameter	Morgao stream (upstream Los Rueldos mine)	Los Rueldos mine drainage	Morgao stream (downstream Los Rueldos mine)
Electrical conductivity (µS.cm^{-1})	168 – 226 (196) N = 3	4543 – 6455 (5710) N = 15	1008 - 1256 (1156) N = 8
Salinity (ppt)	0.09 – 0.11 (0.10) N = 3	2.40 – 3.50 (3.09) N = 14	0.50 – 0.63 (0.57) N = 7
pH (units)	5.44 – 6.34 (5.96) N = 3	2.28 – 2.55 (2.46) N = 15	6.45 – 8.60 (7.61) N = 8
Eh (mV)	773 – 920 (848) N = 3	684 999 (918) N = 14	289 – 981 (681) N = 7
Dissolved oxygen (mg.l^{-1})	1.9 – 4.0 (3.03) N = 3	6.4 – 20 (18.88) N = 14	2.2 – 6.4 (3.89) N = 7
Turbidity (NTU)	36.2 – 108.1 (65.6) N = 3	4.6 – 581 (234.88) N = 14	16.4 – 64.1 (39.74) N = 7
Total As (mg.l^{-1})	< 0.2 (< 0.2) N = 3	6.0 – 12.0 (8.31) N = 16	0.34 – 0.61 (0.45) N = 8

Table 4. Range and average values of characteristic physico-chemical parameters of mine drainage from Los Rueldos mine, and comparison with Morgao stream (N = number of samples considered).

Acid drainage produced from mercury mine effluents and from the waste rock pile on the slope of the mountain flows through bedrock and towards local streams tributaries of the Caudal River. The total flow of acidic polluted water from the Los Rueldos site which flows into the Morgao stream is estimated in 3,200 m^3/year, corresponding to only 1% of the total flow from the Morgao drainage basin, where they are subject to important dilution effects, with the As content being lowered by more than 95%.
Associated to the remobilisation of waste materials in 2002 in La Peña – El Terronal´ spoil heap, for its isolation in a security landfill, a temporal increase of dissolved As in the course of San Tirso River, downstream spoil heap, has ocurred (Figure 2).

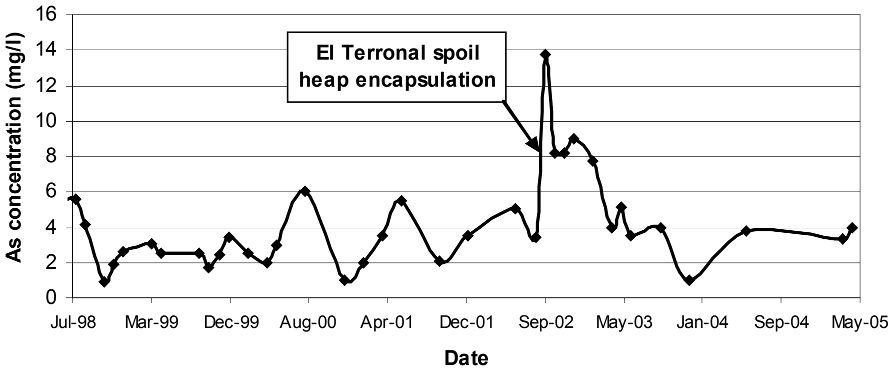


Figure 2: Evolution of As concentrations in the last seven years in San Tirso River, downstream of La Peña-El Terrenal spoil heaps

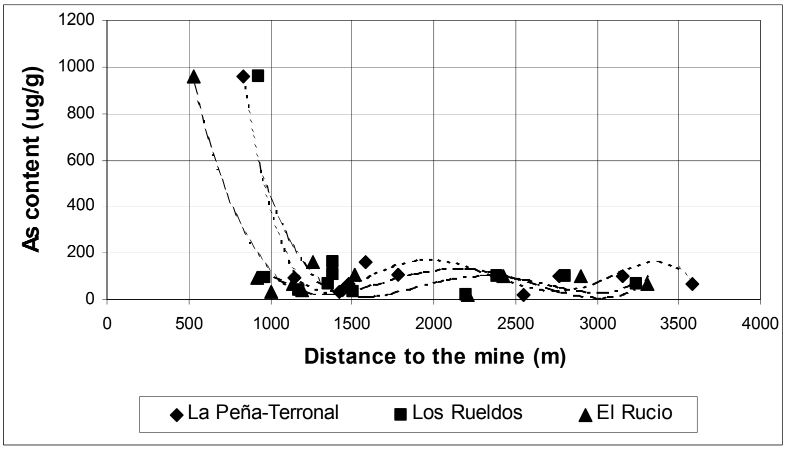
Range of characteristic physicochemical parameters of waters from San Juan and San Tirso Rivers downstream mining and metallurgical operations, measured in 2005 in different periods of the hydrological cycle, are indicated in table 5.

Parameter	San Juan River	San Tirso River
Electrical conductivity (µS.cm^{-1})	902 – 1196 (1021) N = 5	657 – 1085 (844) N = 8
Salinity (ppt)	0.43 – 0.60 (0.50) N = 5	0.31 – 0.52 (0.42) N = 7
pH (units)	8.36 – 8.72 (8.54) N = 5	7.33 – 8.62 (8.35) N = 8
Eh (mV)	291 – 603 (484) N = 5	186 – 334 (265) N = 7
Dissolved oxygen (mg.l^{-1})	2.2 – 4.8 (2.94) N = 5	1.3 – 8.1 (3.87) N = 7
Turbidity (NTU)	9.5 – 580.8 (134) N = 5	3.5 – 32.2 (18.9) N = 7
Total As (mg.l^{-1})	< 0.2 (< 0.2) N = 4	0.8 – 13.8 (5.6) N = 44

Table 5. Range and average values of characteristic physico-chemical parameters of water from San Juan and San Tirso Rivers, downstream mine operations (N = number of samples considered).

Analysis of mine water flowing intermittently through the portal located between Union and Peña shafts show an average pH of 3, conductivity of 4 mS cm^{-1}, 1.6 mg l^{-1} As, 0.049 mg l^{-1} Pb, 0.0005 mg l^{-1} Sb and 0.11 mg l^{-1} Zn. Underground waters in private wells upstream of the spoil heap, which are used for irrigation and as drinking supply for animals, show As contents ranging from 0.001 to 0.015 mg l^{-1}.
The analysis of water in the Caudal River 20 m downstream of the confluence with San Tirso River shows an As content of 1.6 mg l^{-1}; this content decreases to about 0.01 mg l^{-1} at a distance of 150 m from that confluence.
Groundwater flow at the site of the underground mine of La Peña – El Terronal is controlled by the dense network of galleries and the acidic mine drainage produced by circulation of water through the mine flows towards the Caudal River, where it is subjected to dilution. According to geochemical data exposed, it is evident that abandoned mercury mines and spoil heaps have a great deal of influence on the environment, although as consequence of the low volume of polluted mine waters (mine drainage and/or spoil heap leachates), pollution conditions manifest intensively only at the scale of the mine sites and streams flow through. When polluted mine waters are incorporated to streams or rivers with flows comparatively bigger there is a significant dilution process that bears waters downsteam mine operations to conditions similar to the reference values measured upstream mine operations.
Furthermore, abandoned mining operation affect to the urban environment of the Mieres village, where Hg and As anomalies have been detected in urban soils and these anomalies increase in proximity to the mine sites. Figures 3a and 3b show the variation of concentration in As and Hg respectively in surface soils of the urban area as function of the distance to the spoil heaps of La Peña – El Terronal and Los Rueldos (Loredo et al. , 2003b).

A



B

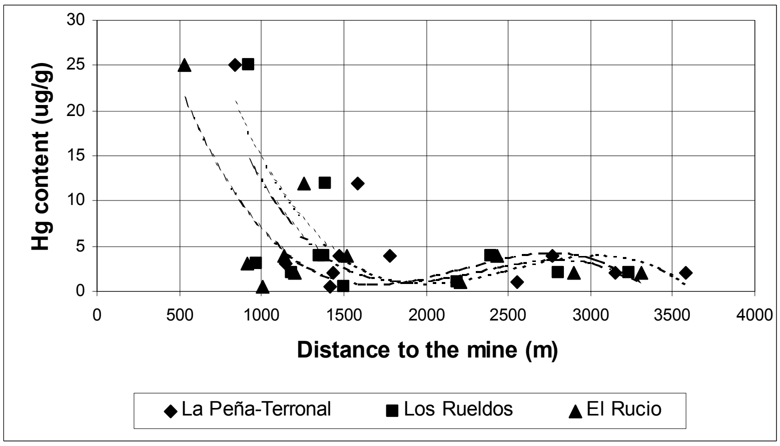


Figure 3. variation of As and Hg concentration in urban soils of Mieres, as function of the distance to abandonedmine sites.

Furthermore than pollution environmental effects on surface and groundwater, mine works as the developed at the site of La Peña- El Terronal, with underground operations deeper than 500 metres, once the pomping has been ceased they introduce big changes in the hydrogeological regime of the catchment, as results of the dense network of galleries, which control the groundwater flow and its connection with surface waters.

CONCLUSIONS
Mineralogical and geochemical data suggest that weathering of As-rich sulphide minerals contributes to the high As contents detected in mine effluents and spoil heap leachates. The potential environmental impacts of this anomalous

As and heavy metals concentrations in soils and waters is important. Results of the study indicate that As is being transported gradually from mineral sulphides in mining wastes to surface waters reaching San Juan and San Tirso River and finally Caudal River, where they experiment big dilutions.
San Juan and San Tirso Rivers receive pollution related to abandoned mine operation in the Caudal River catchment. Significant increments of As concentrations occur as a result of discharge of mine water drainage and mine/metallurgical spoil heaps leachates. Nevertheless, polluted streams receiving directly mine waters and leachates suffer important dilution effects when they incorporate to San Juan and San Tirso Rivers. Currently, this catchment receives polluted waters associated to abandoned mine and metallurgical operations. Main contribution to pollution of the surface watercourses is attributed to Los Rueldos mine drainage and spoil heap leachates, which apport important concentrations of arsenic to the Morgao stream which is incorporated to San Juan River that is an important tributary of the Caudal River in the area of Mieres village. Contributions from La Peña – El Terronal Mines have have been decreased as consequence of the restoration of the spoil heap in 2003, nevertheless arsenic is being yet incorporated to San Tirso River and in consequence to Caudal River from the abandoned mine and metallurgical works. Surface water flowing through the abandoned mine sites in the Caudal catchment in Mieres district is affected, in some areas quite a few, by contact with leachable materials.
Spoil heaps leachates, as well as waters flowing out at some mine sites, are acidic and rich in As and some heavy metals. These waters, very polluted at the source, are diluted when are incorporated to major watercourses, because the flow of this acid mine waters is generally low. During dry periods, the polluting effect of these waters results to be higher, both for the elevated As concentrations that the mine water can reach and for the reduction of river flows.

REFERENCES

Aramburu y Zuloaga, F. 1899. *Monografía de Asturias*. Oviedo.

Baldo, C. 2000. *Impacto ambiental en areas afectadas por minería antigua de mercurio en el Concejo de Mieres (Asturias)*. Doctoral Thesis. Univ. Oviedo. 276 p.

Dory, A. 1894. Le mercure dans las Asturies. *Revue Universelle des Mines*, Metallurg., 32, 145-210

Gutiérrez Claverol, M., Luque Cabal, C. 1993. *Recursos del subsuelo de Asturias*. Servicio de Publicaciones. Univ. Oviedo. 374 p.

Loredo, J. 2000. Historic unreclaimed mercury mines in Asturias (northwestern Spain): Environmental approaches. In: *Assessing and managing mercury from historic and current mining activities*. EPA. 175-180 pp. San Francisco. USA.

Loredo, J., Luque, C., García Iglesias, J. 1988. Conditions of formation of mercury deposits from the Cantabrian Zone (Spain). *Bulletin of Minéralogie*, V.111, 393-400. Paris.

Loredo, J., Ordóñez, A., Gallego, J., Baldo, C., García Iglesias, J. 1999. Geochemical characterisation of mercury mining spoil heaps in the area of Mieres (Asturias, northern Spain). *Journal of Geochemical Exploration*, 67, 377-390.

Loredo, J., Ordóñez, A., Pendás, F. 2002. Hydrogeological and geochemical interactions of adjoining mercury and coal mine spoil heaps in the Morgao catchment (Mieres, North-Western Spain). In: *Mine water hydrogeology and geochemistry* (ed. P. Younger and N.S. Robins), Geol. Soc. London Special Publications, 198, 327-337.

Loredo, J., Ordóñez, A., Baldo, C., García Iglesias, J. 2003a. Arsenic mobilization from waste piles of "El Terronal" Mine (Asturias, Spain). Geochemistry: Exploration, Environment, Analyis, 3-3, 229-237.

Loredo, J., Ordóñez, A., Charlesworth, S., Miguel, E. De. 2003b. Influence of industry on the geochemical urban environment of Mieres (Spain) and associated health risk. Environmental Geochemistry and Health, 25, 307-323.

Loredo, J., Álvarez, R., Ordóñez, A. 2004a. Release of metals aand metalloids from Los Rueldos mercury mine (Asturias, Spain). Science of the Total Environment

Loredo, J., Ordóñez, A., Álvarez, R. 2004b. The problem of mercury contamination in Asturias (Spain). RMZ – Geoenvironment, 51, 133-136.

Loredo, J., Ordóñez, A., Álvarez, R., García Iglesias, J. 2004c. The potential for arsenic mobilisation in the Caudal River catchment, north west Spain. Applied Earth Sciences. Trans. Inst. Min. Metall. B, 113, B1-b11. London.

Luque, C. 1985. *Las mineralizaciones de mercurio de la Cordillera Cantábrica*. Doc. Thesis. Univ. Oviedo. Inedit.

Luque, C. 1992. El mercurio en la Cordillera Cantábrica. In: *Recursos minerales de España*. García Guinea y Martínez Frías (Coords.). C.S.I.C. Textos Universitarios nº15, 803-826. Madrid.

Luque, C, Martínez García, E., García Iglesias, J., Gutiérrez Claverol, M. 1991.

Mineralizaciones de Hg-As-Sb en el borde occidental de la Cuenca Carbonífera Central de Asturias y su relación con la tectónica: El yacimento de El Terronal- La Peña. *Boletín de la Sociedad Española de Mineralogía*, 14, 161-170. Madrid.

Reimann, C. and Caritat, P. 1998. Chemical elements in the environment. Springer. New York.