

USE OF A TAILINGS POND AS AN AEROBIC WETLAND AT THE CLOSED TROYA MINE (GIPUZKOA, NORTHERN SPAIN)

Vicente Iribar ¹, Felix Izco ², Patxi Tames ², Andoni Da Silva ² and Iñaki Antigüedad ¹

¹ Dept. of Geodynamics, University of the Basque Country
Apdo. 644,
48080 Bilbao, Spain
e-mail: gppirsov@lg.ehu.es

² Diputación Foral de Gipuzkoa. Dpto. de Obras Hidráulicas
Plaza Gipuzkoa s/n.
20004 Donostia - San Sebastian, Spain
e-mail: ptames@abrahidr.gipuzkoa.net

ABSTRACT

The underground Troya mine (The Basque Country) exploited a sulphide ore body located in a karstic aquifer. To exploit the ore the potentiometric level was depressed from an elevation of 435 m.a.s.l. to 190 m.a.s.l., and the spring that had drained the aquifer up to that moment dried up. After the mine was abandoned in 1993, groundwater level recovery began; in 1995, with the potentiometric level at 335 m.a.s.l., water started to flow out from the North Adit, which is the mine access of lowest elevation. The discharging water has a high SO₄ content and noticeable dissolved metals, principally Fe and Zn, although the pH is neutral. Water pollution is caused by the oxidation of pyrite and marcasite; this process takes place when the ore minerals are in contact with both air and water in a zone where the mine rooms are partially flooded. The acidity generated by pyrite oxidation is neutralised by calcite dissolution and CO₂ exsolution. During a two-year period (1995-1997) the mine water outflowed directly to Gesala creek, where the fish population was eliminated due principally to ochre precipitation and the presence of toxic metals. As of June 1997, the mine water has been diverted to the old tailings pond of the Troya mine, and now the water entering the creek is pond overflow. The tailings pond is functioning as an aerobic wetland where the dissolved Fe is oxidized and precipitates as Fe(OH)₃; other metals such as Zn and Mn coprecipitate or are adsorbed on Fe(OH)₃. The fish population in Gesala creek has been recovered.

INTRODUCTION

The selection of an appropriate schedule for the treatment of mine influenced waters depends mainly on the flow and quality of the water to be treated, the determining physical factors of the area, the economic resources available and the final water quality desired. Technical speaking, a difference is generally made between chemical (or active) treatment and passive treatment, in principle, passive treatment offers lower-cost maintenance compared with active treatment, but if the flow-rate is high, the land-take needed for passive treatment is enormous. For example, one of the passive treatments for acid mine waters, in principal, involves increasing the

water's alkaline concentration by using anoxic limestone drains, and later using settling ponds and aerobic wetlands, where the iron hydroxide is precipitated (Kleinman, 1997). The rate of Fe and Mn removal in aerobic wetlands are around 10 - 20 g Fe d⁻¹m⁻² and 0.5 - 1.0 g Mn d⁻¹m⁻². Mn is not removed until Fe concentrations are very low; therefore, the size required for an effective wetland is the sum of the areas needed for both Fe and Mn removal (Watzlaf and Hyman, 1995). In a constructed wetland, average removal of iron was 4.76 g Fe d⁻¹m⁻² (Mitsch and Wise, 1998).

On the other hand, tailings ponds tend to be a source of acid water contamination; one of the methods to control acid water generation in the tailings ponds is to avoid the oxidation of

pyritic material by inundating the pond and preventing oxygen contact with pyrite (Kleinman, 1997). An example of the absence of pyrite oxidation in a saturated tailings pond can be found in Boulet and Larocque (1998). This article will describe the origin of water contamination in the Troya mine, as well as the results of the use of the tailings pond for remedying the contamination.

THE TROYA MINE AND THE TROYA AQUIFER

The Troya mine is located in the province of Gipuzkoa, Northern Spain (Figures 1A, B), in a mountainous area with elevations ranging from 300 to 800 m.a.s.l. The mine exploited a 5 m thick Zn-Pb ore deposit located at the top of a limestone bed

(Fernández-Martínez and Velasco, 1996). The first work on access to the mine was undertaken in 1976; in 1986 ore began to be extracted and in July 1993 the mine was shut down. After the mine was abandoned three types of waste products were left: (1) the mine cavity and the unexploited mineral; (2) the tailings pond; and (3) the N and S dumps, where the inert material from excavation of the mine entrances, along with a few metal sulphides, can be found. Troya is an underground mine excavated by means of the room-and-pillar mining technique, and connected to the exterior via the N and S adits. In the interior there are two levels of rooms connected by an inner ramp; the rooms in the N area are at an elevation of between 200 and 350 m, and those in the S lie between 362 and 392 m; the total volume of the cavity is 0.46 hm³. Figure 1C shows the layout of the wor-

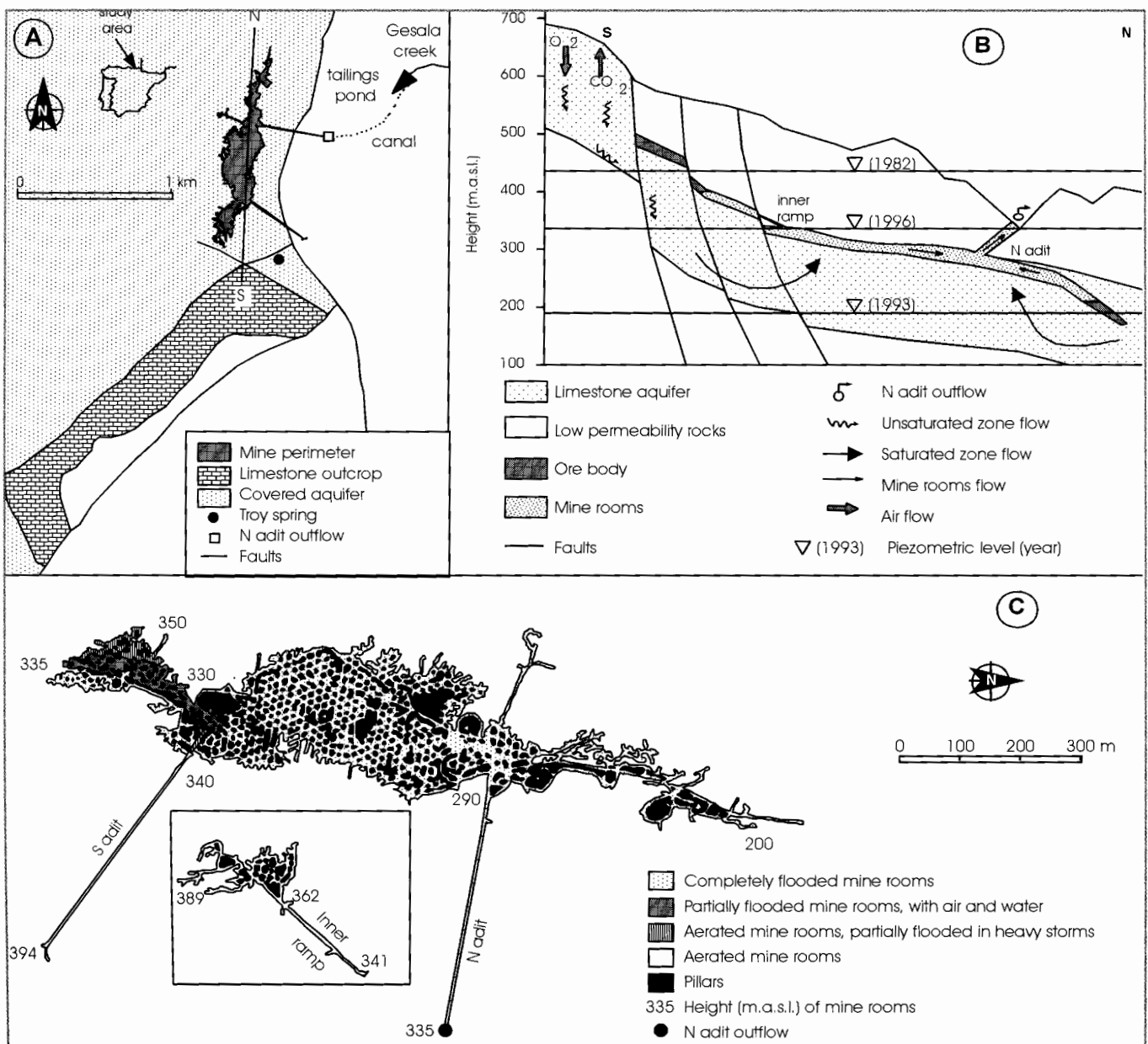


Figure 1. A) Hydrogeological map of the study area. B) N-S schematic hydrogeological cross section, its location is shown in Figure 1A. Mineralization and mine rooms thickness has been exaggerated, usually they are 5 m thick. C) Layout of mine workings, the mine rooms plotted in the continuous rectangle are located in the dotted rectangle.

kings. The original reserves were estimated at 3,700,000 t, and since abandoning the mine it is estimated that some 987,000 t of pyrite-marcasite, 355,000 t of sphalerite, 11,000 t of chalcopryrite and 18,000 t of galena remain, mostly in the pillars.

The 200 m thick limestone bed which hosts the ore body forms the karstic aquifer of Troya. This bed outcrops in the south area and extends to the north in the subsurface; it is confined at the top and the bottom by low-permeability formations (Figures 1A, B). The aquifer is recharged by precipitation infiltration through the limestone outcrop and amounts to some 34 l/s, approximately 50% of the total precipitation (1400 mm/y). Because of the activity involved in exploiting the mineralization, the point of discharge has changed over time. Until 1977 the aquifer was drained by Troy spring, located at 435 m.a.s.l. (Fernández-Rubio et al., 1983), The spring completely dried up in 1982 when draining of the aquifer began. Wells located in the mine were pumped with an average flow of 54 l/s, and the piezometric level dropped to 190 m.a.s.l. (Figure 1B). In January 1994, when pumping ceased, the piezometric level began to rise. In March 1995, when the piezometric level reached around 335 m.a.s.l., the water started flowing out of the N adit, which is the mine access of lowest elevation. Taking into account the current piezometric level, it is assumed that the majority of the rooms in the mine's N area are flooded, but between the 335 and 340 m level, some rooms contain both air and water (Figure 1C).

ORIGIN OF POLLUTION AT TROYA MINE

The N adit outflow has been the main source of pollution at the abandoned mine. In 1976, prior to draining the mine, the Troy spring water was used for urban water supply. Between 1983 and 1993, the pumped water continued being used for urban supply although SO_4 concentration increased until reaching 300 mg/l. Presently, the water flowing from the N adit contains more than 1,000 mg/l of SO_4 and dissolved metals (Table 1). In March 1995, when this water reached Gesala creek (Figures 1A, 3A), the creek's entire fish population was eliminated (Izco et al., 1996), due to the high presence of toxic metals, such as Al and Zn, and the precipitation of Fe hydroxides in the river bed.

The N adit water comes from the aquifer and circulates through the mine rooms. Its chemical composition is the result of the oxidation of pyrite, marcasite and of other sulphides in the mine rooms where ore is in contact with air and water. The acidity resulting from the oxidation of pyrite is neutralised by dissolution of calcite and dolomite (reaching gypsum saturation), and by CO_2 exsolution (Webb and Sasowsky, 1994). Subsequently, as the water makes its way to the N adit, all of the O_2 is consumed, as the discharging water contains dissolved NH_4 , originating from NO_3 reduction and dissolved Fe, Zn and other metals. A hydrochemical balance performed for the first 28 months of the N adit outflow (Iribar et al., 1999), shows that during the period of the balance 2,100 t of pyrite were oxidised, 2,900 t of calcite were dissolved and 1,600 t of $\text{Fe}(\text{OH})_{3(s)}$ were precipitated. The amount of pyrite oxidised is 20% of the pyrite per m in the 335-340 m vertical, which is the zone where the oxidation is assumed to be produced, but it is only 0.3% of the submerged pyrite. Oxygen consumption is equal to 8,420 m^3/d of air, suggesting there is significant air circulation in the rooms; the entrance of air is possible through the limestone outcrop (Figure 1B).

Since 1995, the following chemical changes have been observed in the water flowing from the N adit (Figure 2). The SO_4 and metal content has decreased, this may have been the result of the diminishing ore supply in the area of the pyrite oxidation, or of the precipitation of Fe hydroxides on the pyrite surface, which forms a barrier which prevents the diffusion of O_2 , and continually slows down the rate of oxidation (Nicholson et al., 1990). The evolution of calcium content was similar to that of SO_4 , suggesting that calcite dissolution follows pyrite oxidation. The concentration of Fe, Zn, Ni, Mn, Al and NH_4 dropped rapidly in the first months after water began flowing through the N adit. This was the first flush (Banks et al., 1997), in which the sulphate hydrate crusts formed on the mine walls were washed.

The possibility of plugging up the N and S adits in order to raise the piezometric level to 435 m has been considered. This action could restore the Troya spring, completely flood the mine chambers and avoid mineral-water-oxygen contact, but in addition to plugging up costs, there are 15 mining exploration boreholes below the 435 m level, and water would flow from them causing additional problems, such as landslides.

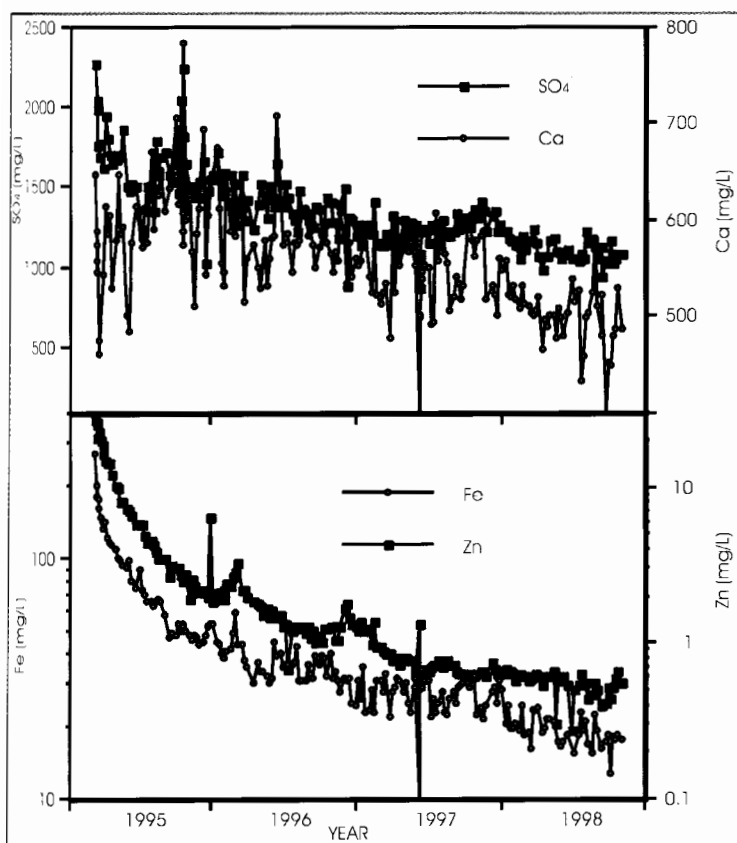


Figure 2. Evolution of SO_4 , Ca, and dissolved Fe and Zn in the North adit outflow. Note that logarithmic scale has been used for Fe and Zn.

	Before diverting to the pond (26 May, 1997)					After diverting to the pond (26 May, 1997)				
	N adit	Canal	Tailings pond	Pond's filtrations	Gesala creek	N adit	Canal	Tailings pond	Pond's filtrations	Gesala creek
PH	6.7	7.9	7.6	7.7	7.9	6.7	7.9	8.1	7.7	8.2
HCO ₃ ⁻	358	297	54	110	269	361	315	211	130	205
Cl ⁻	18	15	22	56	20	14	15	17	41	18
SO ₄ ²⁻	1440	1360	631	755	1300	1150	1180	944	897	909
Ca ²⁺	578	522	234	307	521	510	505	397	360	379
Mg ²⁺	69	65	24	21	61	45	47	38	33	35
Na ⁺	22	20	11	41	22	28	23	25	45	25
NH ₄ ⁺	0.94	0.74	0.21	0.03	0.69	0.54	0.42	0.13	0.01	0.23
Fe	41	25	0.32	0.04	24	21	13	0.57	0.03	0.64
Mn	0.88	0.83	0.81	0.02	0.81	0.50	0.46	0.25	0.02	0.27
Zn	1.94	2.70	8.30	0.04	2.35	0.61	0.95	0.28	0.03	0.24
Ni	0.041	0.034	0.028	0.006	0.030	0.021	0.018	0.015	0.008	0.012

Table 1. Water quality (median values in mg/l) in the Troya system. Metal data are from unfiltered acidified samples. Sampling points are shown in Figure 3A.

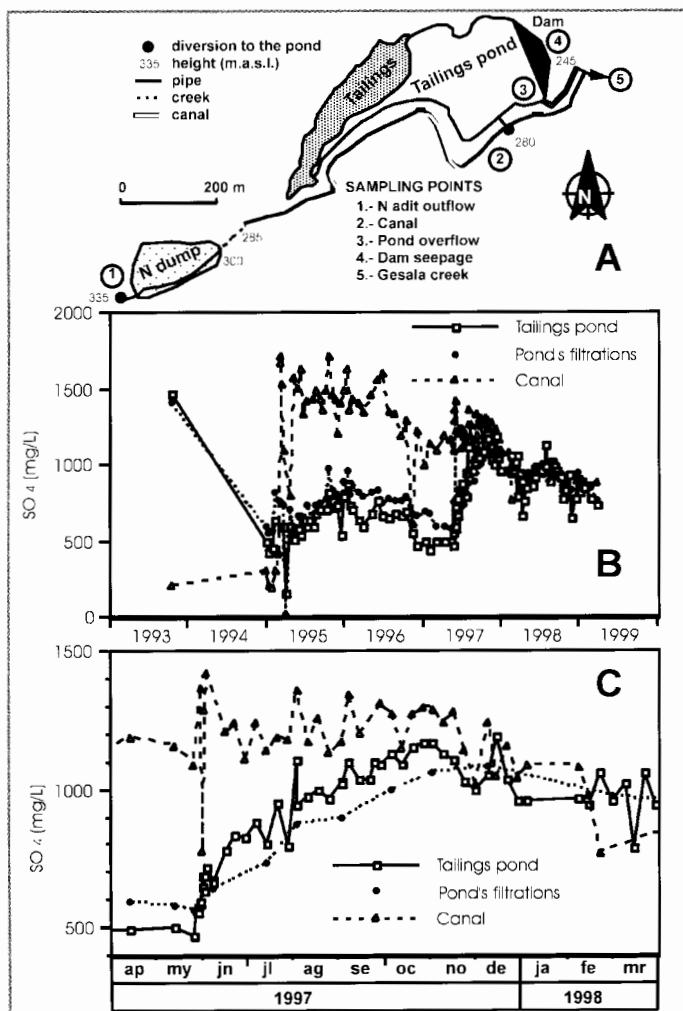


Figure 3. A) Location of the tailings pond and sampling points. B and C) Evolution of SO₄ in the canal, tailings pond and pond's filtrations. Temporal scale in Figure 3B is broader than in Figure 3C.

THE TAILINGS POND AT TROYA MINE

The mineral extracted from the Troya mine was crushed and ground and the mineral values of Pb and Zn were separated in a flotation plant. The tailings from this treatment went to a pond located in the Gesala creek valley (Figure 3A). The pond's retaining dam has a clay core with rock riprap surface protection; maximum tailing height is 30 m, and the pond has a total capacity of 1,050,000 m³. Owing to the fact that the mine was closed earlier than planned, 350,000 m³ of the pond remain unfilled, therefore leaving a pool covering 50,500 m² of surface area and 6 m deep. In order to build the pond, Gesala creek was diverted through a canal which drains a surface area of 0.63 km² plus receiving water from the N adit. The pond, in addition to direct precipitation, drains a surface area of 0.18 km². The filtrations of the dam appear at its foot with an average flow of 7 l/s.

Up until May 26, 1997 the canal led directly to Gesala creek. Since May 26, 1997 the canal water (and hence the N adit water) has been diverted to the tailings pond to take advantage of its purifying capacity, and the water flowing into Gesala creek is pond overflow. This action has changed the pond water's residence time: before diverting the canal to the pond, residence time was approximately two years; following the diversion, residence time dropped to three months.

The tailings are composed basically of pyrite, with a significant metals content (Fe, Zn, Pb, Cu, As, Mn, Ni, Cd, Cr and Hg). Most of the tailings are submerged, but due to the fact that the tailings were dumped at the tail of the reservoir, a tailings delta was formed above the water level of the pond in that area (Figure 3); presently this "delta" is covered with inert revegetated soil.

RESULTS

Since 1993, the Diputación Foral de Gipuzkoa (Provincial Government) has taken samples in the Troya water system. The location of the sampling points and their results can be seen in Figures 3 and 4 and in Table 1.

Since 75% of the water flowing through the canal comes from the N adit, the hydrochemistry at both sampling points is similar. The Fe content is somewhat inferior in the canal, as part of it precipitates and settles between the N adit and the sampling point; however, the precipitation of hydroxides is a relatively slow process (Brooshears et al., 1996; Grundl and Delwiche, 1993) and the Fe concentration in the canal is important.

Before the water from the canal was diverted into the pond, the pond water had a relatively high metal content, especially Zn and Mn, although a low Fe content. The origin of the metals in the pond might be explained by the oxidation of the tailings located above the pond's water level, or by the dumping of the flotation plant in operation until mid-1993. Any dissolved Fe would rapidly precipitate in the pond. When the canal water was diverted to the pond it renewed the pond water in a period of five months as is shown by the concentration of SO₄ (Figure 3). Now, the dissolved Fe in the canal water effectively precipitates in the pond. The pond water is mixed and there is no noticeable stratification; the dissolved O₂ is close to saturation level, the pH has risen to 8.1, and there has been a notable ongoing drop

in concentrations of Mn, Ni, and particularly of Zn (Figure 4) in the tailings pond water. Unlike the evolution of SO₄ in the pond, the drop in the concentration of Zn and Mn was seen almost immediately. Moreover, the concentration of these metals in the pond is less than the canal water and less than that of the water previously found in the pond. The dilution mechanism is not enough to explain this decline, although it may be due to the fact that these metals coprecipitate and are adsorped with the precipitated goethite (McGregor et al., 1998).

In addition to pond overflow, the other contribution to Gesala creek is pond filtration. The evolution of the SO₄ content in the filtrations indicated that the main contribution of the filtrations comes from the pond water, and that the average residence time of the interstitial water of the submerged tailings is on the order of one month. The principal differences in the chemical quality between the pond water and the filtration water are: (1) the filtration water has a higher concentration of Cl and Na, and (2) the metal content (Zn, Mn, Ni and Fe) is much lower in the filtrations. The increase in Cl and Na concentration may be due to the existence of a small saline spring located below the pond, as 'Gesala' is the Basque word for brine. The low metal content in the filtrations might be explained by their absorption by the organic material found on the surface of the pond sediments.

Since the time the water in the N adit was diverted into the pond, the quality of the water that reaches Gesala creek (pond overflow instead of N adit water) has improved, and recuperation of water quality in Gesala creek has been significant (Tables 1, 2). The concentration of metals decreased and the ochre accumulated in the river bed has disappeared, washed away by floods. In terms of fish life, in Gesala creek, which had been home to an important population of *Phoxinus-phoxinus*, the fish population was virtually eliminated in 1995, in 1997, following diversion of water to the tailings pond, recuperation was substantial.

Any action for remedying water contamination in abandoned mines should take the entire mining installation into account, including mine rooms, mine refuse and tailings ponds. In the case of Troya, the necessary surface area of an aerobic wetland for treating the water from the N adit (maximum flow of 80 l/s, and 20 mg/l of dissolved Fe) would have been almost 14,000 m². The use of the tailings pond as an aerobic wetland

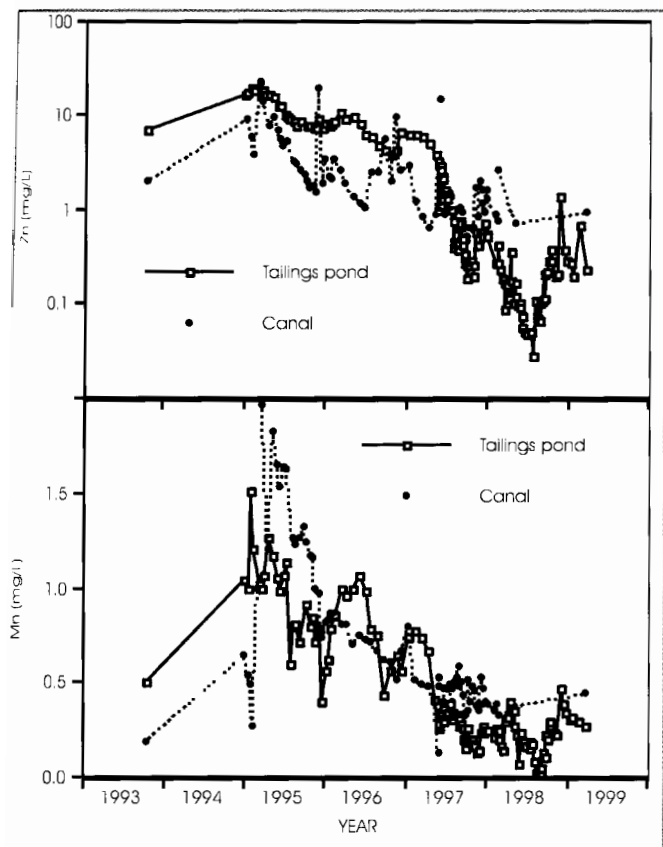


Figure 4. Evolution of Zn and Mn in the canal and the tailings pond. Note that logarithmic scale has been used for Zn and normal scale for Mn.

Year	Location	Fish population		Invertebrates	
		Phoxinus specimens	surface (m ²)	BMWP score	Number of families
1995	Pond's upstream	128	258	127	22
	Pond's downstream	1	364	14	5
1997	Pond's upstream	95	212		
	Pond's downstream	32	380		

Table 2.- Biological impact of mine water in Gesala creek.

has not only been an inexpensive passive treatment system, but the addition of water from the N adit to the pond has enhanced the pond's water quality.

ACKNOWLEDGEMENTS

This work was funded by the Diputación Foral of Gipuzkoa, the University of the Basque Country (UPV 001.310-EA214/96 project), and the CICYT HID96-1315 project (Spanish Government).

REFERENCES

- Banks, D., P.L. Younger, R.T. Arnesen, E.R. Iversen and S. Banks, 1997. Mine-water chemistry: the good, the bad and the ugly. *Environ. Geol.* 32 (3): 157-174.
- Boulet, M.P. and A.C.L. Larocque, 1998. A comparative mineralogical and geochemical study of sulfide mine tailings at two sites in New Mexico, USA. *Environ. Geol.* 33 (2/3): 130-142.
- Brooshears, R.E., R.L. Runkel, B.A. Kimball, D.M. Mcknight and K.E. Bencala, 1996. Reactive solute transport in an acidic stream: experimental pH increase and simulation of controls on pH, aluminium, and iron. *Environ. Sci. Technol.* 30: 3016-3024.
- Fernández-Martínez, J. and F. Velasco, 1996. The Troya Zn-Pb carbonate-hosted SEDEX deposit, northern Spain. *Soc. Econ. Geol., special pub.* 4: 364-377.
- Fernández-Rubio, R., R. Fernández, J.A. Botín and A. Lavandeira, 1983. Preliminary hydrogeological investigations in the Troya Mine (Guipúzcoa). *Hidrogeología y Recursos Hidráulicos, AEHS, Madrid (VIII)*: 115-124.
- Grundl, T., J. Delwiche, 1993. Kinetics of ferric oxyhydroxide precipitation. *J. Contam. Hydrol.*, 14: 71-97.
- Kleinman, R.L.P., 1997. Mine drainage systems. In *Mining Environmental Handbook* (Marcus J.J. Editor), ICP, London: 237-244.
- Iribar, V., F. Izco, P. Tames, I. Antigüedad and A. Da Silva, (in press). Water contamination and remedial measures at the Troya abandoned Pb-Zn mine (The Basque Country, Northern Spain). *Environ. Geol.*
- Izco, F., P. Tames, A. Da Silva, H. Fano, 1996. Afección ambiental producida por la explotación minera en el acuífero urgoniano de Troya (Gipuzkoa). *Proceedings of the Congress on water resources in karstic regions: exploration, exploitation, management, environment, Vitoria-Gasteiz, Spain.* 105-120.
- Machemer, S.D. and T.R. Wildeman, 1992. Adsorption compared with sulphide precipitation as metal removal processes from acid mine drainage in a constructed wetland. *J. Contam. Hydrol.*, 9: 115-131.
- Mcgregor, R.G., D.W. Blowes, J.L. Jambor and W.D. Robertson, 1998. The solid-phase controls on the mobility of heavy metals at the Copper Cliff tailings area, Sudbury, Ontario, Canada. *J. Contam. Hydrol.*, 33: 247-271.
- Mitsch, W.J. and K.M. Wise, 1998. Water quality, fate of metals, and predictive model validation of a constructed wetland treating acid mine drainage. *Water Research* 32 (6): 1888-1900.
- Nicholson, R.V., R.W. Gillham and E.J. Reardon, 1990. Pyrite oxidation in carbonate-buffered solution: 2. Rate control by oxide coatings. *Geochim. Cosmochim. Acta* 54: 395-402.
- Watzlaf, G.R. and D.M. Hyman, 1995. Limitations of passive systems for the treatment of mine drainage. *National Association of Abandoned Mine Land Programs, 17th Annual Conference, French Lick, Indiana, October*, 186-199.
- Webb, J.A. and I.D. Sasowsky, 1994. The interaction of acid mine drainage with a carbonate terrane: evidence from the Obey River, north-central Tennessee. *J. Hydrol.* 161: 327-346.