# Tinto River pollution: remediation versus conservation

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#### ABSTRACT

One of the essential elements on the hydric pollution is its capacity of destruction or change of the established aquatic ecosystems. Then, on the classical descriptions about the acidic mine drainage (AMD) it is unavoidable the reference to its effect in the destruction of the aquatic life. In consequence the water courses intensively affected by AMD have always been considered as environments devoid of life and candidates to decontamination and restoration. However, on the last two decades, the extensive research work developed on extremophiles have added new perspectives to this assumption: Rivers historically polluted by AMD as the Tinto River, with more than 500 years of intensive mining began to be considered as high complex ecosystems with high scientific interest. In view of this alternative the environmental administration has a difficult dilemma: decontamination or conservation.

### INTRODUCTION

Huelva province is located in south-eastern Spain and a great pat of its history, economy, population, culture and environment, have been conditioned by the existence of the named Iberian Pyrite Belt. With a length bigger than 200 km, an average wide of 40 km, and estimated reserves in the order of 750 millions tonnes of sulphide ore, the Pyrite Belt extends from Sevilla province, cross Huelva province from east to west and ends in Portugal.

Exploited from prehistoric times, Tartessus, Phoenicians, Romans and Arabs worked in mines of the belt. However, the biggest mining splendour took place in the second part of the 19th century, caused by the high industrial demand of ore. At this time, the affluence of foreign capital gave place to the opening of more than a hundred of new mines and the reactivation of others mines which have been previously exploited such as Riotinto. In order to develop the growing pyrite mining industry, dams, railways infrastructure, bridges, piers for ore embankment, etc., were constructed. This new activity in surface and underground mining, gave place to innumerable mining structures: tunnels, shafts, open pits, tailing dams, spoil heaps, etc. In these operations, millions tonnes of pyrite have been moved to surface entering in contact with oxygen and water, and millions tonnes of mining wastes (low grade ore, enclosing rocks, slags, ashes, etc.) were produced and stored on land.

As consequence of the contact between sulphides and air and water, the phenomena of acidic water, present historically in the area in a natural way, acquired a new and spectacular magnitude by formation of mine waters. Currently, the mining activity has almost been finished but the great number of abandoned mines and mining wastes constitute "a perpetual pollution machinery": where year after year, the rains give place to surface watercourses and leachates which increase the pollution in river, estuary and coastal waters and sediments.

The present reality is that surface water pollution in the area is associated both to naturally enriched rocks and abandoned mine sites. The increase of secondary permeability in abandoned mine works and waste materials stored on land contribute to increase the potential of geological materials to develop acidic effluents when they are in contact with water. In this frame of reference it will not be possible to achieve the overall goal of the Water Framework Directive relative to the good status for all of Europe's rivers by 2015 (European Commission, 2000).

## **GEOGRAPHICAL FRAMEWORK: THE TINTO RIVER.**

The Tinto River is located in Southwester Iberian Peninsula, in Huelva province. It rises in the Padre Caro peak, at a height of 646 m and it receives a tide influence 67 km. downstream, close to Niebla village, at a height of 40 m. After the loss of its fluvial character the Tinto River waters form an individual estuary of 21 Km. length: Tinto River waters together with Odiel River waters flow into the Atlantic Ocean.

The Tinto River develops a catchment of 730 km<sup>2</sup>, being the Jarrama and the Corumbel Rivers the main tributaries. The climate of the catchment is of dry Mediterranean type, with an annual average temperature in the order of 17,5 °C, with soft winters and hot summers. Precipitations are marked by a strong temporal irregularity, showing an average value of 760 mm/year. Spatially it varies from 850 mm/year in the high part of the catchment to 600 mm/year in the lower part of the catchment.

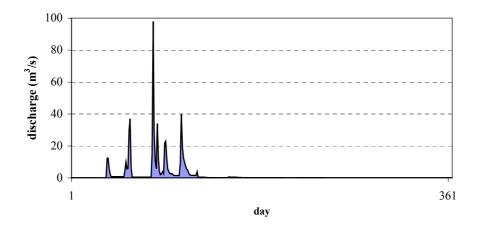


Figure 1. Variation of precipitations in the catchment along the year 2004.

The regulation of two of the tributaries has considerably reduced the average yearly contribution, firstly estimated in 90  $\text{Hm}^3$ . The yearly values of this contribution show quite different values related to the extreme variability of the pluviometry regime in the area. In general terms, it can be asserted that the hydric regime of Tinto River fluctuates between two extreme situations, intense low waters which temporally can be very important, and sporadic floods but with very significant volumetric values. In this way, during the very rainy years, only in 15 days it is produced more than 65% of the total yearly contributions. In the main riverbed, after the rains, the only flow circulating is the coming from groundwater that in this catchment are mainly from mining origin. On the other side, excepted very rainy years during the months of June, July, August and September, and some times in part of May and October too, the flow circulating in the lowest part of the river is practically null, accentuating the phenomena of concentration by evporation.

## THE ENVIRONMENTAL FRAMEWORK: THE TINTO RIVER POLLUTION.

Water pollution related to the long-term fate of mineralized rocks and tailings in this historic mine site occurs in the form of perennial release of contaminated leachates enhanced by specific events associated to seasonal runoff flowing through unreclaimed waste surfaces or mineralized rocks.

All the acidic pollution related to sulphates and metals transported by the Tinto River as far as its mouth, is contributed on the first 10 km of its course. In this section, the River flows through a sub-catchment of 36 km<sup>2</sup>, where the mining exploitations of Peña de Hierro and RioTinto, are located (at this site has been initiated the mining in the area 5000 years ago).

The River receives directly the effluents from Peña de Hierro, Planes Shaft, Alfredo Shaft and indirectly from Atalaya Open Pit. Equally it receives the leachates from the spoil heaps of Peña de Hierro, Tejonera, Dehesa, Nerva-Norte, Zarandas and Nerva-Sur, Naya, Cerda, Cerro Colorado, and others, which occupy an area near 9000000 m<sup>2</sup>. In order to have an approximate idea of the magnitude of pollution in the Tinto River source, it is desirable to show that only the sulphide masses of RioTinto mines, of 500 Millions tonnes, constitute an almost continuous bed of 5 km. length, 750 m wide and 50 m thickness (IGME, 1983). On the other side the volume of spoil heaps in this area is near to 26000000 m<sup>3</sup> and they extend on 2000000 m<sup>2</sup>. It is necessary to have in mind that along 5 km., the river flows confined between pyritic wastes. At the end of the mined area, the Tinto River waters are extremely acidic and they show the typical reddish colour, with the banks showing a yellow colour and without any type of vegetation, which maintains until the mouth in the estuary. Data on water quality at the end of the mined area and for the period comprised between 1990 and 2003 is presented in table 1.

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	Maximum	Minimum	Average
pH (units)	1,6	2,6	2,2
SO₄ <sup>=</sup> (mg.l <sup>₋1</sup> )	23939	6769	16252
As mg.l <sup>-1</sup> )	33,7	3,6	13,6
Cd (mg.l <sup>-1</sup> )	10,2	0,2	1,9
Cu (mg.l <sup>-1</sup> )	144,0	34,1	49,1
Cr (mg.l <sup>-1</sup> )	2,6	0,1	0,5
Fe (mg.l <sup>-1</sup> )	7400	656,4	3269
Mn (mg.l <sup>-1</sup> )	129,0	5,8	54,0
Ni (mg.l <sup>-1</sup> )	51,2	0,2	2,5
Pb (mg.l <sup>-1</sup> )	2,0	0,1	0,5
Zn (mg.l <sup>-1</sup> )	726,1	27,1	364,3

# Table 1. Tinto River source: pH and heavy metals concentrations in water (mg/l), at the end of the mined area. Period 1990-2003.

At this monitoring point the flow of the Tinto River has been estimated in 5.800.000m<sup>3</sup> year (AMA, 1990), although this data must be revised because the measures have been made in years especially rainy. After this point, the river does not receive more polluted contributions but dilution. Then, in the mouth the water pollution is only a 20-30% of the correspondent to the pollution in the upper part of the river. Data on water quality at the mouth of Tinto River in the estuary and for the period comprised between 1990 and 2003 is presented in table 2.

	Maximum	Minimum	Average
pH (units)	1,8	3,1	2,5
SO₄ <sup>⁼</sup> (mg.l <sup>-1</sup> )	15710	178	3285
`As (mg.l⁻¹)	28,0	0,01	1,9
`Čd ́ (mg.l⁻¹)	5,1	0,01	0,5
`Ču ́ (mg.l⁻¹)	365,0	4,6	42,8
Čr (mg.l <sup>-1</sup> )	1,9	0,01	0,1
Fe (mg.l⁻¹)	4.767	7,0	615,0
Mn (mg.l⁻¹)	109,0	0,9	16,1
Ni (mg.l <sup>-1</sup> )	17,4	0,03	0,9
Pb (mg.l <sup>-1</sup> )	1,0	0,01	0,2
Zn (mg.l <sup>-1</sup> )	591,1	8,2	90,1

 Table 2. Mouth of Tinto River in the estuary: pH and sulphate and heavy metals concentrations in water (mg/l). Period 1990-2003.

The water pollution is accompanied along the riverbed by a strong pollution of sediments. The high contents in Fe (21.6%) in these sediments remember the values of this metal in pyrites and complex sulphides from mines (32-42%). In Table 3, appear the average values of pollution in sediments in the high part of the river, in the mouth and 10 km downstream, inside the estuarine zone. Spatial average: average value of 70 samples by year obtained in 5 points of river (upper, medium and low course) during 14 years.

	Mouth	High estuary	Spatial average
	39600	40600	32000
(mg.kg <sup>-1</sup> ) As	857	652	2103
(mg.kg <sup>-1</sup> ) Cd	2	2	3
(mg.kg⁻¹) Cu	550	725	864
(mg.kg⁻¹) Cr	42	61	36
(mg.kg <sup>-1</sup> ) Fe	178250	179500	216000
(mg.kg⁻¹) Hg	3	2	9
(mg.kg <sup>-1</sup> ) Mn	177	138	183
(mg.kg⁻¹) Ni	11	20	11
(mg.kg⁻¹)			
Pb (mg.kg <sup>-1</sup> )	755	765	4058
Zn (mg.kg <sup>-1</sup> )	593	638	954

#### Table 3. Average values of heavy metals in sediments of Tinto River and estuary (mg/kg). Period 1990-2003.

It is important do not forget that the acidic mine drainage produces in the Tinto River two types of environmental deficits: a direct action by pollution of waters and sediments and another one indirect by the pollution that the fluvial discharges produce in the estuary. The contributions of the Tinto and Odiel Rivers to the estuary have been estimated in 17000 kg/h of sulphates and 2200 kg/h of heavy metals. The Tinto River in spite of its chronic low water, in its sporadic discharges contributes with 35% of metallic charge before mentioned to the estuary, and in the case of the iron it reaches the 53%.

In Spain, as it occurs in other European countries, there is not a specific regulation for mine waters then, legislation on mining management on the one hand, and on water management on the other hand, must be have in consideration (Loredo et al., 2004). As consequence of the lack of a specific legislation for mine waters at a national level, the institutions and organisms that must be considered in relation to mine waters management are those in charge of mine and water issues. Then, as competences in mine and water issues are distributed among the Central Administration of the State and the Autonomous Communities, this fact leads to a distribution of competences between different Administrations, and different organisms and institutions inside these Administrations. At an European level, the combination of new European environmental policy proposals with provisions for mine water pollution to a liability regime which would assign liability for an environmental damage caused is a promising solution to provide a high degree of environmental protection in regards to environmental impact from mining in Europe.

The Water Framework Directive presents a breakthrough in European water policy, combining approaches of emission controls tackling pollution at the sources, and water quality standards to be achieved for all water bodies, plus phasing out particularly hazardous substances. The Water Framework Directive demands the establishment of control networks and vigilance programs, and the current networks and programs in Spain are clearly insufficient to fulfil what the Directive requires.

# THE ACIDIC CONDITIONS OF TINTO RIVER: DECONTAMINATION OR CONSERVATION

The first known written reference on Tinto River pollution is an inform sent in 1556 to the king Felipe II by the priest Diego Delgado: "In this river there is any type of fish nor living creature, nor the people or the animals drink these waters. Another property of the water is that if iron is put there, in some days it is consumed; this has been proved by myself and I put a living frog in the river and she was died without leave the water"

Mid twenty century, the Tinto River is nominated as "rubbish river" and "water charged of sulphuric acid, iron salts and others, which impede the animal and vegetal live" (Pinedo, 1963). Thirty years later The General Directorate of the Environment classifies the Tinto River as the river with worst quality of all rivers in Spain, gives to it the nomination of "industrial river" which can receive any type of spills (DGMA, 1987). In 1987, the Environmental Agency of Andalucía (AMA) initiated a Plan for pollution control and rehabilitation of the Huelva estuary. This estuary, formed at the mouth of the Tinto and Odiel Rivers presents big metallic pollution problems in water, sediments and biota. The pollution sources were the fluvial contributions from Tinto and Odiel Rivers and the industrial spills of one of the biggest chemical complexes of Spain, located in Huelva. Then, together with the correction of the industrial spills, the Environmental Agency of Andalucía has undertaken a Correction Plan for Tinto and Odiel Rivers. This Plan was financed by the E.U. and began in 1990. At this time, a group of researchers entered in contact with the Environmental Agency of Andalucía in order to transmit the microbiological importance of the Tinto River and to propose the abandonment of its regeneration.

The microorganisms named extremophiles, which live in extremes conditions for the life, have revolted the interest of a great number of researchers (microbiologists, ecologists, physiologists, biochemists, etc.). The techniques developed have permitted spectacular advances in the knowledge of the microbial world and its importance in the global ecology of the biosphere. In fact, the classical concept of biodiversity, based previously in morphological differences, has evolutioned in the scientific field towards a new concept of phylogenetic biodiversity based in the differences in the genetic sequence. Then, the microbial life assumes a special importance: it is possible to assert that almost the 90% of biodiversity in the earth is microbial (Woese et al 1990, Pace 1997). Into the family of the extremophile microorganisms, the acidophiles are microorganisms living in very acidic environments. The scientific interest on the acidophile microorganisms has followed a path similar to the other extremophiles. Initially, the research was devoted to the role played in the formation of acidic waters (Colmer et al. 1947, Colmer et al. 1949, Temple et al. 1951, Temple et al. 1953, Malouf et al. 1961, Le Roux et al. 1973). On the two last decades the research areas have experimented a great increase and diversification (Gómez et al. 1997, D. B. Johnson et al. 2003, Brettet al. 2003 Gónzalez-Toril et al. 2003).

In spite of the wish of the Environmental Agency to decontaminate the Tinto River, a whole of multidisciplinar researches over extremophile microorganisms (acidophiles) in the river has being developing during the last 15 years. Like other extremophiles the applied techniques and the types of researches have gave place to the publication of new information about the Tinto River, characterising this river as a singular ecosystem gifted of a great diversity of life forms of the three groups: Archaea, Bacteria, and Eukarya (Amaral Zetter et al 2002; González-Toril et al. 2003; López-Archilla et al. 2004).

There are new researches about the possibility that the current extreme acidity is a phenomenon earlier than the appearance of the mining activities in this catchment, 5000 years ago (Fernandez-Remolar et al., 2003; Johnson et al., 2003). In the field of the Exobiology, it can be emphasized the interest exhibited by the NASA in the Tinto River as zone with similarities to Mars planet (Fernandez-Remolar et al., 2003), anyway the development of some projects in course of the Tinto River related to the research of life in Mars, accomplished by AMES-NASA, INTA, CAB, etc., and financed by the Program of Astrobiology Science and Technology for the Planetary Exploration of the NASA, the Ministry of Science and Technology and the Institute National of Aerospatiale Technique (INTA) from Spain. All these scientific facts and their mediatic spreading has converted the Tinto River in a paradigm of the Acidic Mine Drainage, pollutant of the estuary and the littoral in a system scientifically unique.

The immediate consequence of this new valuation of the reality of the Tinto River between diverse environmental circles is that the destruction of the fluvial ecosystem by decontamination plans should be extensively meditated. The same concept of pollution included in the Framework Directive "introduction of substances which can be harmful for the quality of the aquatic ecosystems" recovers a new perspective.

All these facts are reflected in the technical documents of the Network of Protected Natural Spaces of Andalucía (RENPA), the protected spaces network of regional scale more important in number and surface in the European Union. In 2003, the RENPA proposed to include the Tinto River as a protected space on the basis of the Tinto River is a unique enclave in the world, as well for the chromatic beauty as for the exceptional environmental conditions. The waters mainly characterized by acidic pH, red colour and high content in ferruginous salts, with low content in oxygen and polluted from many centuries ago by the ferric sulphate, refuge a great diversity of microorganisms –many of them still without be catalogued- which feed only on minerals and they adapt to extreme habitats. The area was selected by the U.S. Spatial Agency (NASA) to study these forms of life, given to the probable similarity between their environmental conditions and the supposed conditions of the Mars planet (RENPA, 2003).

Finally by the Act 558/2004 of 14 December, the Tinto River is included in the Protected Natural Spaces Network of Andalucía, under the figure of "Protected Landscape". In the introduction of this Act it is included: It results of a great interest by the characteristics offered by the Tinto River, related to the extractive industry, a very acidic pH and a high content in ferruginous salts which allow the life of species surviving to these extreme parameters. It must be emphasized too the importance of the Tinto River for the existence of the aquatic species isolated as consequence of the particular physico-chemical nature of the waters.

In the Act, it is included too that one of the objectives is to maintain the peculiar characteristics of the Tinto River waters which allow the existence of singular species adapted to extreme conditions as consequence of the high acidity and high content in ferruginous salts. And, for that, in the conditions of use and management of the space it is established that: It will not be possible to realize any activity susceptible to alter the elements and the dynamic of the natural processes which develop in this space. The regeneration actions for polluted areas to be developed in this space must take into account the characteristics of the mining landscape and the singularity of the waters.

It is difficult to articulate this protection with the objectives of the Directive 2000/60/CE. The AMD control measures projected for the Tinto River (regulation dam, mining effluents, treatment plant, etc.) need inversion and maintenance costs unapproachable for a mining sector plunged in a heavy economical crisis. This fact, together with the search of new control measures by passive treatments expanded in the time the adoption of solutions.

During the decade of the 1990's the image of the river continued associated to its strong mining pollution, to its uselessness as hydric resource, to the absence of life in waters anyway the absence of flora in its banks, and the harmful of the discharges for the fauna of the Huelva estuary (Wamba et al. 1991, Conde, 1993, CMA, 1995, Sáinz 2000). Some projects have been accomplished on the last years and other are now in course in order to know the applicability of the named passive system to reduce the level of pollution at assumable costs.

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