THE TINTO RIVER: A VERY OLD ACID RIVER OF THE IBERIAN PYRITE BELT

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ABSTRACT

This paper describes the preliminary results of a study that we have begun to do for a complete study of metal contamination in a very polluted river. The study is necessary for to identify, characterise, and develop management strategies and following for its acid river.

The Tinto River is a very polluted river because of the working of the sulphide mines in its basin. The upper part of their common basin (4.000 km²) includes possibly the largest sulphide mineralization in the world (Iberian Pyrite Belt). The Rio Tinto Massif Sulphide Deposit contained about 1000 Mt of sulphides.

The mines have been extensively worked on since the Chalcolithic until the Roman period and the 19th century until our days. As a consequence of the weathering the pyrite is combined together with the oxygen, water and helped by microbial processes, thus hence acid mine drainage. These acid mine drainage with very low pH variying from 1.5 to 2.5, along 93 km from its source zone down to the estuary zone.

These acid mine waters are metal-rich, contain extremely high concentration ranging from 770-1500, 530-950 and 3-5 μmol/l for Zn, Cu, Cd respectively. Furthermore, the sediments of the 70 km basin depict high trace-metal concentration about thousands of ppm for Fe, Cu, Zn.

In order to treat all these problems, we are treating to look for possible solutions the great serious damages in environment (basin and estuary). Making a global evaluations of all factors that are present in this questions as well as climatology, sea-levels, hydrology, contaminant-point, chemical analysis data will be possible to obtain conclusions for the resolution of this problem and the future recuperation of this area.

INTRODUCTION

The Tinto River it is located in the Southwest of the Iberian Peninsula, in the county of Huelva, being, in turn, limit with the county of Seville. It travels from North to South the whole county uniting to the Odiel River in their last kilometres, forming a wide estuary, and ending in the Gulf of Cádiz.

In their to lapse it crosses all the palaeozoic materials first: shales, quartzites and vulcano-sedimentary rocks and to the South it lapses on the Neogene-Quaternary materials of the Guadalquivir Depression: calcareous, sands, conglomerates, loams, clays, sandstones, etc., for, finally, to go into in the swamps of the estuary.

The Tinto it is possibly a acid river from the Tertiary, with a high degree of contamination due to the contributions of acid waters that receives in their basin of the mining exploitations of sulphides and their facilities of benefit of minerals. The river received for these characteristics special numerous denominations through the centuries, Urium "to burn" for the Romans, Lahsar or Lamis, also Libla, Saquia or Azequia of the Arab, going back D.C. to the first half of the XIV century when already figure in the Chronic Geral of Espanha 1344 like Tinto river.

The regime of the river corresponds to the pluvial mediterranean Andalusian of the area (Wamba. 1991) depending its flow in bigger or smaller quantity of the precipitations, that

makes have a maximum at the beginning of the spring, a winter minimum not very accused and, on the other hand, a very lingering summery minimum of 3 to 4 months. It registers grown winter and scarce flow in summer. In periods of rains the river experiences grown very quick that they cease as soon as they make it the rains. Grown happiness has their origin in that had an accident of their high basin and in the little permeability of the lands that, also, they are exempt of vegetation (Figure 1).

Figure 1. Channeling of the Tinto River.

Starting from the dates gathered by the Guadiana Hydrographic Confederation it is obtained to half it valued of instantaneous flow of 4,71 m³/s and an instantaneous flow tip of 100 m³/s, being approximately the dear annual half contribution of 90 million m³ and their hydrographic basin of 720 Km². The estimates of contributions of pollutants are alarming, because they indicate some values annual means of some 150,000 Tm of sulfates, 15,000 Tm of iron, 4,000 Tm of zinc, 1,500 Tm of copper and 450 Tm of manganese.

POLLUTANT SOURCES

The upper part of the Tinto river basin it possibly belongs to the biggest sulphide mineralizations in the world (the Iberian Pyrite Belt). The mines that exist in this basin have been exploited intensely from the Chalcolithic until the Roman period and from beginnings of the XIX century until our days. The quantity of existent sulphides in the group of masses of sulphides of the pyrite belt is considered in 1.000 Mt, of those that great part has been corraded during the Tertiary.

The Iberian Pyrite Belt is located in the Iberian Southwest end of the Massif one and he extends from Sevilla until the banks of the Atlantic, crossing the neighboring Portugal inside the area Southportuguese. The biggest reservations in polymetallic sulphides of all Europe are located in this area, covering an extension of about 280 Km x 40 Km. Inside the Belt it exists a mining district that is broadly well-known in the world environment for their long trajectory miner-metallurgical; it is the Riotinto Mines (Figure 2) located on the head of the river and that during 5000 years they have been intensely exploded for great number of civilisations.
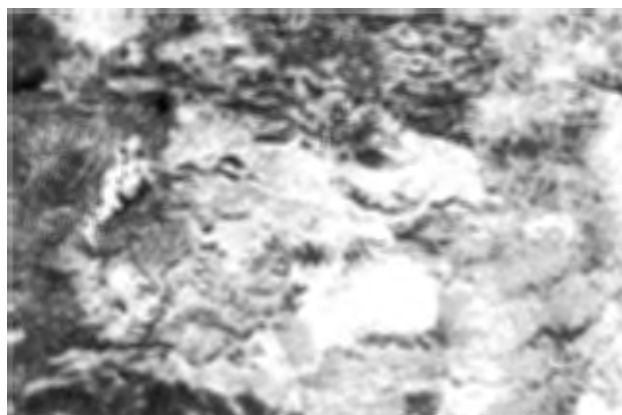

Figure 2. Air photo of the exploitations of Riotinto sulphides.

The sulphides exploitation along the centuries cover a great land extension that has been occupied by all type of such materials as dead wastes, clinkers, servants (roasted sulphides), rafts of flotation residuals, etc. (Figures 3 and 4). This enormous concentration of materials with high concentration of exposed metals to the action of the atmospheric agents is taking place in the course of the time great quantity of lixiviated (acid waters with high content in metals).
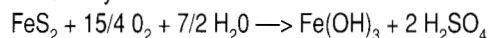

Figure 3. Area of wastes on lands of construction of the drain of ISR.

Figure 4. Dam of acid waters in the vicinity of the mine.

denomination of the next town (Figure 5): Nerva (point number 5), Berrocal (4), La Palma del Condado (Gadea) (3), San Juan del Puerto (2) and La Rábida (1), taking "in situ" data of temperature, pH, Eh and conductivity. Likewise two samples of 250 cc were picked up in each sampling point, one of them previously filtered with filters of 0,47μm that was packed in recipients of polyethylene of narrow mouth, as well as the filters in she behaves and both conserved in refrigerator at 4 ºC.

The samples of filtered water have been analysed by diverse methods (Spectrophotometry, Volumetrie) (analysis carried in the Central Services of Investigation of the Huelva University), obtaining pH data, conductivity, NO_3^-, HCO_3^-, SO_4^{2-}, Ca^{2+}, Cl^-, Na^+, K^+, Mg^{2+}, Fe, Zn, Cu and Mn.
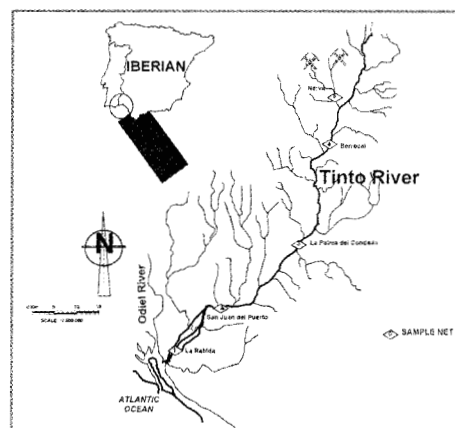

Figure 5. Localization of the control net.

RESULTS AND DISCUSSION

The data, picked up in leaves of I calculate, they were processed to obtain diverse graphic, as well as it stops their statistical study.

The statistical analysis has allowed us to determine the existence of certain connections and groupings among different parameters and to deduce the main factors that they depend, with the final objective on being able to identify the possible origins of the pollutants and to classify the same ones in different groups.

The factorial analysis has been based on the extraction of factors by the method of principal components (Harman, 1980). Besides the 16 components or principal factors, the eigen values, their accumulated and the % variance have been calculated for each one of them (Table 1).

The contribution of each factor in the variance diminishes progressively; starting from these data the norm of Kaiser (1960) has been applied of conserving (to extract) only those main components whose eigen values are bigger than the unit and the more risen better, for what the components have been retained (factors) 1 and 2 that we denominate Factor I and Factor II, respectively; also, they are two factors that they almost explain 69% of the variance.

As the meteorization agents' consequence the sulphides (polymetalics) they combine with oxygen and water to produce acid waters; the reactions are catalysed for microbiological processes (bacterium Thiobacillus ferroxidans and Thiobacillus thioxidans), increasing the speed of the processes a million times. In those reactions, the sulphides (S^{2-}) they are oxidised to sulfates (SO_4^{2-}) being also generated ferrous ions (Fe^{2+}) and protons (H^+); the degradation and dissolution of the sulphides can be summarised by means of the reaction:

$$FeS_2 + 15/4\ O_2 + 7/2\ H_2O \longrightarrow Fe(OH)_3 + 2\ H_2SO_4$$

These acid waters have a very low pH that oscillates between 1.5 and 2.5 along 93 Km, from the birth of the river until the area of the estuary, besides containing high concentrations of metals, varying their value in an important way if it is humid times or you dry off. This produces big environmental alterations in the basin and in the estuary, among those that it highlights the accumulation of sediments with high metallic contents.

METHODOLOGY FIELD SAMPLING AND LABORATORY WORKING

For the study of this alterations, he has been carried out a sampling campaign in a control net formed by five representative points and with access possibilities that they receive the

Factors	Eigen value	%Total of the variance	Accumulated of the variance
1	9,27812	57,988	57,988
2	1,66828	10,427	68,415
3	1,31796	8,237	76,652
4	1,12648	7,041	83,693
5	0,91224	5,702	89,394
6	0,48727	3,045	92,440
7	0,34430	2,152	94,592
8	0,26043	1,628	96,219
9	0,22945	1,434	97,653
10	0,15417	0,964	98,617
11	0,10580	0,661	99,278
12	0,07072	0,442	99,720
13	0,02553	0,159	99,879
14	0,00884	0,055	99,934
15	0,00717	0,045	99,979
16	0,00333	0,021	100,000

Table 1. Extraction of the factors (principal components).

Variable	Factor I	Factor II	Estimating communality*
pH	0.83103	0.986155	0.988730
Eh	0.691936	0.772840	0.955500
T^e	0.767876	0.981915	0.994469
Cond	0.949512	0.966293	0.996442
$SO_4^=$	0.255495	0.492606	0.698370
HCO_3^-	0.847459	0.982214	0.996321
Cl^-	0.024252	0.884568	0.995335
NO_3^-	0.116607	0.369689	0.687034
Ca^{2+}	0.961238	0.985195	0.995238
Mg^{2+}	0.552641	0.779978	0.963575
Na^+	0.031282	0.549438	0.928497
K^+	0.895602	0.988829	0.998618
Fe	0.330631	0.748653	0.987738
Mn	0.479717	0.980216	0.989155
Cu	0.000482	0.807006	0.987532
Zn	0.131569	0.694335	0.853201

* Proportion of explained variance (of each variable) for the group of the factors
Table 2. Factorial matrix of the hydrochemical variables.

The following step has been to calculate the factorial matrix (Table 2) that indicates us the weight of the variables in the extracted factors (I and II). High pesos mean that there are variables that are associated to the corresponding factor. This way taking alone the pesos bigger than 0,9 the Factor I contains to the variable C_a^{2+} and conductivity, and if we take a weight bigger than 0,7, the Factor I would contain, also, pH, temperature, HCO_3^- and K^+.

The communality estimating for the group of the factors I and II (Table 2) it is a good index to know the variability of each variable explained by both. This way, the low values (zero or next to zero) they indicate that the common factors don't explain she swims at all of the variability of the variable, while you value of 1 (or next) they indicate that the variable is completely explained by the common factors. In the corresponding Table it is observed as the factors I and II explain the variability totally of most of the variables and in smaller proportion $SO_4^=$, NO_3 and Zn.

To choose the simplest solution of being interpreted it has subjected to the factorial axes I-II to a rotation Varimax (Kaiser, 1958) whose objective consists on maximising the variance of the factors by means of a type of axes until getting that they approach to the maximum to the variables in that they are saturated (when in the factorial matrix variables exist with high pesos in a factor and first floor in all the other ones, it is said that they are saturated in that factor, and when this happens the analysis factorial cobra sense); the factorial matrix initial becomes this way a rotated factorial matrix (Table 3).

Variable	Factor I	Factor II
pH	0.993052	0.001243
Eh	-0.651764	-0.589953
T^e	0.987780	-0.078778
Cond.	0.843964	0.504002
$SO_4^=$	-0.271946	-0.647033
HCO_3^-	0.990713	0.026501
Cl^-	-0.223413	0.913594
NO_3^-	-0.114928	-0.597060
Ca^{2+}	0.961811	0.245184
Mg^{2+}	0.494528	0.731724
Na^+	-0.121933	0.731143
K^+	0.990000	0.093424
Fe	-0.272768	-0.821128
Mn	0.915782	-0.376242
Cu	0.374988	-0.816327
Zn	-0.036814	-0.832454

Table 3. Rotated factorial matrix (Varimax method).

This rotated factorial matrix is of easier interpretation because each column of this new matrix produces some very high and other pesos they approach to zero, with what is spread to minimise the number of variables that they have high saturations in a factor (Figure 6). It is of highlighting that after the rotation, the factor I is practically saturated in 7 values (Ca^{2+}, HCO_3^-, Mn, K^+, T^e, pH and conductivity) and the factor II in 6 variables (Cl^-, Na^+, NO_3^-, $SO_4^=$, Fe and Zn).
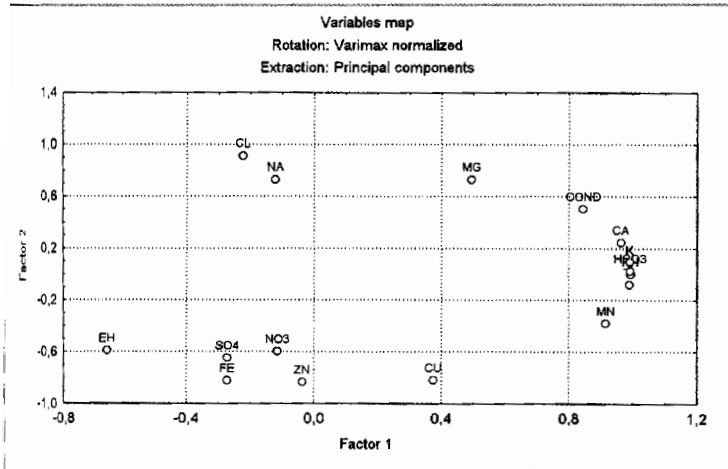
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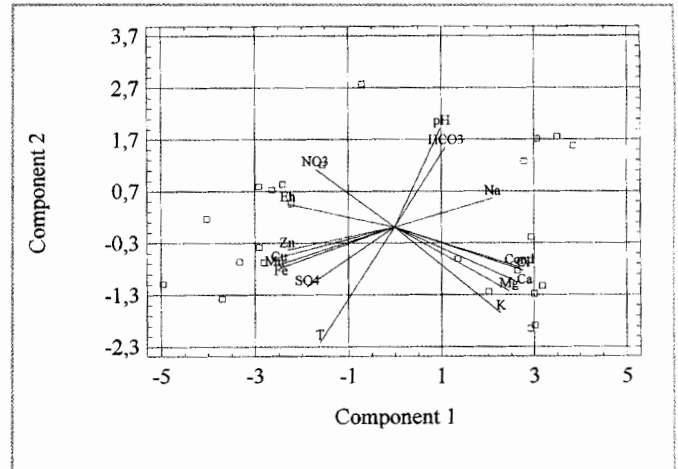Figure 6. Position analysed variables map.

Figure 7. Map of variable-observations.

With this we can know the structure or content of the factors and now we will give him a name.

The factor I is clearly a factor in which the pH controls the dissolution of the elements metallic contents in the geologic materials (shales, volcanic rocks, etc.) of the bed of the river. It is observed that too more contained smaller pH of metals (and vice versa).

The factor II are a factor of precipitation of elements metallic pollutants, bound to derived processes of the mining activity as it is that of the sulphides oxidation in the one that the metals are forming salts like sulfates and nitrates (these last they come from those poured to the river of the residual waters of all the near municipalities). It is observed how the chloride and sodium control the deposit (to bigger salinity of the water, smaller content in metallic elements for deposit of the same ones in the sediments of the river, and vice versa); likewise, it is observed that the Eh also associates to the deposit of metals (the more negative is the Eh, more reducer is the environment and, therefore, bigger deposit of metals).

In the Figure 7 are represented the observation points and the variables simultaneously, being united these to the centre of coordinated for some axes (vectors) among those that you could measure their angular drift. Here one can observe that the angular values among pH-HCO_3^-, Zn-Cu, Mn-Fe, conductivity-Mg^{2+}-Ca^{2+}-K^+ they are very low, that is to say that the cosine of its angles will be very next to the unit, what gives us idea of the hardship of the relationships among even of variables. The longitude of each vector is proportional to the contribution of that variable to the factor.

The variable NO_3^-, Eh and Te goes for free and forming angles of almost 90º with the couples of previous variables, with that that its interrelation practically doesn't exist, being at the end a light relationship among the SO_4^{2-} and the mentioned couples of variables.

In a first analysis cluster, the results have been expressed in dendrograms form and, starting from these (Figure 8), the following comments can be made:

- In first instance they exist a series of associations like: Mn-Zn, K^+-Ca^{2+}, HCO_3^--Cu, to which are added the Fe, NO_3^- and pH, and later on NO_2^- and T^e. To all they are gone adding the Mg^{2+}, conductivity, $SO_4^=$ and lastly Eh. This mass of variables constitutes a great group where they are almost involved 90% of the analysed variables.

- On the other hand another couple of variables exists related to each other (Cl^- - Na^+) that are added to the initial group in the last stadiums. This one could interpret for the influence that they have the waters with high content in marine salts of the outlet of the Tinto river in their mixture with the acid waters of their bed that are waters enriched in metals and anions that have left enriching along their to lapse for the different types of geologic materials until their outlet in the estuary where big quantities of metals are deposited by elevation of the pH before the increase of water salinity.
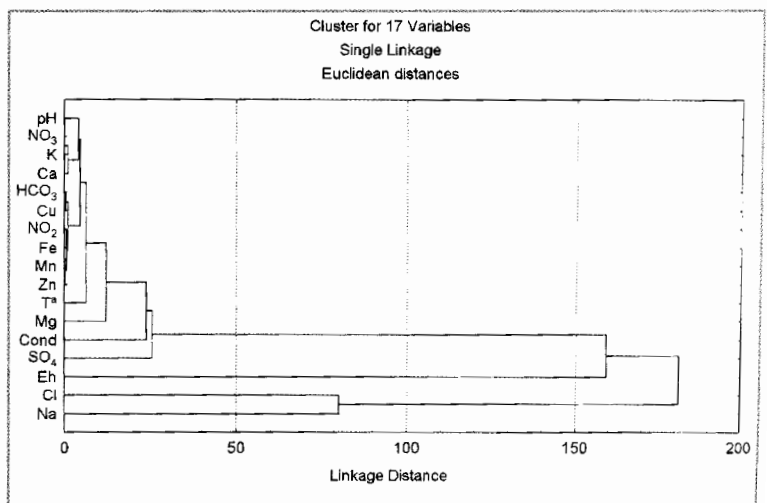

Figure 8. Dendrogram of hydrochemical variables.

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CONCLUSIONS

Starting from this preliminary study of the available data, the following conclusions are extracted:

- In view of the analytic results a decrease of the levels of concentration of the metals is observed in the waters of the Tinto river as we go descending from head to outlet, due clearly to the effect of the dilution and precipitation of metals caused by the mixture of these waters with sea water and with flowing water of the multiple ones with different degree of salinity.
- On the base of the statistical analysis the clear existence of associations, relationships and dependences have been observed among the different parameters being distinguished two big groups: on one hand the strictly derived of the contamination of mining origin and on the other hand those that derive of the own corrosion that the acid waters exercise on the substratum of the bed.

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