


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
Spatial evolution of an AMD stream in the Iberian Pyrite Belt: control factors on the hydrochemistry

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Spatial evolution of an AMD stream in the Iberian Pyrite Belt: process characterization and control factors on the hydrochemistry

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Abstract

This paper presents hydrochemical data of an AMD stream in the Iberian Pyrite Belt, obtained from its source, in the Poderosa Mine Portal, till its confluence at the Odiel River.

The main objective is to establish potential interdependent relations between sulfate and metals' loads and the following physical-chemical variables: pH, electric conductivity (EC), redox potential (EH), and dissolved oxygen (O₂).

All the parameters show a global increasing tendency since the tunnel's exit to the confluence at Odiel River. The TDS and EC are two relevant exceptions. They behave similarly,

showing a decreasing trend and a strong inflection that describes a minimum immediately after the discharging point.

The spatial analysis combined with statistical tools put in evidence the typical AMD processes and the respective physical-chemical implications. Inputs with distinctive hydrochemical signatures impose relevant modifications in the Poderosa creek waters. This indicates low hydrochemical inertia and high vulnerability to external stimulus.

Keywords: AMD; Iberian Pyrite Belt; Odiel River; Poderosa Mine, Cluster Analysis

1. Introduction

The exposition of sulfide minerals to weathering agents is a significant focus of water pollution. This type of pollution responds to two main geochemical processes: a natural one, named acid rock drainage (ARD) and another one caused by mining activity, which is widely known as 'acid mine drainage' (AMD). Commonly, ARD has slow temporal patterns. On the contrary, AMD is often an accelerated process, responsible for strong ecosystems' affection (Gray, 1998; Valente and Leal Gomes, 2009a, 2009b).

Typically, acidification and presence of heavy metals are two major concerns in the AMD affected systems. Water pollution by heavy metals has a very high probability of occurrence due to their solubility in acid environments. The most common mobilized metals are: iron, copper, zinc, lead, nickel, arsenic, mercury, and cadmium (Murphy and Spiegel, 1982). Many of such elements are catalogued as priority contaminants by the USEPA (Tchobanoglous and Burton, 1995). The seriousness of the pollution caused by heavy metals is based on three fundamental reasons: (1) they are not biodegradable, so they would remain indefinitely in water unless transported to other environments; (2) they can suffer bioaccumulation and, then, be transmitted to higher levels of the trophic chain causing biomagnification (Nebel and Wright, 1999); (3) some heavy metals, such as copper, zinc, and manganese become lethal above certain

concentration levels (Begon et al., 1999; Sainz et al., 2002), although they are essential micronutrients for plants and animals.

There are numerous examples around the world of globally affected mining regions since AMD promotes chemical, physical, biological, and ecological interactive effects on the environment (Elbaz-Poulichet et al., 2001; Gray, 1998; Nieto et al., 2007; Sainz et al., 2004; Valente and Gomes, 2007). The Iberian Pyrite Belt, in the SW of Spain, is one of such examples.

This paper presents hydrochemical data of an AMD stream in the Iberian Pyrite Belt (IPB), obtained from its source, in the Poderosa Mine Portal, till its confluence at the Odiel River (Fig. 1). This watercourse would be used as a model to document and understand the water-rock-air interaction processes that could affect the reaction's kinetics in a strongly AMD affected environment.

2. Location setting

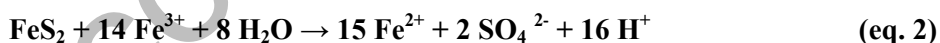
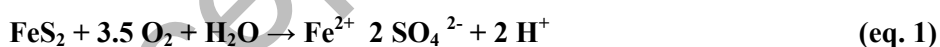
The studied system, named "Poderosa creek", is located in the Iberian Pyrite Belt (SW Spain). IPB is one of the most important metalogenetic regions in the world, where the environmental implications of mining on the receiving watercourses have been broadly described (Aroba et al., 2007; Borrego, 1992, 2002, 2011; Braungardt et al., 1998; Carro et al., 2011; Davis et al., 2000; de la Torre et al., 2009, 2010, 2011; Elbaz-Poulichet et al., 1999, 2000, 2001; Grande et al., 2000, 2003a, 2003b, 2005a, 2005b, 2010a, 2010b, 2010c, 2010d, 2010e, 2011a, 2011b; Grande, 2011; Jiménez et al., 2009; Leblanc et al., 2000; Sainz et al., 2002, 2003a, 2003b, 2004, 2005; Sánchez España et al., 2005, 2006a, 2006b, 2007).

The stream under study has a length of approximately 600 m. It starts at the Poderosa tunnel's mine, which is located 7 km NW from the RioTinto exploitations. Initially, the tunnel ensured the train communication between the underground mining works and the north slope of the hill (Fig. 1). In the past, mining was performed by combining surface exploitation with underground works (by using room and pillar) to a depth greater than 250 m. The ore

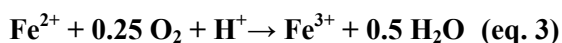
paragenesis presents high levels of copper as chalcopyrite, calcosite and covelite. The tunnel's assured the exit of these minerals, further transported to the Huelva city (Pinedo, 1963). More than 600000 ton of copper ore was exploited only between the 1864 and 1924. The ore was, then, treated by leaching techniques.

Presently, the Poderosa tunnel allows the output of water that is undergoing AMD contamination inside the galleries and the open pits, which are interconnected for over 2000 years (Pinedo, 1963). It flows down to the Odiel River, which is a broadly described river in the AMD literature (Borrego 1992; Borrego et al., 2002; Cánovas, 2005, 2007; Casiot et al., 2005; de la Torre et al., 2010; Grande et al., 2003a, 2003b, 2011a; Jimenez et al., 2009; López-Fernández et al., 2003; Olías et al., 2006; Sáinz et al., 1990, 2000, 2002, 2003a, 2003b, 2005; Sánchez-España et al., 2005, 2006a, 2006b, 2007; Sarmiento et al., 2003, 2004a, 2004b).

The more evident and immediately perceptible feature of the Poderosa creek is the strong color change suffered by its waters. They emerge almost transparent but, rapidly, acquire the typical redness of the AMD streams. The dissolution of metals associated to acid and sulfate mobilization can be generically explained by the pyrite oxidation reactions. There are two main reactions used to describe the oxidation of this mineral, the most common sulfide in nature, according with the oxidant agent: O₂ and Fe(III) (Garrels y Thompson, 1960; Singer y Stumm, 1970) (eq. 1 and eq. 2):



The Fe(III) acts as a powerful oxidant, being more effective than the O₂ and allowing the sulfides' oxidation even in anoxic conditions. The reaction's kinetics depends on the Fe(III) availability. Normally, Eq. 3 is used to describe the reaction step that controls such availability and the overall kinetics of pyrite's oxidation (Alvaro, 2010).



At low pH values ($\text{pH} < 5$), the eq. 3 is catalysed by acidophilic chemoautotrophic microorganisms (*Thiobacillus ferrooxidans*, *Leptospirillum ferrooxidans*) that increase the oxidation rate by a factor of 100.000 (Singer and Stumm 1970; Nordstrom and Alpers, 1999). This biotic contribution leads to acidity intensification, comparing with abiotic oxidation through Fe(III) (Alvaro, 2010; Nordstrom and Southam, 1997; Seal et al., 2008).

The relevance of the major sulfides oxidants (O_2 and Fe(III)) depends specifically on the solution pH. Fe(III) has limited solubility at neutral pH. Therefore, under this condition O_2 will be the dominant oxidant. On the contrary, at low pH values, it will be expected the contribution of both oxidants. Nevertheless, due to the higher kinetics of Fe oxidation enhanced by the bacteria action, this will be the dominant mechanism (Alvaro, 2010; Seal and Hammarstrom, 2003).

The mass balance of pyrite oxidation is rather complex. Consequently, the above equations do not reflect the complexity of the global electron transference mechanism (Toran and Harris, 1989). This chain process requires seven electrons for each sulfur's atom, which represents at least seven discrete steps of electron transfer (Rimstidt and Vaughan, 2003; Seal, 2003). In general, three basic mechanisms, widely described by Velasco et al. (2005) and Alvaro (2010) are pointed out: direct oxidation, indirect oxidation, and oxidation by indirect contact (Crundwell, 2003; Sand et al., 2001; Tributsch, 2001). Complete reviews on the global mechanism involved in pyrite oxidation can be found in the works by Balci et al (2007), Brunner et al (2008), Seal (2003) and Velasco et al. (2005).

In the Poderosa creek, this and other processes should be involved in AMD generation, such as the bioleaching promoted by the chemoautotrophic microorganisms (Sánchez España et al., 2005, 2007).

3. Methodology

The main objective of this work is to establish potential interdependent relations between sulfate and metals' loads and the following physical-chemical variables: pH, electric conductivity (EC), redox potential (EH), and dissolved oxygen (O₂). These interdependent relations could be used to propose a function model, which will be able to describe the spatial evolution of contaminants as response to the reaction processes.

3.1. Sampling and water analysis

To accomplish the main objective, a sampling campaign was performed after the rainy season. It occurred in May 2012, when the tunnel had a flow of approximately 10 L/s. Fig. 1 presents the sampling sites, used to perform "in situ" measurements and to collect water samples. A total of 16 sites (Fig.2.), apart from each other about 10 m, were defined along the entire channel length. The first site is located inside the tunnels (P1), while the last one is at the creek mouth, in the Odiel River (P16). Additionally, two other sites were considered, in order to represent the main tributary inputs: sites P8 and P15. The first one corresponds to a mining effluent that carries industrial waters from Poderosa ore leaching. The second one represents a less contaminated tributary that receives waters from other mining facilities.

The parameters pH, electric conductivity and total dissolved solids were measured in situ, in three consecutive times, using the equipment pH-metro CRISON n° 507 and CRISON n°524, respectively. The other field parameters (EH and O₂) were determined with a Hydrolab Quanta probe.

At each site, double samples were taken. To one of them was added nitric acid, 3%, to prevent metals precipitation before laboratory analysis. The second one was used to determine the content of sulphates. After collection, samples were immediately refrigerated, transported in polyethylene bottles (100 mL), kept in the dark and stored at 4°C until analysis.

Metals concentration was determined using atomic absorption air-acetylene (FAAS), with a Perkin Elmer AAnalyst 800 (Perkin-Elmer, Norwalk), equipped with graphite furnace and hydride generator. Sulphates were determined by ion chromatography (IC) with suppressed conductivity detection (Standard Methods, 4110). Iron redox speciation was performed by using

the phenantroline method. All the reagents had an analytical grade or higher. Certified Patterns were used for Atomic Absorption. The ultra-pure water was produced with a Milli-Q water purification system.

3.2. Statistical treatment

Data resulting from analytical procedures were submitted to statistical treatment using Statgraphic Centurion XV package. This allowed to obtain the statistical summary and, further, to perform cluster analysis (Bisquerra, 1989). Such procedure was applied to find proximity relations between variables and to represent its spatial evolution along the creek. Cluster analysis was performed by applying the Ward method or "second-order central moment". This is a hierarchical method that, firstly calculates the mean of all the variables for each cluster. Then, it calculates the Euclidean distance between each factor and the mean of its group. Finally, it adds the distances from each case. In each step, the clusters that are formed are those that yield the smallest increment in the total sum of the intracluster distances. This statistical tool has been widely applied to AMD affected systems (Borrego et al., 2002, Grande et al., 2003, 2003a, 2003b, 2010, 2011). In short, through the application of this technique, the variables studied can be classified into different "categories".

4. Results

4.1. Spatial evolution

Fig. 3 represents the spatial evolution of field parameters. With the exception of electric conductivity (EC) and total dissolved solids (TDS), all the others show a global increase tendency until the Odiel River. The two cited parameters behave similarly, with a clear inflection in the second site (P2 in Fig.3). Here, they define a minimum, while pH presents a slight increase. At sampling site P9, the parameters EH, O₂ and pH indicate a moderate

increase, in comparison with the previous one. Simultaneously, it is possible to observe a decrease in EC, temperature and TDS. It should be noted that between P7 and P9 there is a water input, related with the mining effluent confluence (P8, in Fig. 3). At sampling site P14, immediately upstream from the confluence of a less contaminated tributary, EH and O₂ suffer an increase, while temperature, pH, and TDS decrease.

The elements As, Sb, Pb, Cd, Ni, Fe II, and Co (Fig.4.) present a decrease in site 2, especially stronger for Fe II. On the other hand, Cu and SO₄²⁻ register an increase with respect to the previous site. At sampling site P7, an increase trend is observed for the set of parameters: As, Pb, Co, Sb, and SO₄²⁻. On the contrary, Cd, Ni, and Fe(II) decrease. At sampling site P8, nearly before industrial effluent input, the metals Mn, Zn and Ni displays an increase, while the rest of the parameters clearly decrease, excluding aluminum which stays equal. At the site P14, the group composed by Cu, Mn, Ni, Pb, and SO₄²⁻ increases again, whereas the rest of the contaminants indicate a decreasing trend. Responding to the discharge of less contaminated water (sampling site P15), the metal Al appears, for the first time, with relevant concentrations. Also, there is an increase in the concentrations of Zn, Cd, Sb, and Fe(III).

4.2. Cluster Analysis

The dendrogram in Fig. 5 shows the grouping of sampling sites, according to its proximity defined by Pearson correlations' coefficient (Bisquerra, 1989). Two major groups are clearly observed: one comprising the sites P8, P14, P15, and P16 and another with the rest of them. Contrary to the first group, the second presents strong correlation coefficients. Moreover, it should be noted the strong affinity between the sites P9 to P13, which are apart from the following grouped sites: P1, P3, P4, P5, P6, and P7. Furthermore, this cluster analysis reveals that P2 (correspondent to the tunnel exit), is slightly related with the group composed by P9-P13.

Identically, Fig. 6 shows the same type of analysis, but now considering the field and laboratory parameters as variables. As in the previous case, two groups were found: one for Zn,

Mn and REDOX, together with Al, DO and pH (with moderate affinity) and another comprising two subgroups. The first regards Fe, Sb, Cd, As, Fe(II), Fe(III), and temperature, while the second includes Cu, Co, SO_4^{2-} , Ni, Pb, EC, and TDS. It should be noted the strong correlation observed between TDS and EC (the highest among the studied variables). On the other hand, temperature and Mn present considerable lower correlation than the rest of the variables.

5. Discussion

Along the creek, the generality of the parameters show an increasing tendency (Fig. 3). This may be explained by the following phenomena: i) higher water's oxidant capacity as distance increases relatively to the anoxic source, as suggested by O_2 behavior; ii) the temperature evolution results from the exposure to sun radiation, which is longer with distance from tunnel's exit; iii) pH trend is somewhat more complex, since it should be controlled by a complex set of processes, such as neutralization, dilution, precipitation, sorption, and dissolution. These processes would lead to increasing pH values, while iron oxidation would be contributing to H^+ liberation, and, consequent to pH decrease.

The parameters EC and TDS present a different behavior, although similar between them. Fig. 3 shows that both lines are identical with an inflection at P2, corresponding to the first oxygenated site, located immediately downstream from a standing water pool at the tunnel's exit. The observed trend should be related with the absence of chlorides, which could mask such relation. This suggests that in AMD environments high EC values are not dependent on metallic load but are related with TDS. Equally, the absence of similarity between pH and EC was already observed and discussed by Grande et al. (2010e).

The spatial evolution of metals, presented in Fig. 4, seems to reveal the effect of natural attenuation processes, mainly dilution and precipitation. At P2, corresponding to oxygenation and sun exposure, it is noted the strong decrease in Fe(II) concentrations. This should be the response to iron oxidation, with consequent acidity increase and further precipitation of Fe(III)

species. Also, sorption phenomena on the suspended matter would promote retention of other elements, such as As, Sb, and Ni.

Somewhat different is the sulfate behavior. This parameter shows a slight increasing tendency that may be related with the presence of particulate sulfides along the creek. This particulate matter suffers oxidation, promoting pH decrease by Fe(II) oxidation and, consequently, sulfate mobilization.

In this scenario, the contribution of biotic oxidation, widely described (Sanchez-España et al, 2007), should also be considered. This biotic action would be enhanced by the increasing temperature and oxygen availability.

The decreasing trend observed for metals at P14 (Fig. 4) can be a response to the input of the industrial effluent, that occurs immediately upstream (Fig. 2). When arriving to the confluence with the Poderosa creek, this effluent has already suffered from oxidation and precipitation processes. During its course of more than 1 km until de confluence with Poderosa creek, the generality of metals was reduced, with the exception of Mn, which needs higher pH values to precipitate (Sanchez-España et al., 2006a). In addition, potential differences in local paragenesis may contribute to the observed Mn concentrations. The same phenomena, although less evident, may be occurring for Ni.

In point 14, the Mn values shot up much higher as a result of the arrival of water from Mn mine, Cobullos Mine, situated on the same side that the Cu mine, El Soldado.

P15 is considerably far from P14 (about 450m), contrary to what happens with the previous sites, which are distant from each other only 10m. Such a long distance may justify the strong decline observed for most of the metals at P15. On the contrary, the metals Mn, Cu, and Zn show an evident rising trend, while Ni and Pb behave more discreetly. These may be related with the presence of an old stockpile located in the vicinity of this site (Fig. 2). In strong runoff conditions, sulfides could be leached, justifying, also, a slight sulfate increase.

Regarding Fe(II) and Fe(III), decreasing concentrations with distance are in accordance with the typical presence of yellow boy. These AMD-precipitates should be retaining other metals by sorption processes, as observed in other AMD systems (Valente and Leal Gomes, 2009a; Sanchez-España et al., 2007).

At P16, near the confluence with the Odiel River, the creek's hydrochemistry reflects the sum of all the inputs. In addition to the previous contributions, there is a new one that carries the effluents from another local mine (El Soldado) (Fig. 2). This small tributary imposes changes in the Poderosa creek due to its distinctive hydrochemical signature, characterized by high pH values (around 4,0). The Al is worthy of mention, since it appears, here, with concentrations above 5mg/L, while it was below detection limits upstream.

5.1. Cluster discussion

The above spatial trends and relations are supported by the cluster analysis. The dendrogram in Fig. 5 shows the grouping of sampling sites, here treated as variables. In general, they are organized in accordance with its spatial sequence. The sites P2 and P8 are exceptions, since they appear displaced, integrating sub-clusters with downstream sites. Regarding P2, such displacement could be reflecting the geochemical gradient imposed by the quick transition to the air-exposed environment. It should be noted that here the water emerges from the tunnel, suffering from rapid contrast in temperature, oxygenation and redox conditions. Therefore, the hydrochemistry at P2 is more similar to its downstream cluster's neighbors (P9-P13), which had time to develop such physical-chemical scenario. Identically, P8 represents the industrial effluent, which had suffered evolution for about 1 km. This may justify its higher similarity to more evolved and further away sites.

Fig. 5 reveals strong interdependent relations between the sites P9 to P12. The explanation to this high proximity lies on the absence of affluent inputs able to modify the water's properties in this section of the creek (approximately 60 m).

On the contrary, the low proximity observed for the most distal cluster (P8, P14, P15 and P16) indicates the difference regarding the upstream sites. It is a consequence of the prominent changes imposed by the second tributary, which has very different hydrochemical features (P15, in table).

The dendrogram of Fig. 6 shows the clusters formed by the analyzed parameters. As discussed previously for the spatial evolution trends (Fig. 4), the cluster analysis also demonstrates the strong relation between TDS and EC. This is evident by the high proximity observed in the central sub-cluster. Somewhat more discrete are the proximity relations between Pb, Ni, SO_4^{2-} , Co, and Cu. In a separate position there is Fe, in its both redox species, together with Sb, Cd, and As. This is the cluster with higher correlation coefficients. On the opposite, there is the cluster with EH and the rest of the variables. This grouping behavior should be related with several geochemical and mineralogical phenomena, already pointed out, such as oxidation, neutralization, precipitation and sorption (Sanchez-España et al., 2006b). Equally, the inputs from two distinctive effluents also contribute to the detachment revealed by the variables less related with EH. These are suffering the influence of Al presence and higher pH values (from P15) as well as the inputs from the stockpile, near P12. Therefore, the first cluster, located at the right side of the dendrogram, groups variables related with alloctonous materials, i.e., not related with the major paragenesis, with EH, O_2 and pH, although with discrete proximity relations.

On the other side, the rest of the variables compose two sub-clusters with strong proximity relations. The group comprising Sb, Cd, As, Fe(II), and Fe(III), represents the paragenetic relation and the sulfides oxidation processes. The central sub-cluster denotes a very intimate association between SO_4^{2-} , Co, and Cu. This is probably due to the control imposed by precipitation and co-precipitation of those metals as sulfate salts.

6. Conclusion

The oxidation of sulfides in AMD is a complex process, which includes reactions such as oxidation-reduction, hydrolysis, and precipitation-dissolution. From this set of reactions results acidity, sulfates, and oxidized iron species. In the studied system, all the parameters typically related with AMD show a global increasing tendency since the tunnel's exit to the confluence at Odiel River. The TDS and Electric Conductivity are two relevant exceptions. They behave similarly, showing a decreasing trend and a strong inflection that describes a minimum immediately after the discharging point (P2).

The spatial analysis combined with statistical tools applied to this creek put in evidence the typical AMD processes and the respective physical-chemical implications. Inputs with distinctive hydrochemical signatures impose relevant modifications in the Poderosa creek waters. This indicates low hydrochemical inertia, and consequently, high vulnerability to external stimulus. Additionally, cluster analysis revealed to be a useful tool to identify and interpret interdependent relations between variables in this AMD affected system.

7. Acknowledgements

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FIGURES

Fig.1. Location map.

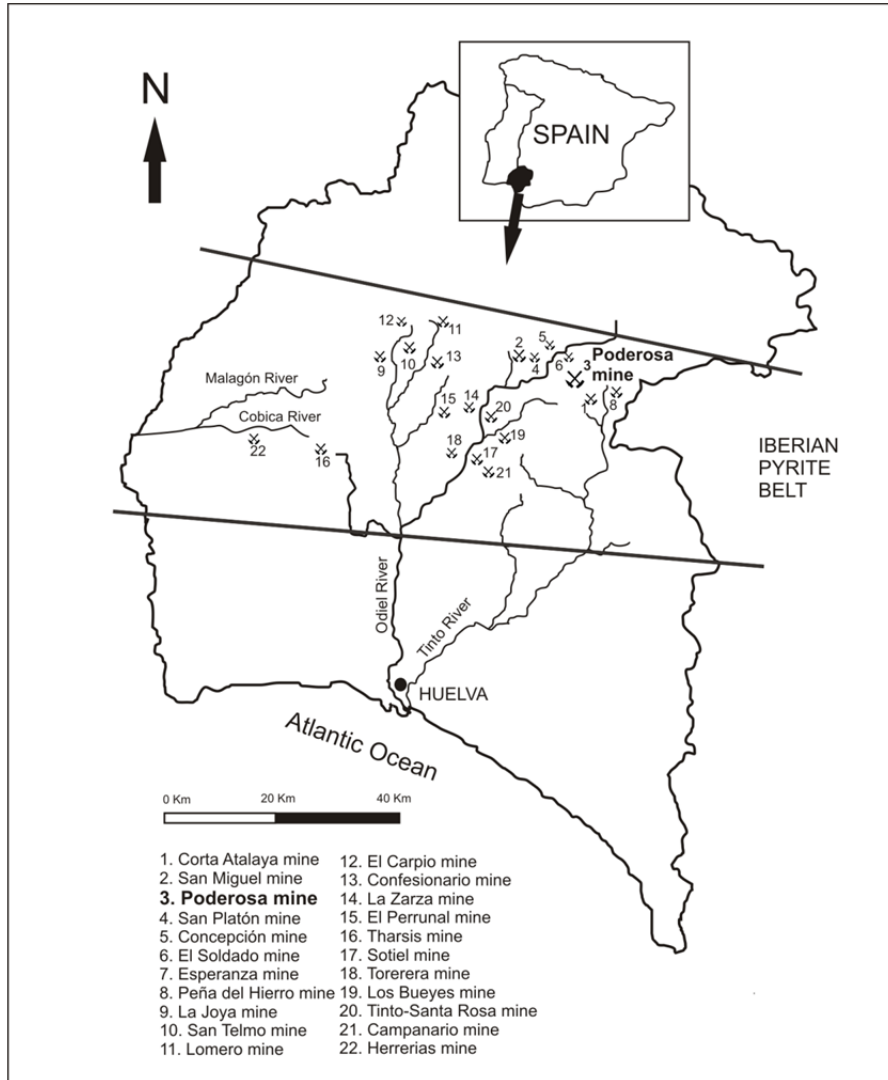


Fig.2. Map representative of the sampling points.

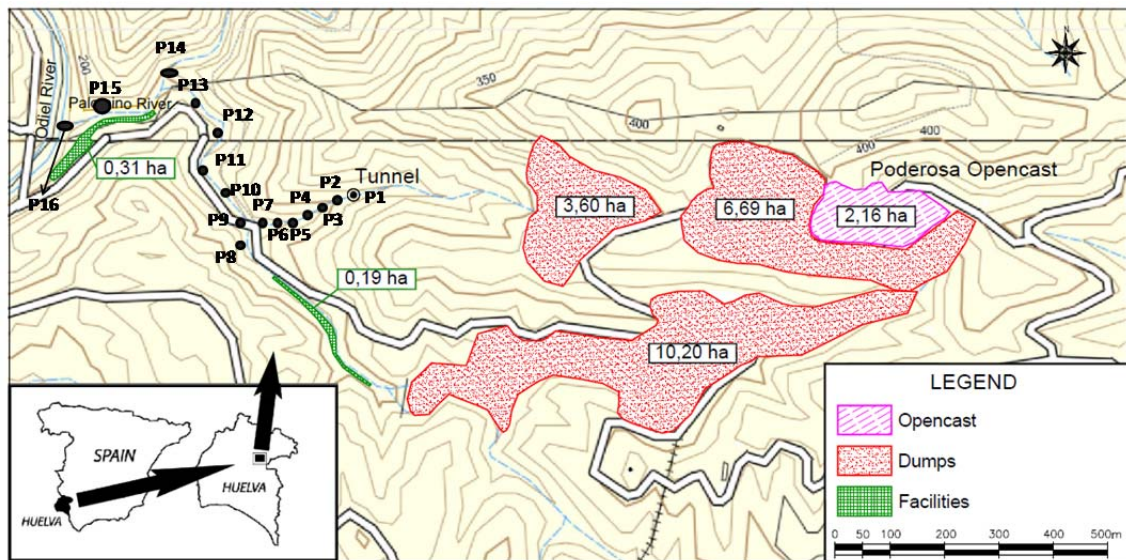
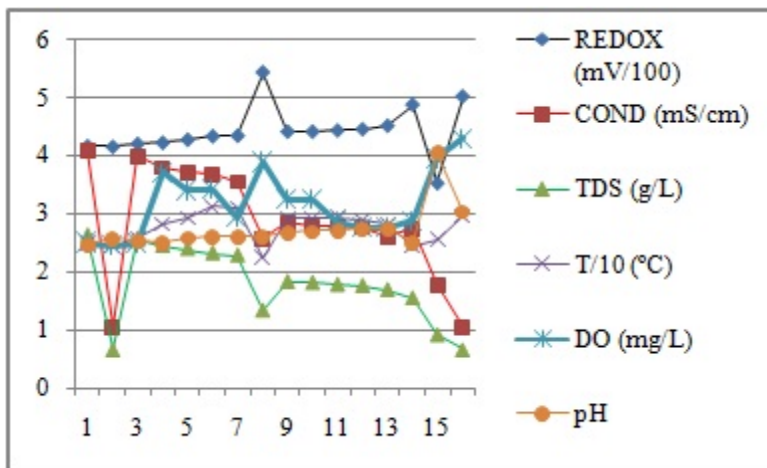


Fig.3. Graphical spatial evolution of the parameters measured in situ.



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Fig.4. Evolution spatial parameters analyzed in the laboratory.

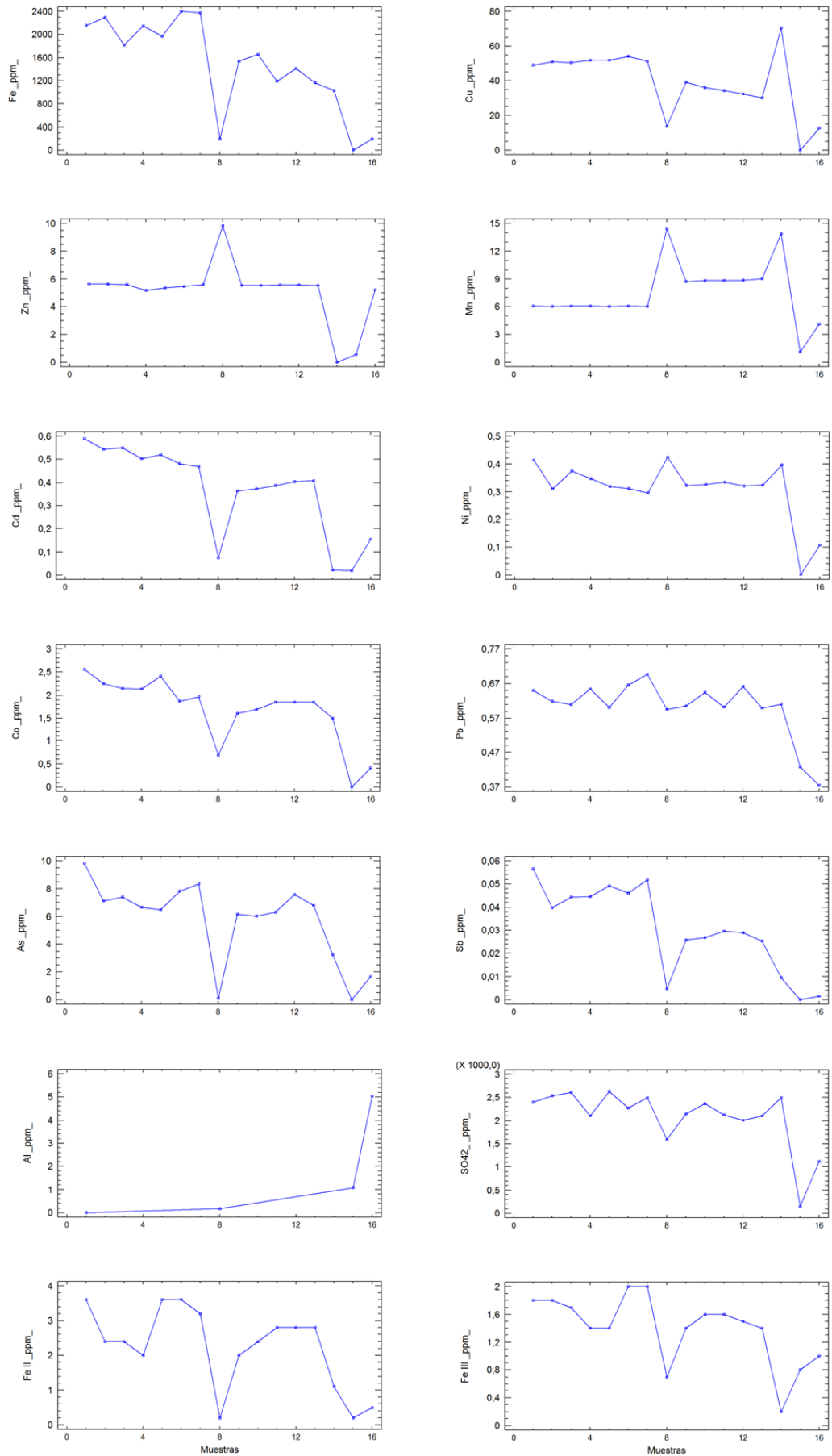
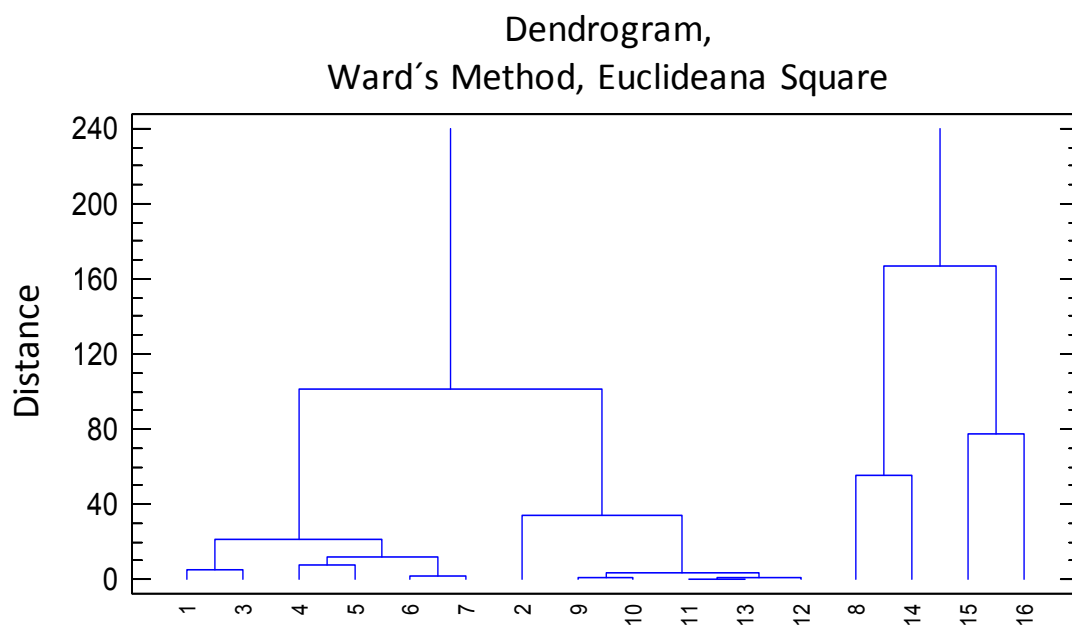
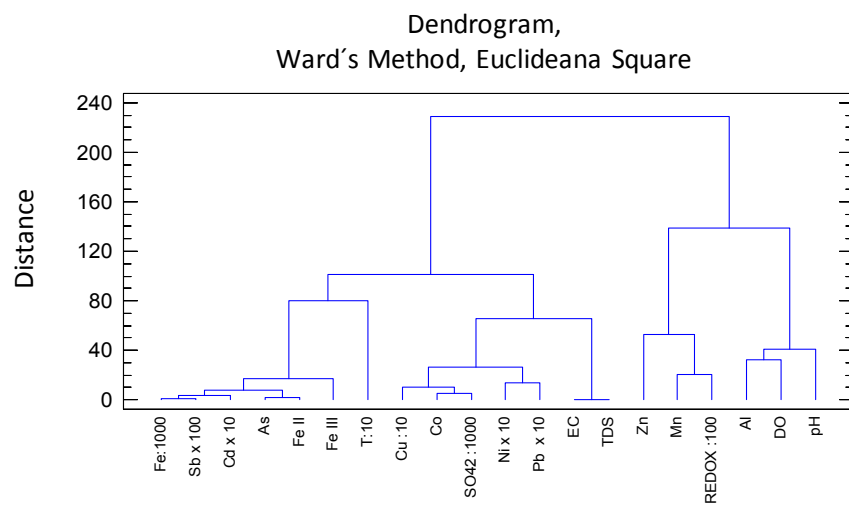


Fig.5. Dendrogram of sampling points.



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Fig. 6. Dendrogram of physico-chemical parameters measured in situ and analyzed metals



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