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Assessment of natural attenuation of acid mine drainage pollutants in El Bierzo and Odiel basins: A case study

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Abstract

In the past, mining activities have generated major acid drainage sources, which usually carry dissolved metals that flow into the main rivers of the affected basins. The study looks at natural attenuation processes in local, sub-basin and basin areas, in the El Bierzo and Odiel basins of Spain, where coal and metal mining activities were formerly conducted. In this study, sampling and *in situ* monitoring of pH, Eh, dissolved oxygen, conductivity, temperature, flow, turbidity, acidity, alkalinity, Fe^{2+}, Fe^{3+} and total Fe were carried out during the hydrological cycle. Chemical analysis was also performed on water samples, following the water quality data of the ICA Network of the Spanish Environment Ministry for a period of 10 years. The results show that the main natural attenuation processes were: dilution by mixing with clean water, oxidation and hydrolysis of dissolved metals, reduction of anaerobic sulphates, and precipitation of secondary minerals.

Keywords: *Acid mine drainage; natural attenuation; dilution; oxidation; hydrolysis*

1. Introduction

Acidic water is a well-recognized source of environmental impact and is toxic to aquatic fauna and flora. Mine drainage carries heavy metals into the surrounding environment, polluting aquatic ecosystems, as well as contaminating drinking water supplies and irrigation systems. The chemistry of mine drainage depends on many factors. The initial chemistry depends on the type and abundance of metal-bearing sulphides in ore and the country rock, kinetic rates of ore and wall rock dissolution, permeability of the ore deposit or mine tailings, and the host rock's acidity buffering capacity and microbial activity [1, 2].The oxidation of sulphide minerals such as pyrite is usually due to mine drainage with low pH and high sulphate and metal concentrations [3].

The discharge of mine drainage from underground or surface mining into surrounding rivers leads to the pollution of surface water at local, sub-basin and basin levels. The natural attenuationof mine drainage, including the adsorption and precipitation of metals and acidity dilution has been studied by several researchers in diverse mining districts of the world [4,5,6,7,8,9]. Mining activities in the past have generated uncontrolled waste and tailings deposits and today they are a major source of acid mine drainage. This situation has significant effects on the pollution load of the area's water network, affecting water quality and degrading the river ecosystems. In some cases, the affected waterways have seen improvements and natural attenuation processes which have led to the recovery of biota and water quality [10].

This recovery of river ecosystems is notable when the acidic mining discharge has low flow and low metal concentrations where the effluent mixes with clean water, oxidation and hydrolysis of dissolved metals, anaerobic sulphate reduction, precipitation of secondary minerals and sorption of trace elements take place and generate a natural attenuation process [11]. This paper assesses the natural attenuation of acid mine drainage in local, sub-basin and basin areas, based on the case study in the El Bierzo basin (Figure 1) and Odiel river basin (Figure 2) in Spain. A systematic analysis of water quality at the acidic mining discharge point and along the river was conducted, where natural attenuation processes have been identified under certain conditions, resulting in a reduction in metal and sulphate concentrations, as well as an increase in pH values.Currently in the El Bierzo basin, most of the tributaries of the Tremor river collect acid drainage coming from abandoned underground mines, with the acidity variation of pH 2.9 to 4.8 classified as high-acid, and of Fe concentrations ranging from 70 to 100 mg/l [12]. Comparatively, the river water of the La Silva sub-basin has less acidity, with pH ranging from 5 to 7.8 and close to neutral values. In the Odiel basin, which is presently exhausted, metal mining was formerly conducted in the Iberian Pyrite Belt for the massive sulphide deposits of Huelva province. This has resulted in leaving a legacy of abandoned mines and attendant spoil tips, including enormous sulphide waste rock piles, tailings and flooded pits. These mine wastes are significant sources of severe environmental pollution from acid mine drainage into the Odiel and Tinto river systems [13].

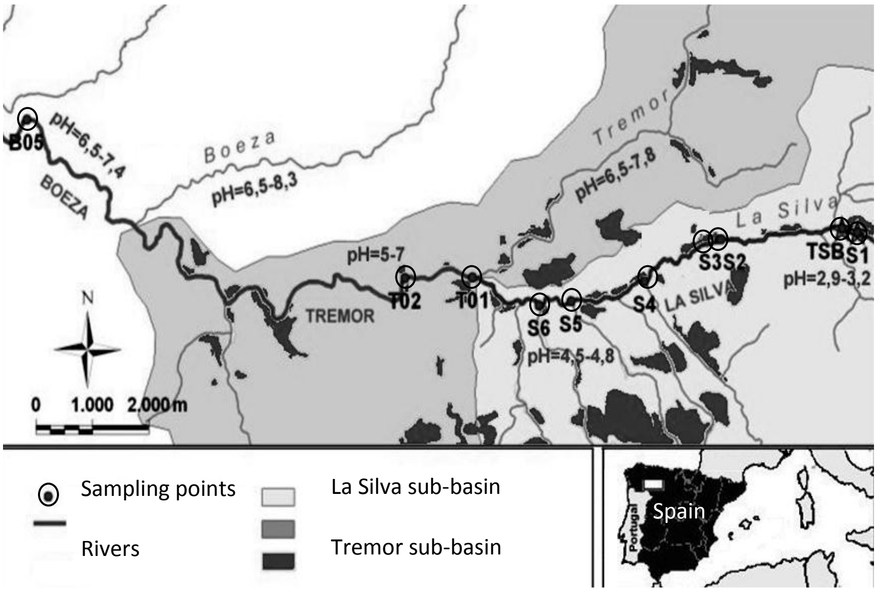

Figure 1. Mining areas in the El Bierzo basin formed by the La Silva and Tremor sub-basins and sampling points

2. Methodology

To investigate the surface water affected by acid mine drainage in the El Bierzo and Odiel river basins, several sampling campaigns were conducted in these rivers in 2006 and 2007. This involved in situ measurements of pH, Eh, dissolved oxygen, conductivity, temperature, water flow, turbidity, acidity, alkalinity, $Fe^{2+,}$ Fe^{3+} and total Fe, using portable equipment and instruments (HANNA HI 9025C, HI 9033 and HI93703, CRISONOXI 330 and a HACH digital titrator).

The acidity was titrated with NaOH 0.16 N up to pH 8.3 (phenolphthalein indicator), while sulphosalicyclic acid was used to determine iron content. Water samples were also collected for laboratory chemical analysis, in HDPE 125 ml bottles, after washing with 10% nitric acid and rinsing with water from the sampling point. Water samples were filtered at 0.45 microns and acidified with HNO_3 up to pH <2, refrigerated at 4 C° for transport to the laboratory. Water data of the North Hydrographic Confederation was also conducted, analysing monthly water quality data from the ICA network of the Environment Ministry over a 10 year period.

3. Results and discussion

3.1. Natural attenuation of water pollutants near “Bocamina 1” in the el Bierzo basin

The “Bocamina 1” drainage, located near the La Laguna hill, between VillamartindelSil and San

Pedro Mallo villages of the El Bierzo basin, undergoes a predominantly ferrous to ferric phase transformation in the first 300 m of its length, with the oxidation of Fe^{2+}, the content of which decreases with the increase in distance, with a corresponding increase in the Fe^{+3} concentration, while the total Fe in solution decreases at the same time, possibly due to the presence of organic matter, which adds to the alkalinity and contributes to solid phase formation (Fe and Al hydroxides) (Figure 3a). This attenuation is verified by the accumulation of precipitates in the riverbed and an increase in pH from 3.1 to 3.9 (Figure 3b), indicating that the drainage ditch (with vegetation) acts as a treatment device, which reproduces the natural attenuation mechanisms downstream of the acid water discharge point [14]. At 400 m, there is a supply of clean water (pH 7.6) with a flow that is 4 to 6 times greater, increasing the pH to 6.9. Finally at 500 m, the pH rises to 7.5 and the redox potential drops to 100 mV (Figure 3b).

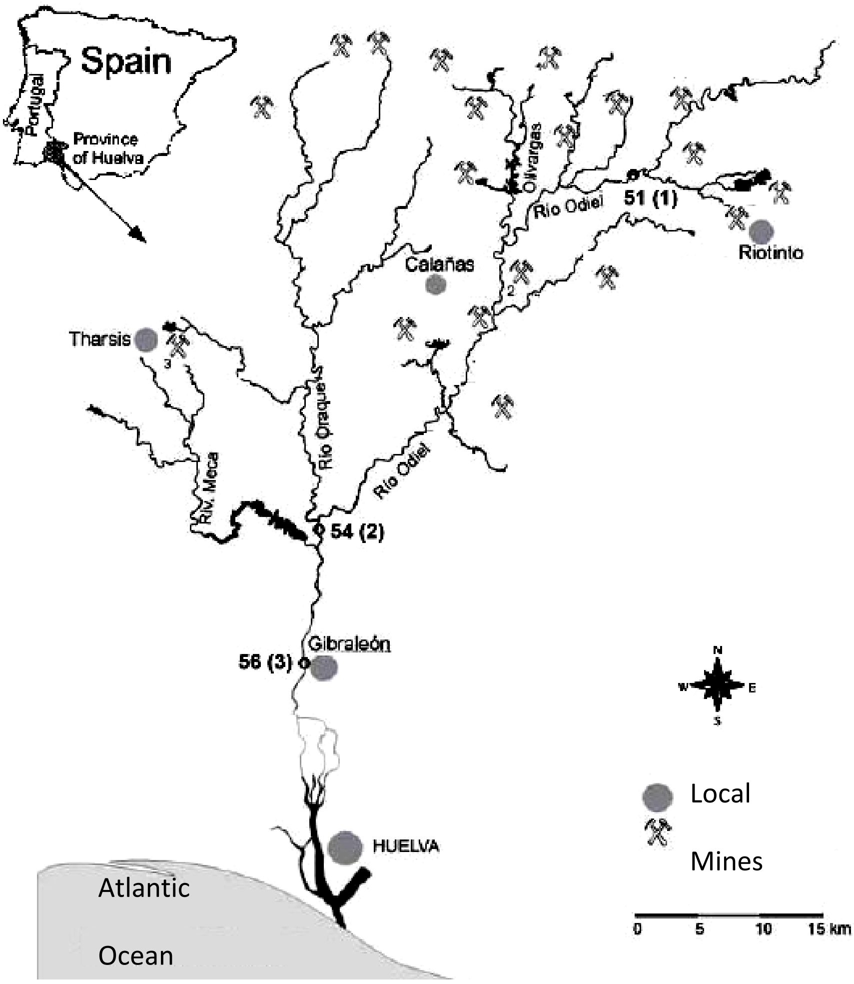

Figure 2. Odiel basin river system, local mines and sampling points

3.2. Natural attenuation of water pollutants in the La Silva and Tremor sub-basins

There has been significant coal mining activity in the Bierzo basin, with large road excavations in recent years, which have led to water contamination upstream of the Silva river sub-basin with pH between 2.7 and 3.3, conductivity of 1000-5000 µS/cm, Fe=100 mg/l, Al=200 mg/l, Mn=7.2 mg/l, Cu=2 mg/l, Zn=4 mg/l, Ni=3.2 mg/l and SO_4=740 mg/l (Figure 4a).At 900 m, Fe decreases from 90 mg/l at pH 3, to zero concentration at pH 4, possibly because the dissolved Fe is hydrolyzed and precipitated, forming solids such as Fe oxyhydroxides, as in the following Reaction (1):

$$8Fe^{3+}+SO_4^{2-}+14H_2O\rightarrow Fe_8O_8(SO_4)(OH)_6+22H^+ \quad (1)$$

Al also drops from 200 mg/l at pH 3 to 80 mg/l at pH 3.3, probably due to dilution. Later, between 900 m and 2700 m, the reduction is buffered and the pH varies from 3.3 to 4.5 with Al hydrolysis and precipitation.

In the final segment, from 2700 m to 7000 m, the reduction process of Al content continues and the concentration goes from 70 mg/l at pH 4.5 and almost disappears at pH 5 (Figure 4a). This occurs as per the following Reaction (2).

$$Fe^{3+}+3OH^{-}\rightarrow Fe(OH)_3 \quad (2)$$

The secondary minerals that are precipitated are metastable, in the transformation of ferrihydriteFe(OH)$_3$ to goethite FeO(OH) and finally to hematite Fe_2O_3, or in the transformation of schwertmannite to goethite, expressed by Reaction (3):

$$Fe_8O_8(SO_4)(OH)_6+2H_2O\rightarrow 8FeO(OH)+SO_4^{2-}+2H^+ \quad (3)$$

The removal of mineral water acidity due Fe oxidation and hydrolysis increases the pH of the water and leads to mineral formation, namely, of Al (pH 4.5 to 5) as well as gibbsite ($Al(OH)_3$), hydrobasaluminite ($Al_4[(OH)_{10}/SO_4]$ .12-36H_2O) and Aluminite ($Al_2[(OH)_4/SO_4]$ .7H_2O), which precipitate and remove trace elements such as Zn, Pb, Cd, Cu, Ni and others by coprecipitation and adsorption (Figure 3b).

In the case of Cu, which is adsorbed into the ferrihydrite, the Reaction (4) is as follows:

$$Cu^{2+} + 2H^+ \equiv Fe(OH)_3\rightarrow 2H^+ + Cu^{2+} \equiv Fe(OH)_3 \quad (4)$$

where,

≡ indicates adherence to the solid surface

The removal of Fe, Al and Mn in the initial segment, or upstream, reaches significant percentages, over 90% in the case of Fe (pH = 3.7) and Al (pH 4.8) and near 60% for Mn. This is mainly due to the formation of Fe and Al solid phases (oxihydroxides, oxihydroxisulphates), which precipitate and remove metal acidity, although this generates acidity which must be neutralized, but in general, the water pH increases. Mn oxidation occurs at high pH (4.5 to 8), eliminating about 30% and the remaining 70% through coprecipitation and sorption with Fe oxyhydroxides (45%) and Al (25%) (Figure 5).Downstream of the La Silva stream, the pH reaches 5.3, as it joins to the Tremor river, which has six times the flow of the la Silva stream. This river has a pH near to neutral, conductivity between 275 and 345 µS/cm and alkalinity of 30 to 35 mg/l $CaCO_3$. At lower altitudes, it joins with the Boezariver, which has similar characteristics. The Tremor and Boeza segment is 10000 m long, where the pH remains neutral and there is a drop in Cu and Zn concentrations, as their soluble part does not coprecipitate with Fe and Al oxyhydroxides, forming solid Cu and Zn hydroxides instead (pH between 6 and 8) (Figure 5b), as shown in the following equations (5) and (6):

$$Cu^{2+} + 2H_2O \rightarrow Cu(OH)_2 + 2H^+ \quad (5)$$

$$Zn^{2+} + 2\ H_2O \rightarrow Zn(OH)_2 + 2H^+ \quad (6)$$

Almost all ecotoxic metals are capable of forming solid phases such as hydroxides [Fe $(OH)_3$, $Al(OH)_3$, $Zn(OH)_2$, etc.]. The precipitation of these hydroxides removes dissolved metals, in addition to enhancing the sorption of other pollutants, as in the case of arsenic coprecipitated with $Fe(OH)_3$.

The removal of sulphates can be linked to the consumption of sulphates during the formation of secondary minerals in acid environments, and due to the presence of organic matter in certain bed anaerobic areas, where alkalinity occurs in the form of HCO_3^- from the CO_2 generated in the biological reduction of sulphates by the following Reaction (7):

$$SO_4^{2-} + 2\ CH_2O + H^+ \rightarrow HS^- + 2H_2O + 2CO_2 \quad (7)$$

Bacterial sulphate reduction is the main mechanism producing sulphides precipitation; once HS^- ions are formed in solution, divalent metals react and precipitate as mineral sulphides with low solubility, according to Reaction (8):

$$HS^- + Me^{2+} \rightarrow MeS + H^+ \quad (8)$$

Me^{2+} represents ions of Cu^{2+}, Zn^{2+}, Cd^{2+}, Pb^{2+}.

Another kind of sulphate reduction is when it acts as an electron acceptor, forming H_2S and HCO_3^-, wherein for each reduced SO_4^{2-} mole, 2 alkalinity moles are produced by Reaction (9):

$$SO_4^{2-} + 2\ CH_2O + H^+ \rightarrow H_2S + 2\ HCO_3^- \quad (9)$$

The H_2S is released mainly in gas form, which reduces the water acidity, and generates solid metal sulphides on reacting with dissolved metals presented in Reaction (10):

$$H_2S + Fe^{2+} \rightarrow FeS + 2\ H^+ \quad (10)$$

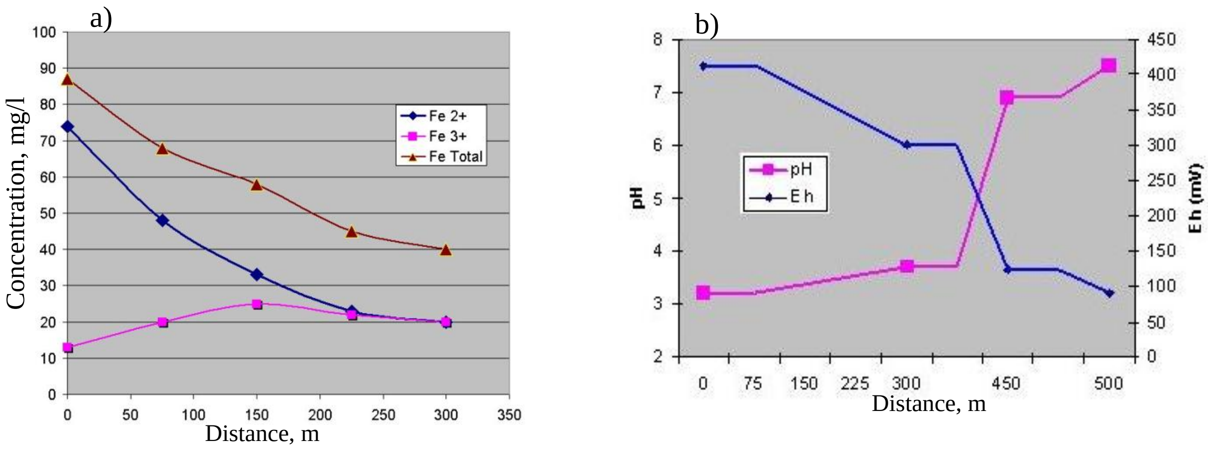

Figure 3. Behaviour of Fe^{2+}, Fe^{3+} and total Fe concentration (a) and pH-Eh (b)

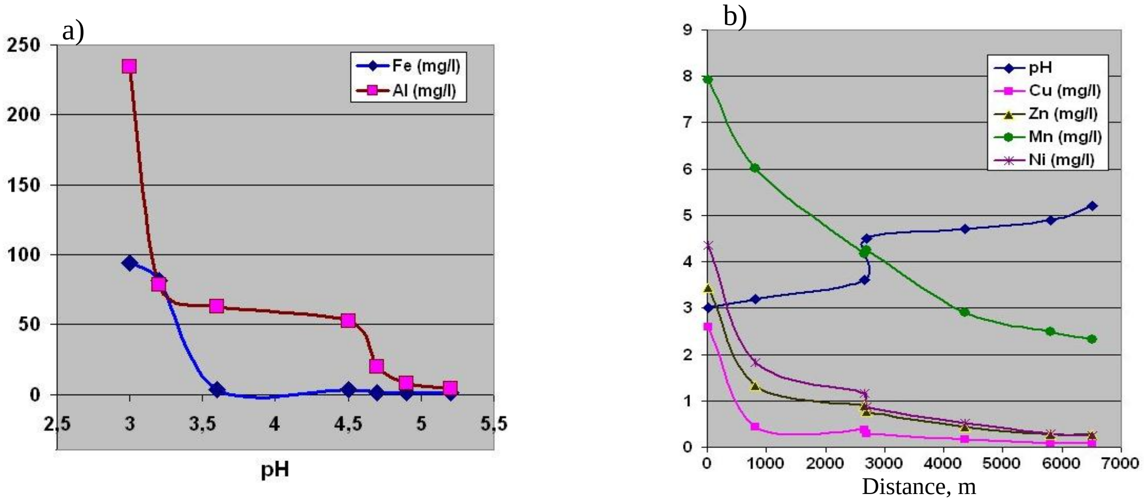

Figure 4. Behaviour of Fe and Al concentrations (a) and removal of Cu, Zn, Mn and Ni based on pH (b) in the La Silva river

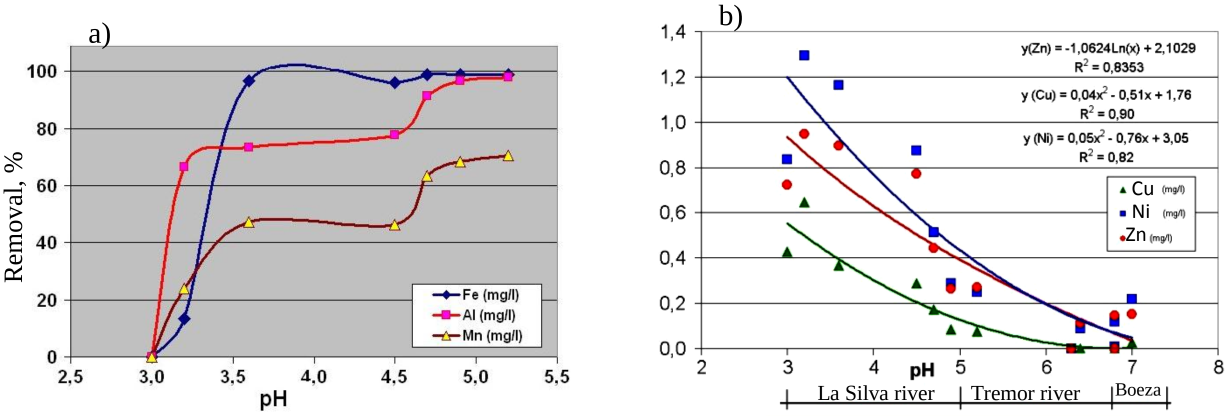

Figure 5. Fe, Al and Mn removal upstream (a) and downstream (b) of the La Silva, Tremor and Boeza rivers

As a result of the last two Reactions, 2 moles of bicarbonate and 1 mole of acidity are produced, thereby removing sulphates and dissolved metals by increasing the pH and alkalinity (Figure 6a). Additionally, there is also a reduction of As, Sb and Mo when complex sulphide minerals of Fe, Al and SO_4 are formed, as well as Zn and Cu sorption on the surface of the colloids or the initially formed amorphous solid phases.

This reduction of sulphates in water is also reflected in the electrical conductivity values, which drop from over 5000 µS/cm at the discharge points (pH = 2.9 to 3.2) to 50 µS/cm in the final segment (Boeza river) at neutral pH (Figure 6b).Generally, the phenomenon of attenuation by dilution and precipitation reduces the metal concentration and increases the water's pH. The main course of the basin covers three river systems (the Tremor, La Silva and Boeza rivers), where this is an improvement in water quality.

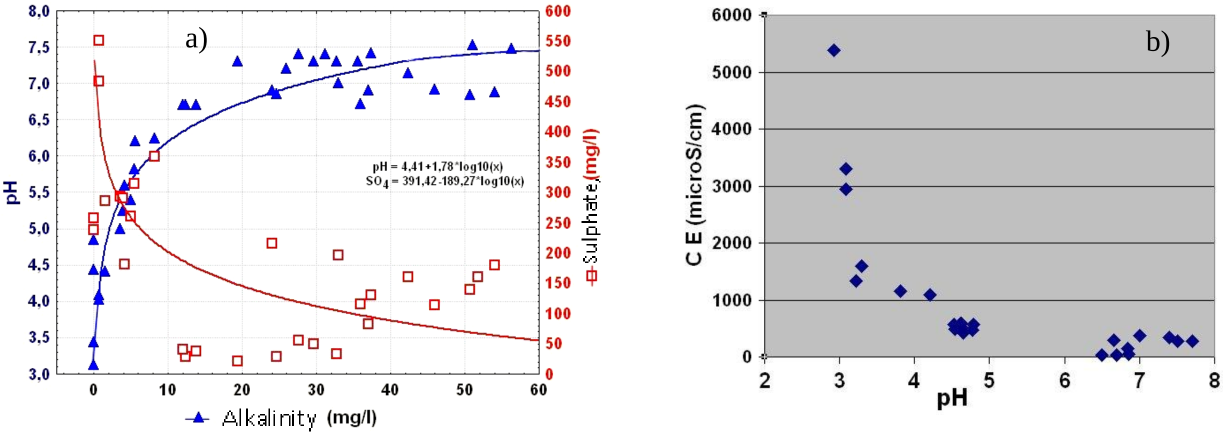

Figure 6. Sulphate removal based on pH and increase in alkalinity (a) and conductivity variation based on pH (b)

3.3. Natural attenuation of water pollutants in the Odiel basin

In the Odiel basin, located in the Iberian Pyrite Belt of south-western Spain, surface water quality data were measured between 1990 and 2001 of the ICA Network along 60000 m of the Odiel river, in sampling station 51 (1) up to Rio Tinto village, in stations 53 and 54 (2) near Calañas Village and station 56 (3) in Gibraleón Village (Figure 2). In this segment almost all acid mine drainage coming from abandoned mines (Concepción, Esperanza, San Platón, Poderosa, Rio Tinto, San Miguel, Sotiel, AguasTeñidas, Confesionarios, Valdelamusa, Lomero-Poyatos, San Telmo, Tharsis, Almagrera and others) is discharged between stations 1 and 2. In this segment of the Odielriver, there are some supplies of clean water from small tributaries from areas without mining facilities.

Before receiving the acidic water discharges of the Odiel, they have a pH ranging between 7 and 8 and alkalinity between 100 and 150 mg/l $CaCO_3$ eq.; after receiving the mine drainage (pH 2.5 - 3) the river flows downstream in a polluted state. The basin is characterized by a clearly seasonal water system with significant interannual irregularity (1000 l/s in winter and 200 l/s in summer).

The oxygenation of the Odielriver produces the chemical and biological oxidation of some soluble metal ions such as Fe^{2+}, which are transformed into Fe^{3+} and are precipitated as iron oxyhydroxides. The hydrolysis of both, Fe^{3+} and Al^{3+} form compounds that are precipitated, immobilising significant quantities of Fe and Al, in addition to coprecipitation by the adsorption of certain trace elements, enabling an increase in pH, thus forming a complex process of natural attenuation.

The hydrolysis reactions of Fe and Al are reversible, since, on the one hand, acidity can be added to the medium, and on the other, Fe^{3+} and Al^{3+} can be removed or released, resulting in a buffering system while maintaining the water pH without variation in certain river segments, until all the available Fe and Al is used up, which favours the total precipitation of Fe^{3+} at an approximate pH of 3.5 [15].

In the event of aluminium hydrolysis (buffering at a pH between 3.8 and 4.5), the precipitates of which give a whitish colour to the water (gibbsite, $Al(OH)_3$), this has a purely chemical system behaviour, contrary to the case of iron, which may involve biological mediation. These processes, together with the effects of dilution by the mixing of acid drainage with less contaminated water, lead to significant acidity attenuation.

As a result of all these processes and perhaps primarily due to dilution in the Odiel river segment studied between stations 51 and 54 of the ICA network, an improvement can be seen downstream in the water quality of the river, as seen in pH behaviour, although this improvement is less marked in the dry season (summer) than over the winter months (January-February), when there is rainfall (Figure 7).

During the summer (August) and in dry years, a lower pH and higher metal concentration are observed, together with Fe, Al and SO_4 contents that are also higher in summer and lower in winter (Figure 8a). In addition, these concentrations are higher in the upstream river stations (stations 1 and 2), when compared with stations (3) downstream of the mining area (Figure 8b).

In general, in the river segment assessed, there is an increase in pH and a decrease in metal concentration, illustrated in the Figure 8 represented by Fe, possibly due to the dilution phenomenon.

4. Conclusions

Under certain conditions, when the acid effluent ceases or acid mine discharges are low in comparison with the water volume in the receiving bodies, these water bodies show an improvement in quality downstream.

In the dissolution and mobilization of contaminants, great influence is exerted on the pH and the available concentration; and an increase in pH leads to the formation of more stable solid phases, although in certain chemical conditions, some metals may also be mobilized at neutral pH.

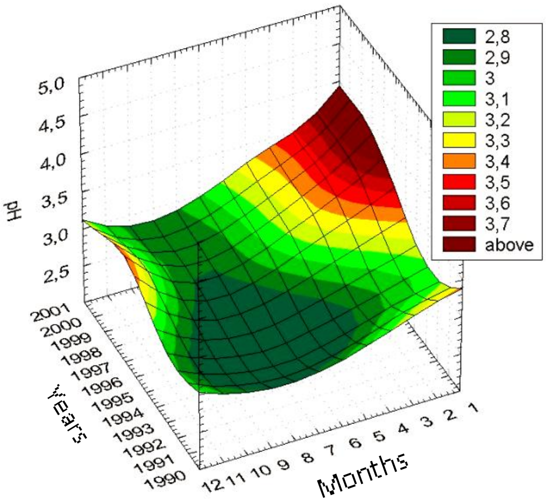

Figure 7.pH behaviour between 1990 and 2001 in the assessed Odiel river segment

The main acid mine drainage attenuation processes identified are: dilution by mixing with clean water, oxidation and hydrolysis of dissolved metals, an aerobic sulphate reduction, precipitation of secondary minerals and sorption of trace elements.

The increase in pH due to dilution enables the formation of more stable solid phases, which remove metal concentrations, thus neutralising the system.

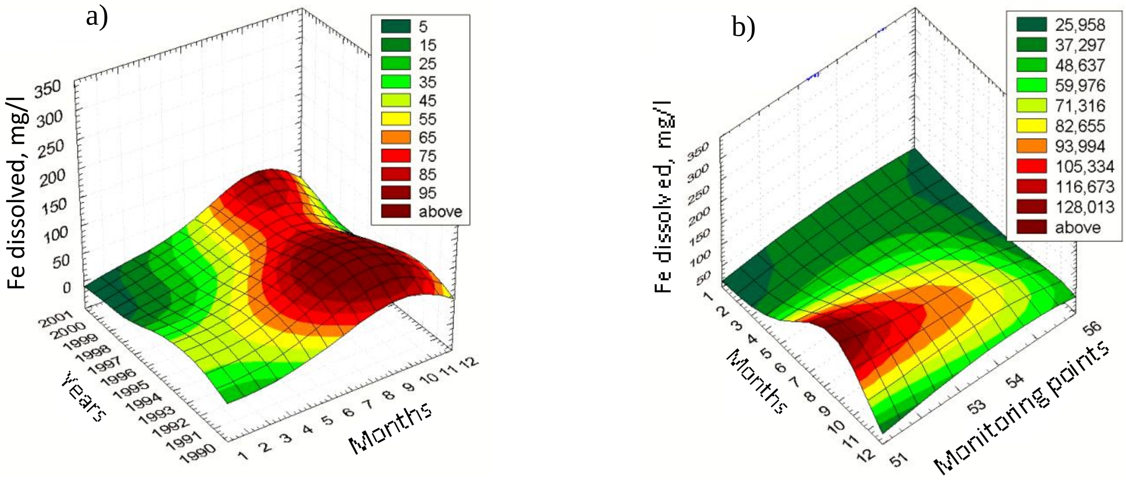

Figure 8. Metal concentration in summer (July-August-September) and dry years (a) and attenuation at sampling stations downstream and during winter (January-February) in the Odiel river between 1990 and 2001

The precipitation processes of secondary Fe and Al minerals in acidic media eliminate mineral water acidity and remove Zn, Cu, As and other elements by sorption and coprecipitation processes, thus producing natural attenuation.

This attenuation depends on the presence of chemical compounds that have the capacity to react with hydrogen ions, reducing acidity in the medium. If in the final balance, the quantity of compounds that generate alkalinity is greater than that of acid generators, the system is attenuated until reaching a pH of close to neutral.

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