Water Quality variations in the Tinto River during high flood events

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ABSTRACT

The Tinto river is strongly affected by acid mine drainage (AMD) originated in the Riotinto Mining District, with a mean pH value close to 2.6 and very high concentrations of sulphates (2500 mg/l) and metals (Fe 400 mg/l, Al 75 mg/l, Zn 62 mg/l). However the water quality shows seasonal variations through the year. It is known that during high flood events the concentration of contaminant decrease, although the total load transported by the river increase. We have studied the water quality variations in the Tinto river during several floods in autumn 2004. During intense rainfalls, water samples were collected every two or three hours with an automatic sampler. Samples were filtered and several elements (sulphates, As, Ba, Ca, Cd, Co, Cu, Fe, K, Mg, Mn, Na, Ni, Pb, Si, Zn, etc.) were determined in the laboratory by ICP-OES. The discharge was obtained from a stream-gauging station located at the sampling point. Most of elements show a decrease in concentration during the flood, probably due to dilution with the rain water, though exist some differences in the relative decrease from one element to another. However, other elements show an increase in concentration with the discharge, as is the case of Pb and Ba.

INTRODUCTION

The Tinto river drain a metallogenic area known as the Iberian Pyrite Belt (IPB) that hosts a large number of sulphide deposits, which has been subject of mining from prehistoric times. There is evidence to indicate that the Tinto river has transported considerable quantities of metals for over 4500 years, though during the last 150 years a more intensive mining has been carried out in the IPB. Nowadays, there is no sulphide mining in the IPB, however there are enormous amounts of mining wastes in the Tinto basin, which will continue to generate AMD for a long time to come.

The Tinto basin has a surface area of 1700 km^2 and a river lenght of 100 km, and is underlain by impermeable materials, so it has a low natural regulation. River flow displays a very strong inter and intraanual variation, in response to the rainfall regime. The average rainfall varies between 550 mm in the lower part of the basin and 1000 mm in the upper part. Tinto river flows into a coastal wetland known as the Ría de Huelva estuary, where joins to Odiel river, forming a very important Natural Reserve, famous for its ornithological diversity. Because of the environmental concern, several works have tried to estimate the anual metal discharge to the Ría de Huelva, but they haven’t considered high flood events. The lack of information about high flood events must be misleading on the total contaminant discharge transported by the river.

Tinto river has a mean pH value close to 2.6 and very high concentrations of sulphates (2500 mg/l) and metals (Fe 400 mg/l, Al 75 mg/l, Zn 62 mg/l, etc.). However the water quality shows seasonal variations through the year. During the summer the metal and sulphate concentration in the river increases due to the intense weathering of the sulphides and higher evaporation. Under these conditions, soluble iron hydroxysulphates precipitates on the margins of the river, and metals such as Cu, Al, Zn, etc., are affected by coprecipitation and adsorption processes in these salts (Cánovas *et al*., 2005). The highest sulphate and metal concentrations occurs with the arrival of the first rains, when these soluble salts are dissolved. During wet season metals concentration decrease and lowest values are reached during winter, which is a product of rainfall dilution effects in the river.

The major part of element transport in a river takes place during these high flood events because the variation in flow is much higher than the coinciding variation in concentration, so previous estimations of contaminant discharge to the estuary are underestimated. However, little it is known about how elements behave in acid waters in response to the dilution effect during high flood events.

This paper present a preliminary investigation of several floods (firsts after the summer) recorded in autumn, and their influence on the Tinto river water quality.

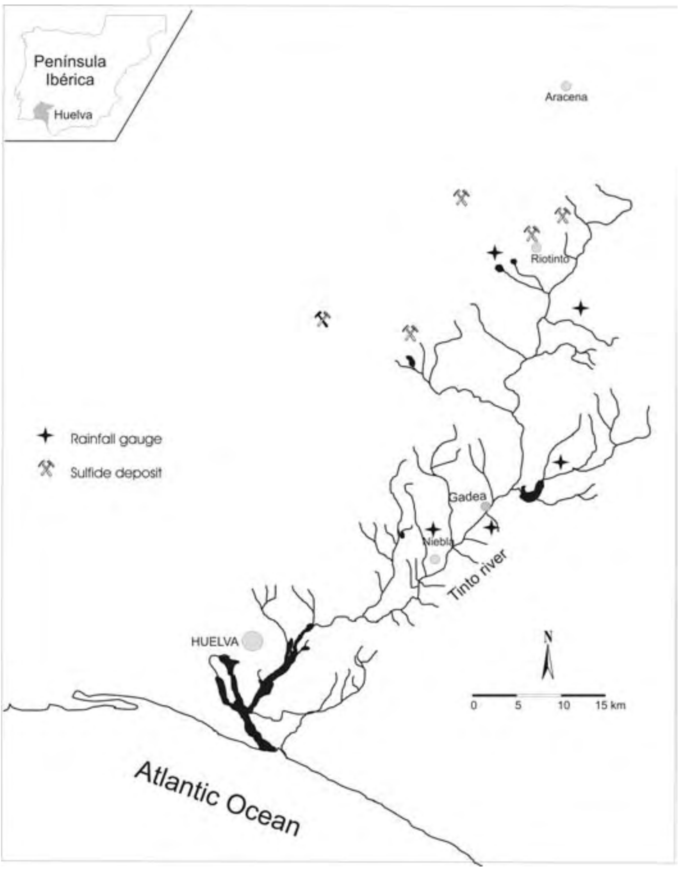

Figure 1. Location of the Tinto river, the main rainfall gauges located on its basin and the Gadea control station.

METHODOLOGY

Sample point is located close to where tidal influence appears. This point has been used as a stream-gauging and water quality control station for different organism (Guadiana Hydrographic Confederation and Environmental Council of the Andalusia Regional Government).

At this point was set up a Xian 1000 portable autosampler from Bühler Montec. Samples were pumped by an air pump vacuum system. Autosampler included a sample container of 24 bottles and an outlet pipe made of polyethylene. Bottles were previously washed in 10% nitric acid and then with milli-Q water (18.2 MΩ). The frequency of the sampling was every two, three or six hours depending on the weather forecast, and being more frequent during flooding (2 hours).

Specific electrical conductivity, pH, temperature and Eh were measured in all samples *in situ*. Samples were filtered through 0.45 µm pore Teflon filters and acidificied with suprapure nitric acid and all the samples remained refrigerated until analisis.

The chemical analysis was undertaken at the Central Research Services of the Huelva University following a custom-designed protocol specific to these types of water (Ruiz *et al*., 2003). Cations were analysed using Inductively Coupled Plasma optical Emission Spectroscopy (ICP-OES) on a Jobin Yvon (JY ULTIMA 2) spectometer.

Rainfall data were achieved from a net of rainfall gauges (composed by 5 stations) distributed all over the catchment (Fig. 1). Discharge data were obtained from two types of flow-meter, an ultrasonic flow-meter property of the Environmental Council of the Andalusia Regional Government, and a stilling well flowmeter property of Guadiana Hydrographic Confederation. The last type of flow-meter has some problems when a flooding happens, so we can contrast results from the two types of flow-meters. Ultrasonic flow-meter has some fluctuations (from 9th to 13th october) due to changes in pressure (level is detected by differences of pressure) as can be seen in the hydrograph (Fig.2). According to these data, we have distinguished three different flood events (Fig. 2).

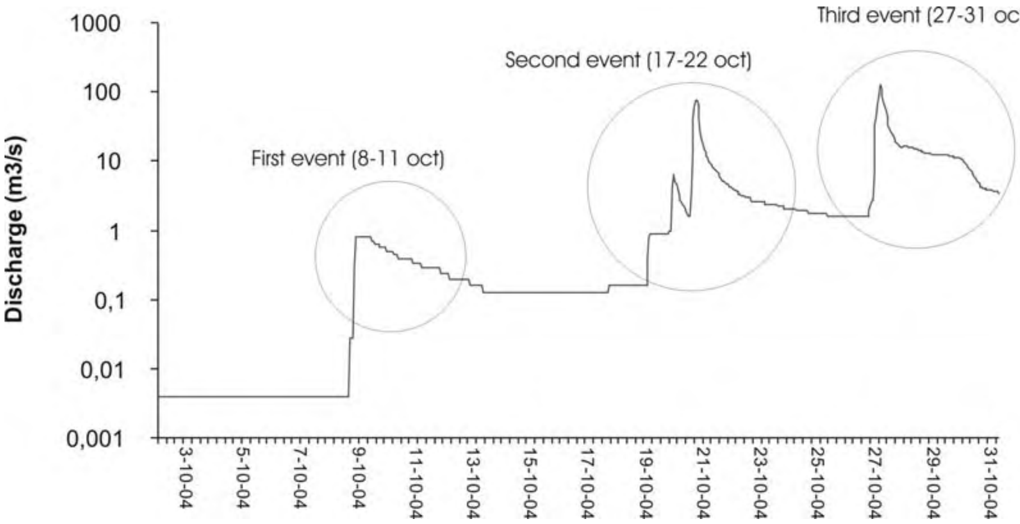

Figure 2. Hydrograph of the different high flood events recorded in October in the Tinto River.

RESULTS AND DISCUSSION

During the summer, river flow decreased significantly. Average river flow was of 0.24 m^3/s in June, and at the end of the dry season was only of 4 l/s. Due to an intense evaporation and a rise in sulfide oxidation processes by bacterial activity, it can be observed an increase in electrical conductivity (achieving 4 mS/cm at the end of the dry season) and in metal and sulphate concentration. For this reason, quite a lot of mineral phases are supersaturated, precipitating as soluble salts, chiefly Fe oxyhydroxidesulphates (melanterite, copiapite, coquimbite, etc), on the margins of the river and on the mine dumps and tailing dams located on its watershed (Hudson-Edwards *et al*., 1999; Buckby *et al*., 2003).

Below, the influence of the different rainfall events after the dry season on the Tinto river water quality is dicussed.

First rainfall event (8-11 October)

The first few rains after the dry season were recorded on 8th and 9th of October (9 and 1 mm respectively). As a result river flow increased until 0.78 m^3/s on the 9th October (Fig. 2); the hydrograph crest was reached after a few hours the end of the rainfall.

During this event, the autosampler did not work. However, from manual sampling data, a flashout of the soluble salts precipitated on the margins of the river was observed, increasing strongly electrical conductivity (from 3.67 to 8.07 mS/cm) and metal concentration (Fe from 99 to above of 1100 mg/L, SO_4 from 1628 to 9574 mg/L, As from 0.01 to 0.51 mg/L, Al from 89 to 483 mg/L, Pb from 0.08 to 0.28 mg/L, Zn from 25 to 144 mg/L, etc.). The rise in concentration was very strong for Fe (12 times increased) and As (50 times increased); the rest of metals increased their concentration between 4 and 6 times. pH values kept stable around 2.27.

The process by which the soluble salts are flushed out with the arrival of the first rains in autumn has been mentionated in reserches on rivers affected by AMD (Sandén *et al*., 1997), specially on the Tinto and Odiel rivers (Olías *et al*., 2004, Cánovas *et al*., 2005) and in this situation when these salts are flushed out, the higher contamination level is reached in both rivers.

Second rainfall event (17-22 October)

In this event, rainfalls were more intense than in the first event (18, 7, 6 and 33 mm recorded on 18th, 19th, 20th and 21st October respectively). Before this rains, river flow was 0.123 m^3/s. On 19th, river flow increased heavily until values close to 1 m^3/s, altough electrical conductivity and pH values did not change (Fig. 3). Some metals increased slightly their concentration (Fe from 1134 to 1385 mg/L, Cu from 139 to 148 mg/L, Cd from 0.67 to 0.74) while others metals didn´t change their concentration (Al, Mn, Cu, Zn, etc.).

It is not clear why there is no significant change in the element concentration with a rise so high in river flow (one order of magnitude). This could be explained by the fact that in this event, the concentration of disolve elements could be in equilibrium with the soluble mineral phases precipitated during the summer (melanterite, copiapite, coquimbite, etc.). The arrival of runoff water with a minor amount of salinity would dissolve these soluble salts without changing element concentration.

This process would continue until these salts were dissolved completely or were completely flushed out by a more important high flood event.

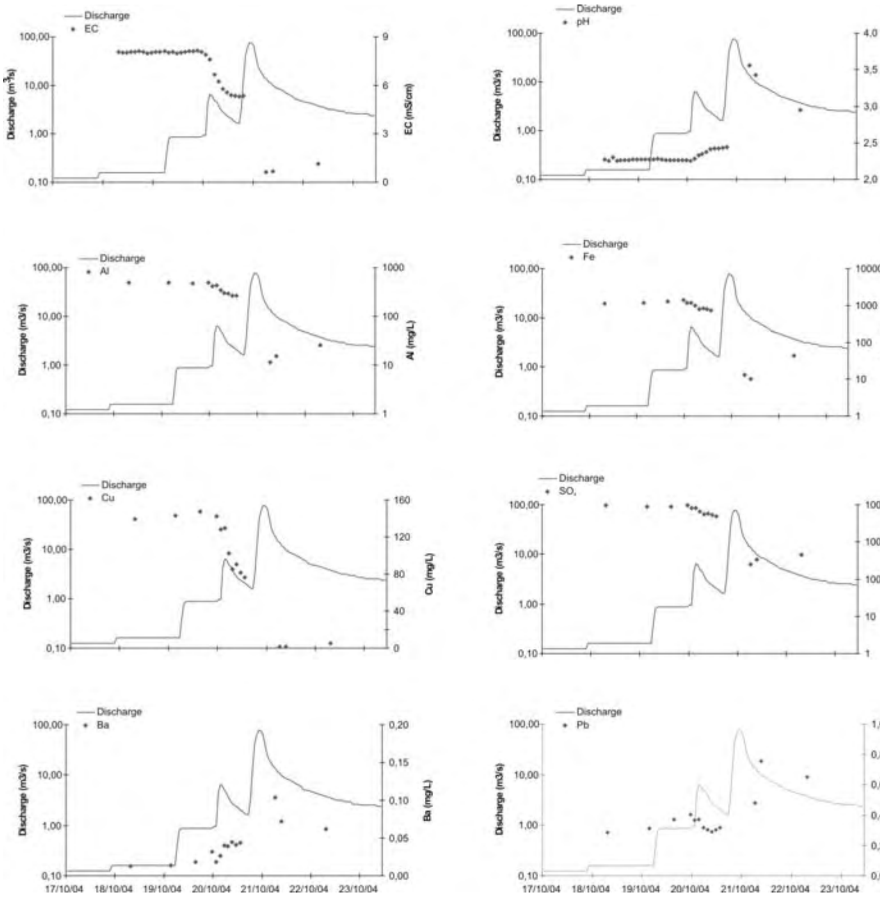

Figure 3. Evolution of EC, pH, sulphate and metals concentration in relation to the river flow during the second rainfall event

River flow increased again on the 20th, reaching a maximum value of 6 m^3/s. As is shown in Figure 3, electrical conductivity decreased progressively until a value of 5.5 mS/cm and pH values displayed a slightly increase around 2.44. The crest of the hydrograph did not ocurr at the same time than the minimum value of electrical conductivity, recording a lag of about a day. Walling and Foster (1975) showed that variations in the concentration of certain dissolve elements tended to lag behind associated changes in discharge and this lag is increased progressively downstream. This lag is inversely related to antecedent catchment wetness and rainfall magnitude, so the lag between the crest of the hydrograph and the minimum value in electrical conductivity on the 21st is lower than on the 20th.

River flow increased again on the 21st, due to the intense rainfall and higher soils moisture, reaching a maximum of 76 m^3/s, higher than others crest in this event.

This flooding swept a great amount of suspended materials that buried the outlet pipe of the autosampler, so it was off during a few hours, but we were able to take some samples manually. Due to the great rise in flow level, electrical conductivity decreased heavily (0,63 mS/cm) like the metals and sulphate concentration (Fe 13 mg/L, Al 11 mg/L, Cu 2 mg/L, Mn 7 mg/L, Zn 3 mg/L and SO_4 247 mg/L), while pH reached a value of 3.6 (Fig. 3).

During the recession hydrograph electrical conductivity, metals and sulphate concentration rose in value but not reaching previous values. Electrical conductivity became stable around 2 mS/cm, pH around 2.8, and Al, Fe and Zn concentration approached around 66, 110 and 14 mg/L respectively. In this flooding, an important wash out was carried out and soluble salts precipitated during the summer disappeared from the margins of the river, decreasing the contamination levels. However, Ba and Pb displayed a different behaviour in relation to the rest of metals. Ba showed an increase during the flooding (Fig. 3) while Pb showed an slightly decrease during the flooding on the 20th, though later increased its concentration, reaching a maximum durin the flooding on the 21st. This behaviour could be associated to the fact that the solubility of Pb and Ba is controlled by barite ($BaSO_4$) and anglesite ($PbSO_4$). Therefore when sulphate concentration decrease, Ba and Pb concentration increase.

Saturation states of minerals in water have been calculated with PHREEQC (Parkhurst & Appelo, 1999). Results show that all the samples were supersaturated in barite (saturation index between 0.1 and 1) reaching the maximum saturation index during the flooding. All the samples were slightly undersaturated in anglesite (saturation index between -0.4 and -0.9), so in principle we could dismiss the possibility that Pb concentration could be controlled by anglesite dissolution and/or precipitation. However, this control by anglesite could be effective upstream, close to the sulphide deposits, where the saturation index is higher.

Pb has a great affinity to be adsorbed by particle surfaces, so this behaviour could alternatively explain its maximum concentration during the flooding, due to a higher amount of suspended solids transported by the river. The rest of the element showed a similar evolution, altough as can be seen in Figure 4, there are some differences between some of them.

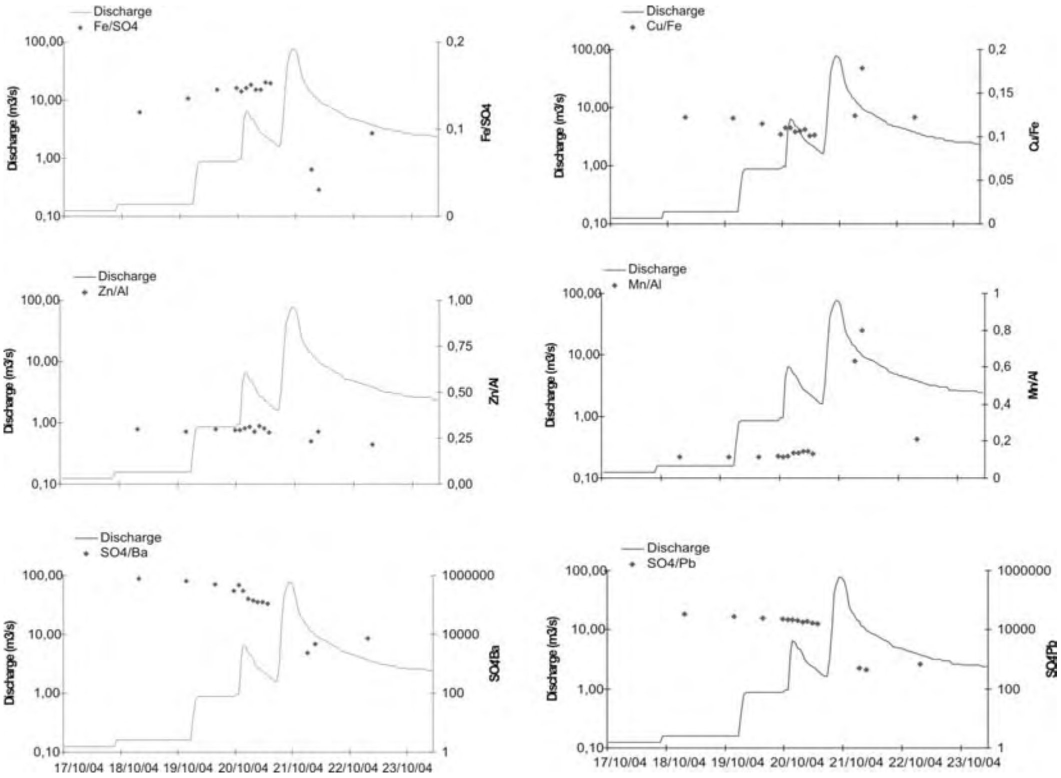

Figure 4. Ionic ratio evolution between metals and sulphate in relation to the river flow during the second rainfall event.

Sulphate concentration increased in relation to Fe during the flooding due to the important precipitation of iron oxyhydroxides associated to the rise in pH. An increase of the rest of metals was produced in relation to Fe concentration for the same reason. One of these metals, Mn, showed a slight variation in response to a rise in pH value, due to its conservative behaviour in acid waters (Cánovas *et al*, 2005).
Al and Zn showed similar variations during the flooding (Fig. 4) due to the similar behaviour in response to the dilution effect of runoff water. Cu had a different behaviour in relation to Mn, Al and Zn, showing an stronger decrease during the flooding.

Third rainfall event (27-31 October)

During this rainy event, rainfalls of 65, 5 and 4 mm were recorded on 27th, 28th, and 29th October. A strong increase in river flow was recorded on 27th, reaching 127 m^3/s in only six hours (Figs. 2 and 5). At the crest of the hydrograph, electrical conductivity decreased until 0.51 mS/cm. The same decrease was undergone by metals and sulphate concentration (SO_4 157 mg/L, Fe 14 mg/L, Al 7 mg/L, and Cu, Mn, Zn 2 mg). pH values increased until 3.4 and, in the same way than the previous event, Pb and Ba concentrations increased, altough Pb concentration showed an initial decrease.

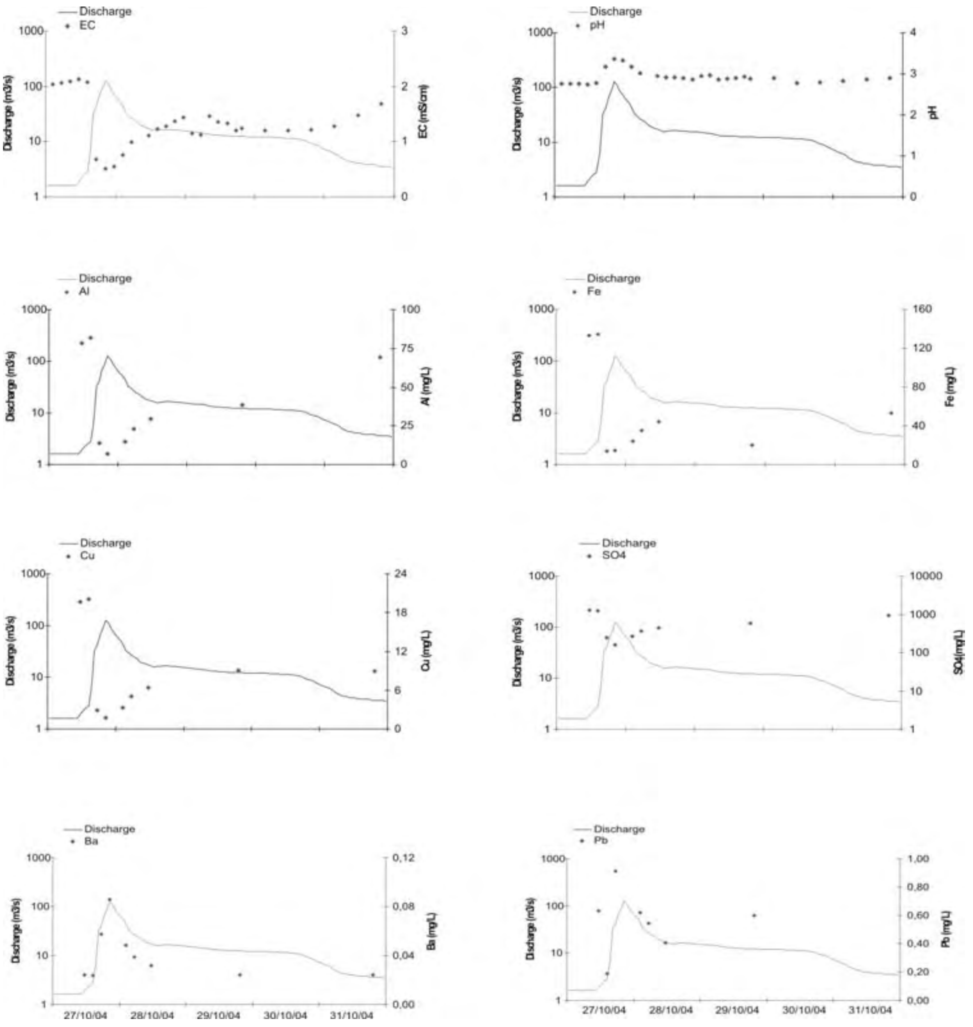

Figure 5. Evolution of EC, pH, sulphate and metals concentration in relation to the river flow during the third rainfall event.

Once the river flow decreased progressively, electrical conductivity, sulphate and metals increased continuosly. There is a period where electrical conductivity decreased from 1.5 to 1 mS/cm and pH increased slightly (Fig. 5). We do not have a sample from this period. However, the change in water quality cold be associated to the arrival of water from an area not affected by acid mine drainage, altough no increase in river flow is observed.

Saturation indexes of barite and anglesite during this flooding are similar to the previous event. Evolution of ionic ratio between metals also showed a similar behaviour in relation to the previous event.

CONCLUSIONS

In this work, Tinto river water quality has been monitorized during the first flooding in autumn in a sample point located close to the mouth of the Ría of Huelva. During the dry season, river flow decreased and due to the intense evaporation and an increase in biological sulphide oxidation processes, metals and sulphate concentration increased, precipitating soluble salts (melanterite, copiapite and coquimbite) on the margins of the river and on mine dumps and tailing dams.

These salts are very soluble and were redissolved with the arrival of the first rains after the summer. In that situation, highest pollution levels were reached, with a pH value of 2.2, electrical conductivity of 8 mS/cm, and Fe, Al, Cu and Mn concentration around 1200, 480, 140, 140 and 55 mg/L respectively.

Small increases of river flow hardly changed water quality, so elements concentration must be controlled by solubility of salts precipitated during summer until these slats are completely dissolved.

With the arrival of the first great flooding (with a value of 67 m^3/s), these salts are washed out and metals and sulphate concentration reached values lower than those reached during the summer. During the flooding, most of elements decreased in concentration, although Pb and Ba concentration increased. Ba concentration must be controlled by barite solubility, so when sulphate concentration decrease, Ba concentration tend to increase.

At the sampling point, river water is slightly undersaturated in anglesite and therefore the behaviour of Pb is not as clear as Ba. Pb concentration may be influenced by the increase of particles in suspension, due to its great affinity to be adsorbe in particle's surface.

The evolution in the concentration of the rest of the metals is similar during the flood. However, when the ionic ratio between elements is considered, some differences are shown. Fe is the metal which has the highest decrease during a rise in river flow, due to its precipitation as Fe oxyhydroxide when pH is increasing, buffering the system. Cu may be affected by precipitation or/and adsorbtion during the flooding, and Al and Zn have a similar in response to the dilution effect. Mn is the most conservative metal dissolved in the Tinto river waters.

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