

Evaluation of the dissolved contaminant load transported by the Tinto and Odiel rivers (South West Spain)

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Abstract

The Tinto and Odiel rivers are heavily affected by acid mine drainage (AMD). However, the exact quantities of contaminants transported into the Huelva estuary and the Gulf of Cadiz are unknown. The existing previous investigations are, in general, based on studies with few data or incorrect methodology, and are therefore unreliable. This study aims to present a reliable estimation of the dissolved contaminant load transported by both rivers for the periods 1995/96 to 2002/03. The methodology used is based principally on the correlation between contaminant concentration and flow rate. The results show that both rivers transport enormous quantities of dissolved contaminants: 7900 t yr⁻¹ of Iron (Fe), 5800 t yr⁻¹ Aluminium (Al), 3500 t yr⁻¹ Zinc (Zn), 1700 t yr⁻¹ Copper (Cu), 1600 t yr⁻¹ Manganese (Mn) and minor quantities of other metals. These values represent 60% of the global gross flux of dissolved Zn transported by rivers in to the ocean, and 17% of the global gross flux of dissolved Cu.

Key words: Tinto and Odiel rivers, contaminant metal load, acid mine drainage

1. Introduction

The Tinto and Odiel rivers drain an area which hosts many polymetallic massive sulphide deposits in a region known as the Iberian Pyrite Belt (IPB), whose original reserves were in the order of 1700 million tonnes (Sáez et al., 1999). The extraction of these minerals commenced in prehistoric times although the large-scale exploitation of these deposits did not start until the second half of the XIX Century (Leblanc et al., 2000). There exist some hundred deposits within the Odiel and Tinto basins amongst which the districts of Riotinto, Tharsis and Sotiel-Coronada are best known. The legacy of such intense mining activity has left kilometres of galleries, a multitude of pits, enormous waste dumps and other mining waste where oxidation of pyrite and associated sulphides can occur, producing an acid leach containing large amounts of toxic metals and a highly contaminating power called acid mine drainage (AMD). Although at present there are no active mines in the IPB the Tinto and Odiel rivers continue to carry high levels of contaminants due to the longevity of the contamination processes of AMD (Younger, 1997).

Globally AMD is considered to be one of the main causes of contamination of the hydrological resources (Nordstrom & Alpers, 1999), and the Tinto and Odiel rivers are probably one of the most strongly affected by AMD. The Tinto river has a pH around 2.5 and a very high concentration of metals (López Archilla & Amils, 1999; Braungardt et al., 2003; Achterberg et al., 2003). Although less well known, as the conditions are not so extreme as in the Tinto, the Odiel river is more affected given that the size of the polluted fluvial network is greater, with pH values around 3.1 (Olías et al., 2004).

These two rivers end in a common estuary called "Ría de Huelva" (Fig. 1), which is heavily contaminated by metals (Nelson & Lamothe, 1993; Ruiz, 2001; Grande et al., 2003). During estuarine mixing, metals are removed from solution in relation to pH and salinity increase (Elbaz-Poulichet et al., 2001a; Braungardt et al., 2003; Achterberg et al., 2003). Nevertheless, the inputs from the Ría produce a plume of contaminants in the Gulf of Cadiz which enters into the Mediterranean Sea (van Geen et al., 1997; Elbaz-Poulichet et al., 2001b).

Despite the numerous publications dealing with the fate of metals in the estuary and the contamination of adjacent coastal waters, the metal fluxes discharged by the Tinto and Odiel rivers remain uncertain as they rely on a limited number of data (Braungardt et al., 2003; Sainz et al., 2004; Sarmiento et al.,

2004). This does not allow to take into account in the flux calculation the variability in discharge and concentrations in relation to the Mediterranean climate of the area, which alternate long periods of drought and short but intense rainy events.

The main objective of this work is to provide a reassessment of the dissolved contaminant load discharged by the Tinto and Odiel rivers to the Ría de Huelva. For this purpose, the variations of metal concentrations as a function of river discharge have been examined over 8 hydrological years (from 1995/96 to 2002/03).

2. Methodology

2.1. Analytical data used

The analytical data used for this study are results of sampling programs in the Tinto and Odiel rivers undertaken between the periods 1995/96 to 2002/03. This time frame was selected due to the high abundance of available sample data. In the Odiel river the sample station is located in the town of Gibraleón and in the Tinto river samples were taken at the town of Niebla.

We have compiled analytical results at the aforementioned sample stations from the following organisations:

- Control Network of the Guadiana Hydrographic Confederation, with a sample periodicity of approximately 15 days, although there are some months without analysis. We have acquired samples taken between September 1995 and October 2002. Along with other parameters analytical results include sulphate, Arsenic (As), Cadmium (Cd), Copper (Cu), Iron (Fe), Manganese (Mn), Lead (Pb) and Zinc (Zn).
- Analysis undertaken by the Environmental Council of the Andalusia Regional Government that started in March 1996 with a weekly sample rate and from December 1997 on a fortnight basis. We have data until August 2003. The same parameters were determined as in the control network mentioned before.

- Analysis undertaken in the “Control of Littoral Waters Plan” of the Environmental Council of the Andalusia Regional Government, using sample rate of approximately 1 sample per 3-month period. These controls commenced in 1988 and are the source data used by Sainz et al. (2004) to determine the contaminant load transported by the Tinto and Odiel rivers. We have only used them where they exclusively coincide with the above-mentioned time frame between September 1995 and August 2003. The analyses include all of the above elements with the exception of sulphates.

Together with the aforementioned analyses we also have available samples taken by our team on a weekly basis commencing in February 2002 in which a large number of elements were analysed. In this study we have only used elements that are coincident with the pre-existing sample programs (sulphate, As, Cd, Cu, Fe, Mn, Pb, Zn) together with other toxic metals that reach high concentrations that are not included in the previous list of analysis undertaken by organisations listed above (Aluminium (Al), Cobalt (Co) and Nickel (Ni)).

In order to ensure the consistency of the data set used, that includes data from the Guadiana Hydrographic Confederation and the Environmental Council of the Andalusia Regional Government, together with our own data, first we confirm that the protocol for data acquisition and data quality assurance at the different laboratories was similar to the one followed at the University of Huelva discussed below. In this way, for example the laboratory of the Environmental Council of the Andalusia Regional Government is accredited under the ISO/IEC/EN 17025 standard "*General Requirements for the Competence of Calibration and Testing Laboratories*" (ENAC Lab # 119/LE296). Moreover, to check how comparable is the data from the different data sets, since February 2002 we designed a sampling campaign with the aim of, as much as possible, sampling the same days that the organizations mentioned above from which we are using the data.

2.2. Analytical techniques

This section deals only with the sampling undertaken by us, which followed a protocol similar to that described by Johnson (1986). However, as discussed above, it should be noted that in the days where data from various sources was available there was a good between the different data sources.

For cation determination the samples were collected in 250 ml high-density polythene bottles previously washed in 10% nitric acid and then with mili-Q water (18.2 M Ω), and only prewashed in mili-Q water (18.2 M Ω) for samples used for anion determination. Conductivity and pH were measured in situ and later the samples were filtered through 0.45 μ m pore teflon filters. The samples destined for cation determination were acidified with suprapure nitric acid and all of the samples remained refrigerated until analysis.

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., 2003a), that was contrasted with international (SRM 1640, IRMM-N3) and natural calibrated standards (Ruiz et al., 2003b, Tyler et al., 2004a,b). The cations were analysed using Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES) on a Jobin Yvon (JY ULTIMA 2) spectrometer fitted with an ultrasonic nebuliser (CETAC U5000AT+) to improve the sensitivity of the equipment (Tyler et al., 2004a,b). The anions were determined by ion chromatography using a Dionex DX-120 machine fitted with an AS 9-HC of 4 x 250 mm column and a 4 mm ASRS-ULTRA suppressing membrane.

2.3. Flow data

The flow rate data originate from daily readings at stream gauging stations of the Guadiana Hydrographic Confederation. In the Odiel river the stream gauging station coincides with that of the analytical sample point, thus we can calculate the contaminant load by multiplying the concentration of the elements by the average daily discharge.

However in the case of the Tinto river, the stream gauging station is 9 km upstream from the point used for the analytical sampling (Figure 1), thus the use of a correction coefficient is necessary because there are several large streams unaffected by AMD that join the Tinto river between the two points, resulting in a dilution of contamination and an increase in flow.

The correction coefficient was calculated in function of the corresponding drainage basin area at the stream gauging station (756 km²) and at the point downstream used for analytical sampling at Niebla (950 km²). Supposing similar conditions for both sites, i.e. soil type, vegetation, etc, the flow

contribution at Niebla will be higher by a correction factor equal to the relationship between both drainage basin surface areas ($950 \text{ km}^2 / 756 \text{ km}^2$), which results in 1.256.

Given this, to calculate the contaminant load for the Tinto river we should multiply discharge (or the contaminant load obtained at Niebla) by 1.256. This correction has not been taken into account in previous investigations.

A frequently encountered problem was missing flow data, such that in the 8 years of our selected time frame there are 12 months of missing data for the Tinto river and 23 months for the Odiel river. In this last case there is a long period without information between November 1997 and March 1998.

3. Results and Discussion

3.1. Hydrological regime of the rivers

With the available data an average flow obtained for the studied time period (1995/96 to 2002/03) is $1.6 \text{ m}^3 \text{ s}^{-1}$ and $29 \text{ m}^3 \text{ s}^{-1}$ for the Tinto and Odiel rivers respectively. In the wettest years these values increase to $2.5 \text{ m}^3 \text{ s}^{-1}$ and $67 \text{ m}^3 \text{ s}^{-1}$, however in the driest year the average flow rate of the Tinto river was reduced to just $0.2 \text{ m}^3 \text{ s}^{-1}$ (during this year there are numerous missing flow data for the Odiel).

It must be taken in to account that the considered time frame it was wetter than normal; the average precipitation recorded at the 9 rain gauges (Figure 1) included in this study between the period 1995/96 to 2002/03 is 980 mm, however if a greater time period is considered between 1980/81 to 2002/03 the average reduces to 812 mm.

In Figure 2 the horizontal axis represents daily flow ordered from lowest to highest and the vertical axis represents frequency in which the rivers reach or exceed these flows rates. The resulting curves for both rivers are similar and demonstrate the high irregularity of the flow rates. In the Odiel river 80% of the daily flow rates were recorded at below $10 \text{ m}^3 \text{ s}^{-1}$ and just 7% of the total days had a flow above $100 \text{ m}^3 \text{ s}^{-1}$. For the Tinto river in 27% of the total days the river was practically dry (discharge $<0.01 \text{ m}^3 \text{ s}^{-1}$) and 80% of daily flows are less than $1 \text{ m}^3 \text{ s}^{-1}$, with just 4% above $10 \text{ m}^3 \text{ s}^{-1}$.

3.2. Elemental contaminant concentrations

There are 416 samples from the Tinto river available for the eight year study period, giving an average of 52 data per year, with a minimum of 36 samples per year and a maximum of 80. The number of samples for the Odiel is 419, also averaging at 52 data per year, with a minimum of 43 and a maximum of 76 samples.

The total number of elemental data analysed are shown in Table 1, those elements with lower concentrations (mainly As, Cd, and Pb) have fewer results as the analyses frequently reported below the detection limit. Analytical results for Al, Co, and Ni are only available for our own weekly sampling program, which commenced during 2002, thus the number of available analyses for these elements are lower than others.

In agreement with the previous studies (López-Archilla & Amils, 1999; Braungardt et al., 2003) the conditions in the Tinto river are more extreme than in the Odiel river, with average pH values of 2.6, sulphate content 2455 mg L⁻¹, Fe 393 mg L⁻¹, Al 75 mg L⁻¹, Zn 61 mg L⁻¹, Cu 27 mg L⁻¹, Mn 11 mg L⁻¹ and lower values of As, Cd, Co, Ni, and Pb. The average pH of the Odiel river is slightly higher (3.3), the sulphate and metal content also are much lower than the Tinto river, especially As content (62 times lower than the average in the Tinto) and Fe (31 times lower than the Tinto). The concentration of Cd, Cu and Zn is approximately 4 times lower than the Tinto, however the concentrations of Mn, Ni and Pb are similar in both rivers (Table 1).

3.3. Contaminant load calculation method

One method of calculating the monthly contaminant load is to average the monthly analytical results and multiply it by the monthly discharge. This method however can produce a large error in periods where there has been flow rate variation. If the same “weight” is given to an analysis obtained during low water to one obtained in high water or storm periods we are over evaluating the contaminant load, because in the entire monthly calculation the storm supposedly contributes a much greater volume of water.

To resolve this one can take in to account the daily flow for the sample in question to balance the importance of this sample in to the context of monthly contribution of the river. For a number of samples (n) in a month the weighted monthly average would be:

$$C_{mp} = \frac{C_1Q_1 + C_2Q_2 + \dots + C_nQ_n}{Q_1 + Q_2 + \dots + Q_n}$$

This weighted average concentration is multiplied by the monthly discharge to calculate the monthly load for each element.

Despite this the method is also not exact when there are peaks in flow rates that have not been recorded because storm activity produces a strong dilution effect on the contaminant concentration (Olías et al., 2004). Statistically there is little possibility of sampling these storms effects that occur during only a few days of the month. For example five samples were taken from the Odiel river in November 2001. Figure 3 shows that these five samples do not coincide with period of highest flow rate and in only 3 days 93 hm³ (84% of the monthly contribution) were discharged, such that the recorded contaminant concentration should be much lower than the rest of the month. In this case if we calculate the contribution using the weighted monthly average once again the contaminant load is overestimated.

Another method of estimating the contaminant load is based on establishing relationships between flow and the concentration of the dissolved elements. When the flow increases in a river generally a decrease in concentration of dissolved substances is observed due to the dilution effect of the less concentrated surface runoff (Langmuir, 1997). This effect has been verified in the Odiel river where a decrease of the contaminant levels during winter due to higher flow rates is apparent (Braungardt et al., 2003; Olías et al., 2004). If it were possible to establish a relationship between elemental concentrations and flow rates using the daily average flow rates we could calculate the contaminant concentration of this day and thus the load transported by the river.

However, these correlations are not always simple to establish. For example at the start of the hydrological year, in autumn, the first rains produce the dissolution of the weathering products of pyrite accumulated during the summer, such that the salts deposited by the intense evaporation along the river margins when dissolved by the increased flow produce an inverse relationship by actually increasing the concentration. This process, called 'rinse out' or 'flush out', have been observed in the

Tinto and Odiel rivers (Hudson-Edwards et al., 1999; Olías et al., 2004), and in others rivers affected by AMD (Wirt et al., 1999; Keith et al., 2001).

During winter and once these salts have been washed away by the river, the contaminant concentrations fall well below those measured at the beginning of autumn. If on the other hand not enough precipitation occurs to produce this washing effect the elevation of the contaminant concentrations will occur during the winter (Olías et al., 2004). Equally if during spring there is a relatively long period of drought, with an increase in temperature soluble sulphate salts can precipitate along the banks of the river, which will be eventually re-dissolved during a flood, producing the same autumnal wash effect although on a lesser scale (Olías et al., 2004).

Thus the relationship between flow and contaminant concentration is not constant over the entire year, but is dependant on the time of year, the previous precipitations, temperature, and possible reservoir releases in the drainage basin, etc. There also exist a number of elements such as As and Pb whose behaviour do not show any significant correlation with flow and where this is the case this methodology cannot be applied.

In this study where possible, the contaminant load has been calculated using it relationship with the flow rate. The method followed has been to identify for each hydrological year periods where the relationship exists and calculate for each one of these periods the regression equation between flow and elemental concentration. The best fit is obtained using a potential function as shown by Langmuir (1997). Once the regression equation is obtained the elemental concentration for each daily discharge is calculated and from this is calculated the contaminant load transported on this day. The sum of these daily contributions will therefore give the monthly contribution for each element.

Figure 4 is an example of the relationship between Cu and flow for the hydrological year 1996/97 in the Tinto river and shows the different periods used to obtain the regression lines. As can be seen in this figure, there is an increase in the Cu concentration in autumn associated to the washing of the soluble salts with the first rains after the summer drought, the so called 'rinse out' effect. In contrast, the lower Cu concentrations are recorded in winter, when the river flux is higher.

The overall annual correlation is low; however there are periods with a notable increase in correlation dividing up the data. The first period (15/11/96 to 05/12/96) corresponds to the first important washing after autumn in such a way that concentrations increase with the flow rate. The second period (06/12/96 to 21/04/97) corresponds to winter and the progressive decrease of flow rates in spring. This evolution is interrupted by an increase in flow rates in April (22/04/97 to 24/05/97). Later the river completely dries up and subsequently in June, in response to new rainfalls, the river flows once again, producing an increase in elemental concentrations with flow due to the re-dissolution of salts previously deposited (Figure 4).

The correlation between flow rate and contaminant concentration also change among different years depending on the hydrologic conditions. As an example, Figure 5 shows the evolution of flow rate and Mn concentration in the Odiel river during two hydrologic years, together with the correlation between discharge and Mn concentration in the 3 periods differentiated. The hydrologic year 1999/00 was dry, with a mean flow rate of $7,1 \text{ m}^3 \text{ s}^{-1}$, while the year 2000/01 was very rainy, with a mean flow rate of $67 \text{ m}^3 \text{ s}^{-1}$. As can be seen in Figure 5, the correlation obtained is completely different for the three periods. In the winter of 2000, there is a Mn concentration of $6,2 \text{ mg L}^{-1}$ for a flow rate of $1 \text{ m}^3 \text{ s}^{-1}$, and a concentration of $2,8 \text{ mg L}^{-1}$ for a flow rate of $10 \text{ m}^3 \text{ s}^{-1}$. In contrast, in the winter of 2001 the Mn concentration increase up to 24 and $7,6 \text{ mg L}^{-1}$. This clearly shows that higher precipitations produce a more intense leaching in the mining areas (Sainz et al., 2002).

Not always are there such good correlations. In some cases, the presence of samples with anomalously high metal concentrations are probably linked to recent mining activity, to the contrary samples with anomalously low concentrations are likely to be linked to major releases of good quality water from reservoirs. The contaminant load for these periods without a good correlation has been calculated using the weighted average method. Where there is inadequate correlation with flow it is not even possible to calculate the contaminant contribution using the weighted average method (for example the presence of peaks in flow without analytical results), and therefore the contribution of this element is not calculated, as is the case where there are months of absent flow data.

Results obtained in this way had to be correlated with monthly precipitation rates recorded at 9 different rain gauge stations distributed throughout the Tinto and Odiel drainage basins (Figure 1) as a

way of completing monthly data where there was no available flow rate recorded or where it was not possible to calculate the contaminant load using the previously described methods.

3.4. Contaminant load transported by the Tinto river

In the case of As, Pb, and other elements where there is no correlation with flow the contaminant load is calculated using the weighted monthly average. For peaks in flow that have not been sampled no calculation is made.

In the Tinto river there exists a period between October and November 2000 where there were much higher elemental concentrations of contaminants (Figure 6); Fe concentrations were greater than 5000 mg L⁻¹, As greater than 30 mg L⁻¹, almost 25000 mg L⁻¹ of sulphate, 600 mg L⁻¹ of Zn, etc. These very high concentrations are not repeated in any other year and there is no similar elevation for the same period in the Odiel river. The only reasonable explanation we can offer for these very high concentrations is that they are caused by the dumping of mining waste possibly associated with the conclusion of mining activity at Minas de Riotinto. Thus with low flow rates there is a very high contaminant contribution above all in Fe and As. These anomalous data are not taken in to account for the correlation between precipitation and contaminant load.

Once the figures of the monthly loads were calculated using the aforementioned methods the relationship between contaminant load and monthly precipitation rates was calculated. Despite obtaining strong correlations, some anomalous data are apparent. For example, that when precipitation levels for any given month are close to zero the Fe contribution remains close to 500 t month⁻¹. This is due to the fact that precipitation levels for any given month (above all when levels are high) influencing the flow rates of the following months. Such that even when no rainfall is recorded, if rainfall during the previous month was important the river levels remain high enough to continue transporting an elevated quantity of contaminant load.

Figure 7 shows the cross correlation function between discharge and rainfall monthly values for the Tinto and Odiel rivers. The highest correlation is obtained for lag number of 0, that is, rainfall for a given month has a direct effect on the discharge increase for this month. However, there exists also a

significant correlation between the rainfall of a given month and the discharge in the following month, given that the part of the precipitation that will be temporally retained by soil infiltration and/or aquifers recharge will later drains to creeks and rivers with some delay. The correlation between the rainfall of a given month and the discharge in the following months, after the first one, is already very low, being close to the confidence level.

To resolve this effect, the correlation was established between contaminant load and precipitation of the considered month plus half of the previous month, which accounts for the “memory” effect of the river discharge with respect to rainfall in the previous month. By using half of the precipitation of the previous month it will not have the same repercussions on the flow as the precipitations of the month in question, as shown by his lower correlation coefficient (Fig. 7). In this way, the correlation between precipitation and contaminant load monthly values improve notably, obtaining the relationships shown in Table 2.

By using the precipitations and the regression equations obtained (Table 2) we can calculate the contaminant load of the months where no flow data is available or where having this information an inadequate correlation between flow and concentration was obtained and we were not able to apply the weighted monthly average method.

Table 3 shows the annual quantities obtained for the different elements. The greatest contribution in to the estuary logically corresponds to sulphates that are in the range of 19000 to 69000 t yr⁻¹, with an average close to 37000 t yr⁻¹. With respect to metals the highest amounts correspond to Fe with an annual average of 5100 t yr⁻¹, a minimum of 2500 t yr⁻¹ and a maximum of 9300 t yr⁻¹.

Although it has only been in the last few years that Al has been analysed, this element in terms of contaminants transported by the Tinto river has values of 963 and 1493 t yr⁻¹ for the years 2001/02 and 2002/03 respectively. Following the order of importance the average contribution of Zn, Cu and Mn are: 860 t yr⁻¹, 470 t yr⁻¹ and 160 t yr⁻¹, respectively.

For As, Cd, Co, Ni and Pb the following quantities were obtained which are far lower with averages of 12, 4, 9, 2 and 15 t yr⁻¹ respectively. It should be noted that Pb and As estimations are subject to a greater error than the others given that they normally do not show any correlation with flow and have

had to be calculated using the weighted monthly average or using the relationship with precipitation (Table 2).

Figure 8 represents the relationship between the annual precipitation data and the contaminant load calculated for the different elements (Al, Co and Ni are not represented as only 2 years of data are available). Pb and As show a high correlation coefficients because a greater number of monthly readings has been estimated from the precipitation. However, this figure clearly shows that the contaminant load transported by the rivers each year is dependent on the annual precipitation regime.

3.5. Contaminant load transported by the Odiel river

In the Odiel river a highly anomalous sample is apparent on the 17/01/97, where the river water not only had a high flow rate but also very high concentrations of elemental contaminants combined with an increased conductivity and a decrease in pH. Figure 9 shows the relationship between flow rate and Fe concentration between December 1996 and February 1997 and the only day that does not follow the general trend is on the 17/01/97. Similar results are obtained on graphs of the other elements, however elemental concentrations in the Tinto river on this day are totally normal. All of this evidence leads to believe that the cause of the anomaly is due to dumping at one of the mining installations. For the calculation of the contaminant load for this day we have considered the analytical values obtained.

Table 4 shows the relationships obtained between monthly precipitation plus half of the precipitation of the previous month and the values of contaminant contribution calculated using the flow rate or the weighted average concentration methods. Using these calculations extrapolations to complete the data set have been made in months where no flow data was available or where no calculation could be made using the described methodology.

Table 5 shows the annual contribution of the Odiel in to the estuary for the period 1995/96 to 2002/03. The average annual contribution of sulphate is 147000 t yr⁻¹, varying between 35000 and more than 300000 t yr⁻¹. In the case of metals the greatest contribution corresponds to Al with values close to

4500 t yr⁻¹ during the hydrological years 2001/02 and 2002/03. The following quantities in order of importance correspond to Fe, Zn, Mn and Cu with average values of 2800, 2600, 1450 and 1250 t yr⁻¹.

The contribution of As, Cd, Co, Ni and Pb, as in the case of the Tinto river, occur in much lower quantities. Despite this in the Odiel river the average contribution of Ni (32 t yr⁻¹) and above all Co (62 t yr⁻¹) are higher than those of As (23 t yr⁻¹), Cd (7 t yr⁻¹) and Pb (12 t yr⁻¹).

Finally Figure 10 shows the relationship between annual rainfall and the contaminant load of the Odiel river. As in the previous case it is noteworthy that there is a greater uncertainty in the As and Pb calculation, such that the previous data for these elements should be regarded only as orientative.

3.6. Contaminant inputs to the Ría of Huelva and Gulf of Cádiz

This work deals with the transported load in solution. The concentration of suspended particles is low compared with the dissolved species (Braungardt et al., 2003) although could be an important influencing factor for elements with a high affinity for particulate matter such as Pb.

Table 6 shows the average total values of the contaminant load of both rivers together with the estimated percentages of the contribution from each river in the total balance. It is evident that despite the concentrations being higher in the Tinto river, the Odiel river provides higher quantities (with the exception of Fe and Pb) due to its greater flow rate. The contribution of Co and As are approximately double in the Odiel, Cu and Zn some 3 times higher, sulphates and Al some 4 times higher, Co 7 times higher, Mn 9 times higher with the maximum difference being in Ni (17 times higher in the Odiel than in the Tinto).

As the considered time period is somewhat more humid than the normal, the average contaminant load for an extended time frame could be slightly lower.

3.7. Comparison with other acid rivers

It is not common to find in the literature estimations of the annual contaminant loads transported by acidified rivers contaminated by acid mine drainage. In the following section comparisons are made between the values presented in this study for the Tinto and Odiel rivers to values cited in literature.

Arambarri et al. (1996) estimate for the river Guadamar, whose drainage basin borders the Tinto on the east, the following values: 2990 t yr⁻¹ Fe, 1411 t yr⁻¹ Mn, 613 t yr⁻¹ Zn and lower amounts of other metals, all coming from the mines at Aznalcóllar. However the authors calculate the transported load by multiplying the average elemental concentration by annual flow of the river, which, as previously discussed, implies an overestimation of the values.

Banwart and Malstrom (2001) calculated the discharge of the dumps at the Aitik mine in Sweden, which has a dimension of 2.6 km², prior to them being “dry covered” (to reduce the production of AMD). They obtained a discharge of 101 t yr⁻¹ Cu and 7116 t yr⁻¹ of sulphate.

Nordstrom et al. (1999) calculated a discharge to the Sacramento River, prior to undertaking remedial work, of 300 t yr⁻¹ Cu, Zn and Cd derived from the Iron Mountains, the greatest producer of AMD in the state of Colorado (USA).

Gray (1998) quantified the average discharge of two mining wastes to the Avoca River in Ireland at 159 t yr⁻¹ Fe, 62 t yr⁻¹ Zn and 4 t yr⁻¹ Cu.

Kimball et al. (2002) using a tracer test during late summer base flow calculated that Cement Creek (Colorado, USA), before it joins the river Animas, transported 486 kg day⁻¹ of Fe, 287 kg day⁻¹ of Al, 146 kg day⁻¹ of Mn and 50 kg day⁻¹ of Zn, despite the treating of the discharge from the Sunnyside mine.

In conclusion, with the exception of the data obtained by Arambarri et al. (1996) whose values we believe to be highly overestimated, our results in the Tinto and Odiel rivers are far higher than any other rivers affected by AMD.

If as Braungardt et al. (2003) did, we compare the values obtained by us with the estimations published by GESAMP (1987) of the global gross flux of dissolved metals transported by rivers in to

the oceans, we obtain some very surprising results: the load transported by the Tinto and the Odiel rivers represents 17% of the global gross flux of Cu and 60% of the Zn (Table 7). This gives an idea of the extreme degree of contamination that the two rivers suffer.

4. Conclusions

Although there exists several previous studies that attempt to calculate the amount of dissolved contaminants transported by the Odiel and the Tinto rivers, these studies are based on few analytical data and/or use inadequate methodologies for this type of calculations.

Due to the high variability of the contaminant concentration in relation to flow, contaminant concentration estimations based on calculating the average monthly concentration using several periodic samples is only adequate when the flow during the month is approximately constant. Where flow is highly variable during storms for example, a more reliable estimation method is to use the relationship between flow and concentration.

The data that we present highlight the enormous amount of metal being transported by the Tinto and Odiel rivers in to the Ría de Huelva and the Gulf of Cadiz. The average quantities transported by both rivers annually are: 183000 t of sulphate, 7900 t Fe, 5800 t Al, 3500 t Zn, 1700 t Cu and 1.600 t Mn. The amount of As, Cd, Co, Ni and Pb are much lower, with respective values of 36, 11, 71, 36 and 27 t.

The quantity of contaminants transported annually depends on the precipitation regime, as there is a good relationship between contaminant load of each element and the annual precipitation. The time period considered in this study (1995/96 to 2002/03) is somewhat more humid than normal, thus quantities calculated maybe higher than if a longer time period were selected.

Estimations for As and Pb have a greater degree of uncertainty as they do not normally show any relationship with flow, and have been estimated using the weighted monthly average method or using their relationship with precipitation. Also the quantities of Al, Ni and Co have only been estimated for two years.

With respect to the importance of each river, there exists great differences in the amount of contaminants entering the estuary depending on which element is selected. For example the Tinto river supplies more Fe and Pb, but for other elements the greatest contribution comes from the Odiel, with maximum values for Co, Mn, and Ni where the supply is 88, 90 and 94% of the total respectively.

The contaminant load estimates in this work are far greater than those calculated in other acidic rivers (Arambarri et al., 1996; Banwart & Malström, 2001; Nordstrom et al., 1999; Gray, 1998; Kimball et al., 2002). The Tinto and Odiel rivers are extreme cases of rivers contaminated by acid mine drainage, such that the Zn transported by these rivers to their common estuary represent 60% of the global gross flux of this element in to the oceans, according to the estimations of GESAMP (1987).

Acknowledgements

The authors wish to thank the Guadiana Hydrographic Confederation, and the Environmental Council of the Andalusia Regional Government for the information provided for this study, which has been financed through projects "Evaluation of the contaminant load to the Huelva estuary", financed by the Environmental Council of the Andalusia Regional Government, and REN2003-09590-C04-03 financed by the Spanish Ministry of Education and Science.

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Figure Captions

Figure 1. Sketch map of the Tinto and Odiel rivers showing the location of the sampling points, stream gauging stations, rain gauges, and main mine localities.

Figure 2. Relationship between flows, sorted from lowest to highest, and the frequency in which they are surpassed during the study period

Figure 3. Flow of the Tinto river in November 2001 with an indication of the sample date. Example of how the estimation using the average monthly concentration is inadequate for calculating the contaminant load

Figure 4. Relationship Cu-Flow for the entire year 1996/97 and highlighting the different periods used for the contaminant load calculation

Figure 5. Mn concentration and discharge evolution for the years 1999/00 and 2000/01, indicating the different regressions obtained for the contaminant load calculation

Figure 6. Evolution of the Fe and As concentration in the Tinto river displaying a maximum in autumn and winter of 2000 that is probably related to the dumping of mining wastes.

Figure 7. Cross correlation function between discharge and rainfall monthly values for the Tinto and Odiel rivers (point line indicates confidence limits).

Figure 8. Relationship between precipitation and annual contaminant load transported by the Tinto river

Figure 9. Relationship between flow and Fe content in the Odiel showing an anomalous point probably corresponding to dumping of mining wastes

Figure 10. Relationship between precipitation and annual contaminant load transported by the Odiel river

Table 1. Summary of studied analytical data (E.C. – Electrical Conductivity)

	TINTO RIVER					ODIEL RIVER				
	Data No.	Mean	Min.	Max.	Sta.Dev.	Data No.	Mean	Min.	Max.	Sta.Dev.
pH	385	2.63	1.80	6.80	0.50	391	3.35	2.40	6.30	0.56
E.C. ($\mu\text{S cm}^{-1}$)	385	3231	253	15000	2074	391	1608	160	4670	969
SO_4^{2-} (mg L^{-1})	348	2455	58	25256	3031	339	978	51	3821	709
As (mg L^{-1})	346	0.86	0.00	34.48	3.37	241	0.01	0.00	0.40	0.04
Cd (mg L^{-1})	390	0.25	0.00	5.34	0.51	381	0.06	0.00	0.31	0.04
Cu (mg L^{-1})	394	27.2	0.02	365.0	38.8	396	6.0	0.03	37.6	4.0
Fe (mg L^{-1})	381	393.5	0.02	5080	648	383	12.8	0.03	171.0	18.9
Mn (mg L^{-1})	381	11.4	0.561	113.0	13.8	384	10.8	0.5	43.4	8.2
Pb (mg L^{-1})	317	0.19	0.03	1.52	0.22	299	0.11	0.00	1.18	0.11
Zn (mg L^{-1})	389	61.8	0.73	591.0	80.1	391	16.8	0.36	86.4	13.3
Al (mg L^{-1})	74	75.0	6.8	239.8	45.8	62	29.8	3.5	80.4	19.7
Co (mg L^{-1})	74	0.49	0.05	1.27	0.24	62	0.28	0.07	0.80	0.18
Ni (mg L^{-1})	74	0.14	0.02	0.43	0.08	62	0.16	0.02	0.50	0.13

Table 2. Relationship between monthly precipitation and contaminant load transported by the Tinto river (see text for discussion)

	Equation	R ²
SO_4^{2-}	$y = 26.63x - 333.3$	0.74
As	$y = 0.008x - 0.232$	0.54
Cd	$y = 0.003x - 0.069$	0.72
Cu	$y = 0.376x - 8.573$	0.69
Fe	$y = 3.259x - 2.601$	0.62
Mn	$y = 0.120x - 1.624$	0.83
Pb	$y = 0.017x - 0.801$	0.64
Zn	$y = 0.619x - 6.116$	0.71
Al	$y = 1.001x - 11.88$	0.60
Co	$y = 0.007x - 0.135$	0.58
Ni	$y = 0.002x - 0.034$	0.62

Table 3. Obtained results of the annual contaminant load transported by the Tinto river

	Rainfall mm	SO ₄ ²⁻ t yr ⁻¹	As t yr ⁻¹	Cd t yr ⁻¹	Cu t yr ⁻¹	Fe t yr ⁻¹	Mn t yr ⁻¹	Pb t yr ⁻¹	Zn t yr ⁻¹	Al t yr ⁻¹	Co t yr ⁻¹	Ni t yr ⁻¹
1995/96	1366	68928	16.9	7.5	973	9274	268	26.2	1614			
1996/97	1098	26894	15.2	3.0	303	3732	163	26.0	734			
1997/98	1210	47304	10.8	4.9	661	5711	215	17.7	1212			
1998/99	376	19167	1.9	1.5	172	2711	89	1.8	444			
1999/00	835	28657	8.5	2.7	323	5135	124	8.0	728			
2000/01	1140	51109	34.0	7.5	699	8000	215	17	1114			
2001/02	886	19616	3.9	1.4	213	2518	88	6.5	370	957	6.9	1.8
2002/03	935	31039	8.2	3.0	410	3518	142	14.5	687	1492	10.5	2.6
Mean	981	36589	12.4	3.9	469	5075	163	14.8	863	1224	8.7	2.2
Min.	376	19167	1.9	1.4	172	2518	88	1.8	370			
Max.	1366	68928	34.0	7.5	973	9274	268	26.2	1614			

Table 4. Relationships between monthly precipitation and contaminant load transported by the Odiel
(see text for discussion)

	Equation	R ²
SO ₄ ²⁻	y = 136.5x - 4482	0.73
As	y = 0.025x - 1.142	0.61
Cd	y = 0.058x - 0.118	0.62
Cu	y = 1.189x - 42.18	0.62
Fe	y = 2.786x - 106.8	0.62
Mn	y = 1.268x - 35.03	0.71
Pb	y = 0.008x + 0.000	0.51
Zn	y = 2.292x - 64.42	0.62
Al	y = 3.355x - 2.027	0.91
Co	y = 0.055x - 1.236	0.85
Ni	y = 0.030x - 0.711	0.85

Table 5. Obtained results of the annual contaminant load transported by the Odiel river

	Rainfall	SO ₄ ²⁻	As	Cd	Cu	Fe	Mn	Pb	Zn	Al	Co	Ni
	mm	t yr ⁻¹	t yr ⁻¹	t yr ⁻¹	t yr ⁻¹	t yr ⁻¹	t yr ⁻¹	t yr ⁻¹	t yr ⁻¹	t yr ⁻¹	t yr ⁻¹	t yr ⁻¹
1995/96	1366	149666	39.1	9.8	1489	2643	1679	13.1	2656			
1996/97	1098	205668	22.7	9.4	1310	3720	1502	10.9	2740			
1997/98	1210	199170	33.3	9.3	1728	3977	1950	14.5	3514			
1998/99	376	34902	3.6	2.1	288	611	387	4.5	690			
1999/00	835	54631	12.2	3.8	451	1854	516	5.4	877			
2000/01	1140	305296	41.2	7.7	3015	5686	3256	18	6591			
2001/02	886	98619	12.7	6.2	600	1376	1021	15.6	1683	4439	60.5	34.0
2002/03	935	129756	19.9	8.7	1133	2910	1306	12.2	2143	4675	64.4	33.8
Mean	981	147213	23.1	7.1	1252	2847	1452	11.8	2612	4557	62.5	33.9
Min.	376	34902	3.6	2.1	288	611	387	4.5	690			
Max.	1366	305296	41.2	9.8	3015	5686	3256	17.9	6591			

Table 6. Average values of the contaminant load transported by the Tinto and Odiel rivers

	TINTO		ODIEL		TOTAL
	t yr ⁻¹	%	t yr ⁻¹	%	t yr ⁻¹
SO ₄ ²⁻	36589	20	147213	80	183803
As	12	35	23	65	36
Cd	4	36	7	64	11
Cu	469	27	1252	73	1721
Fe	5075	64	2847	36	7922
Mn	163	10	1452	90	1615
Pb	15	56	12	44	27
Zn	863	25	2612	75	3475
Al	1224	21	4557	79	5781
Co	9	12	62	88	71
Ni	2	6	34	94	36

Table 7. Comparison of the contribution of the Tinto and Odiel rivers with global river flux estimations of GESAMP (1987)

	Tinto and Odiel Rivers Flux t yr ⁻¹	Global gross flux (GESAMP, 1987) t yr ⁻¹	Fraction %
As	36	10000	0.00
Cd	11	340	3.3
Cu	1721	10000	17.2
Fe	7922	1400000	0.6
Mn	1615	280000	0.6
Pb	27	2000	1.3
Zn	3475	5800	59.9
Co	71	1700	4.2
Ni	36	11000	0.3

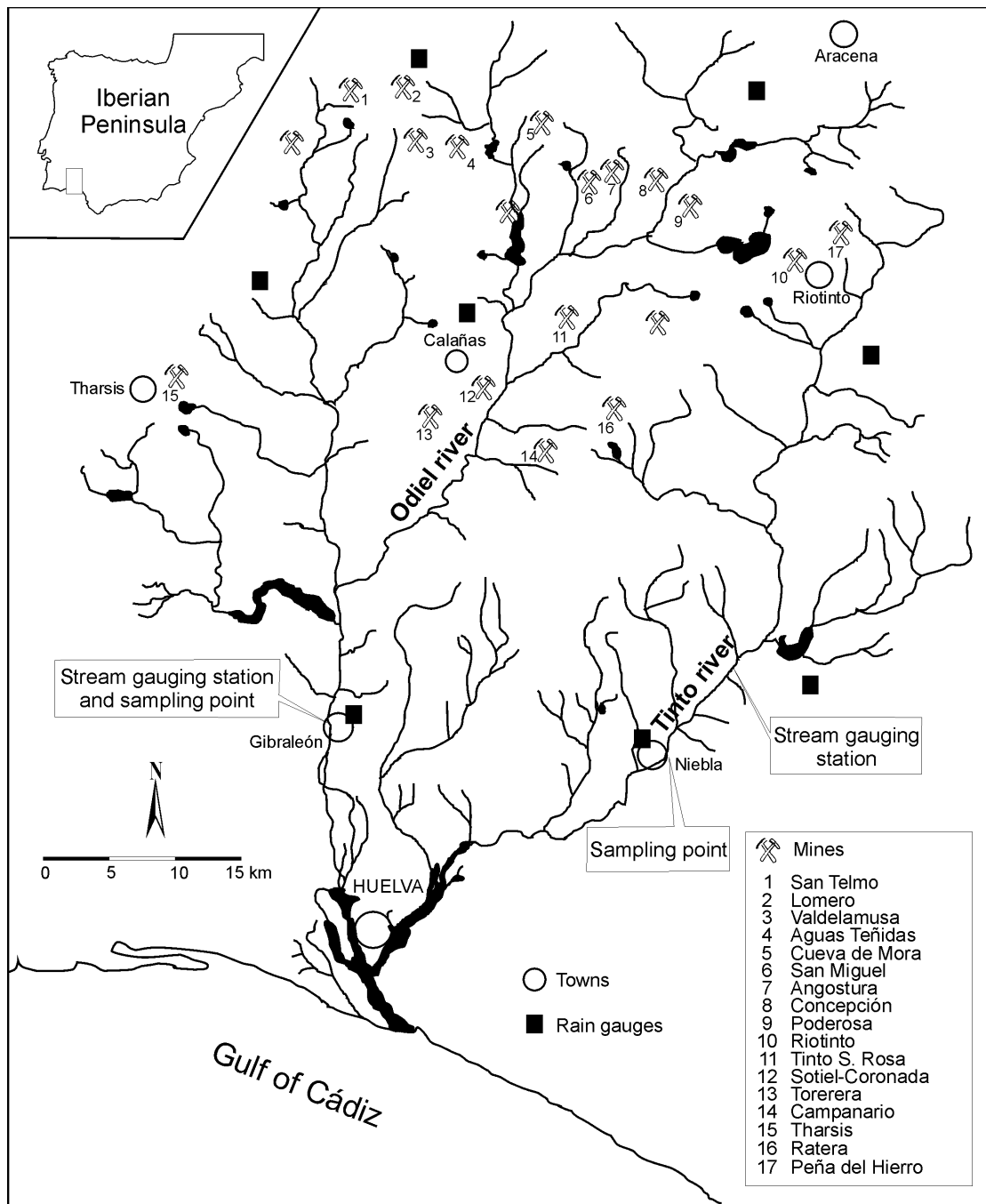


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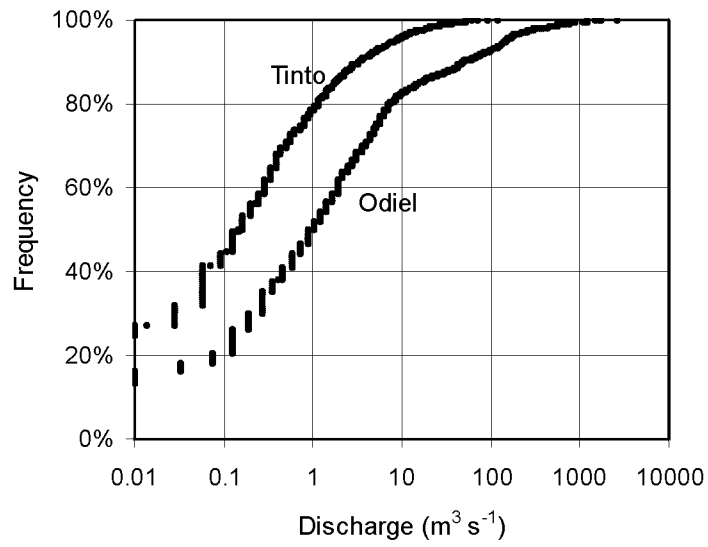


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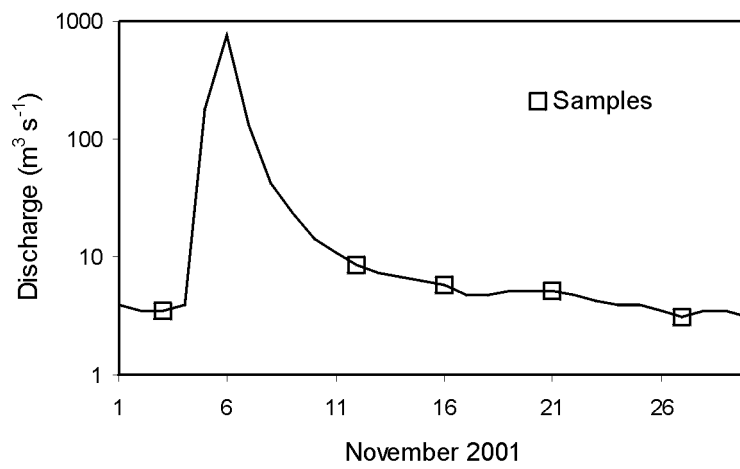
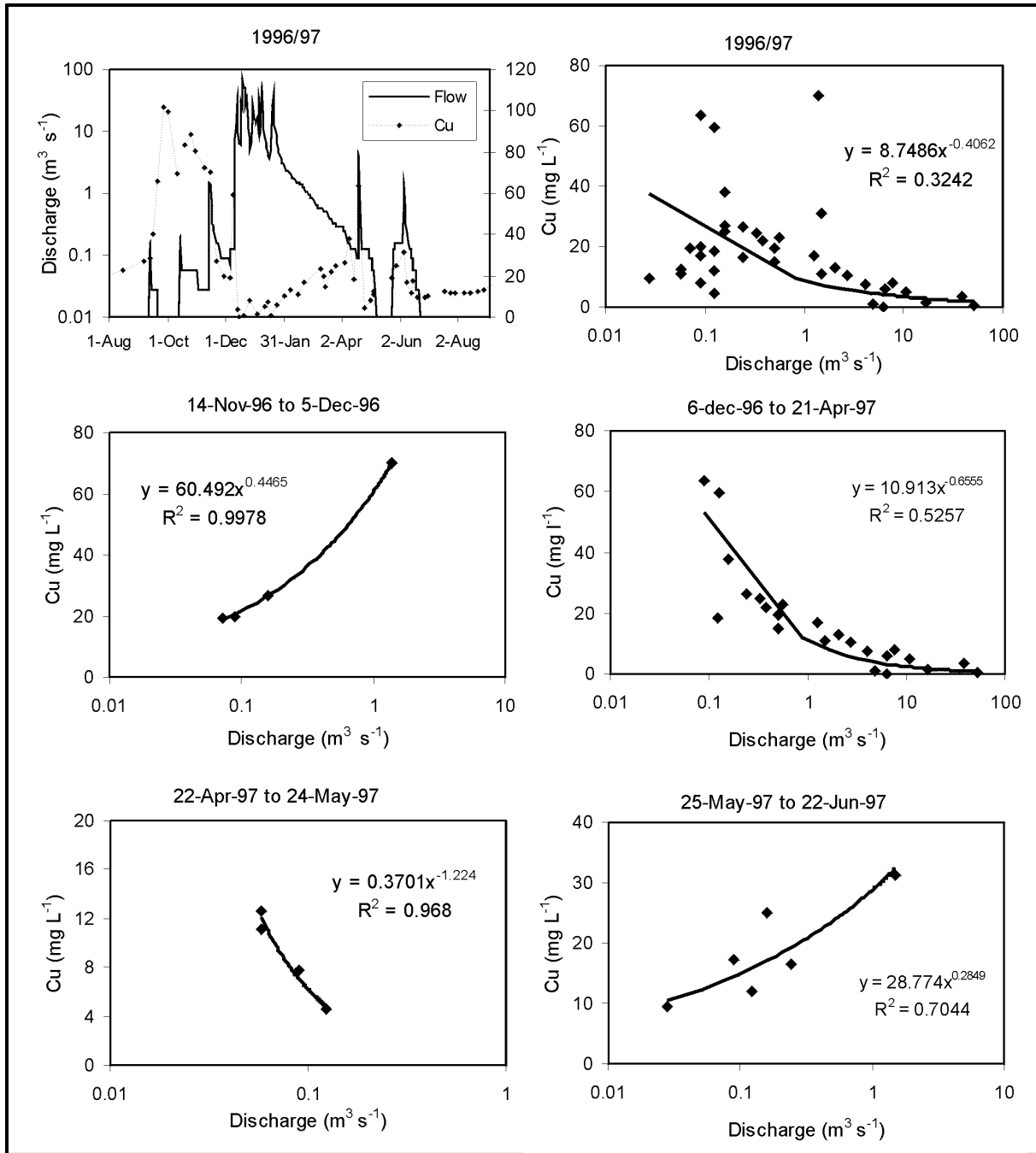


Figure 3

Figure 4.



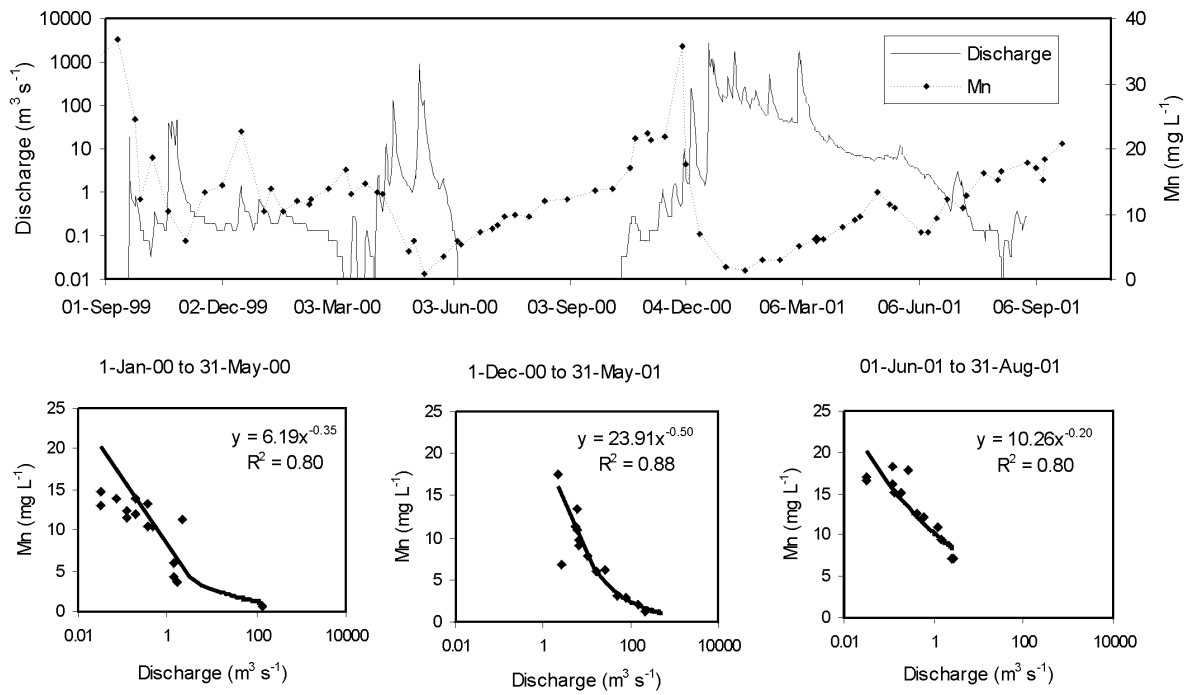


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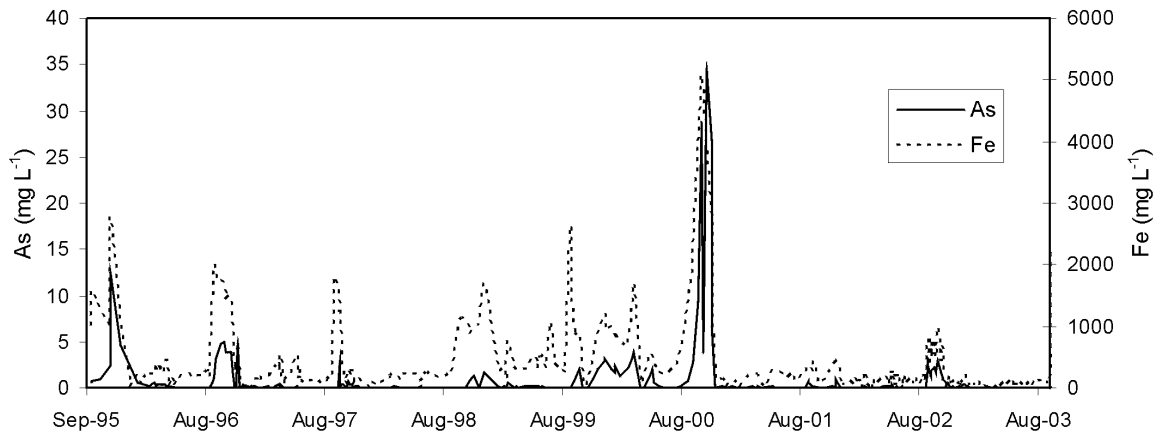


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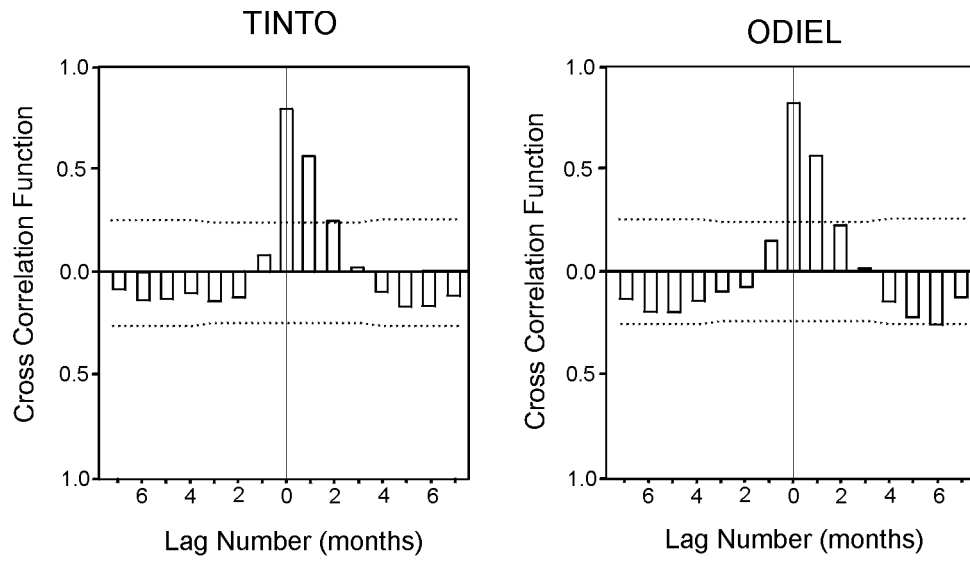


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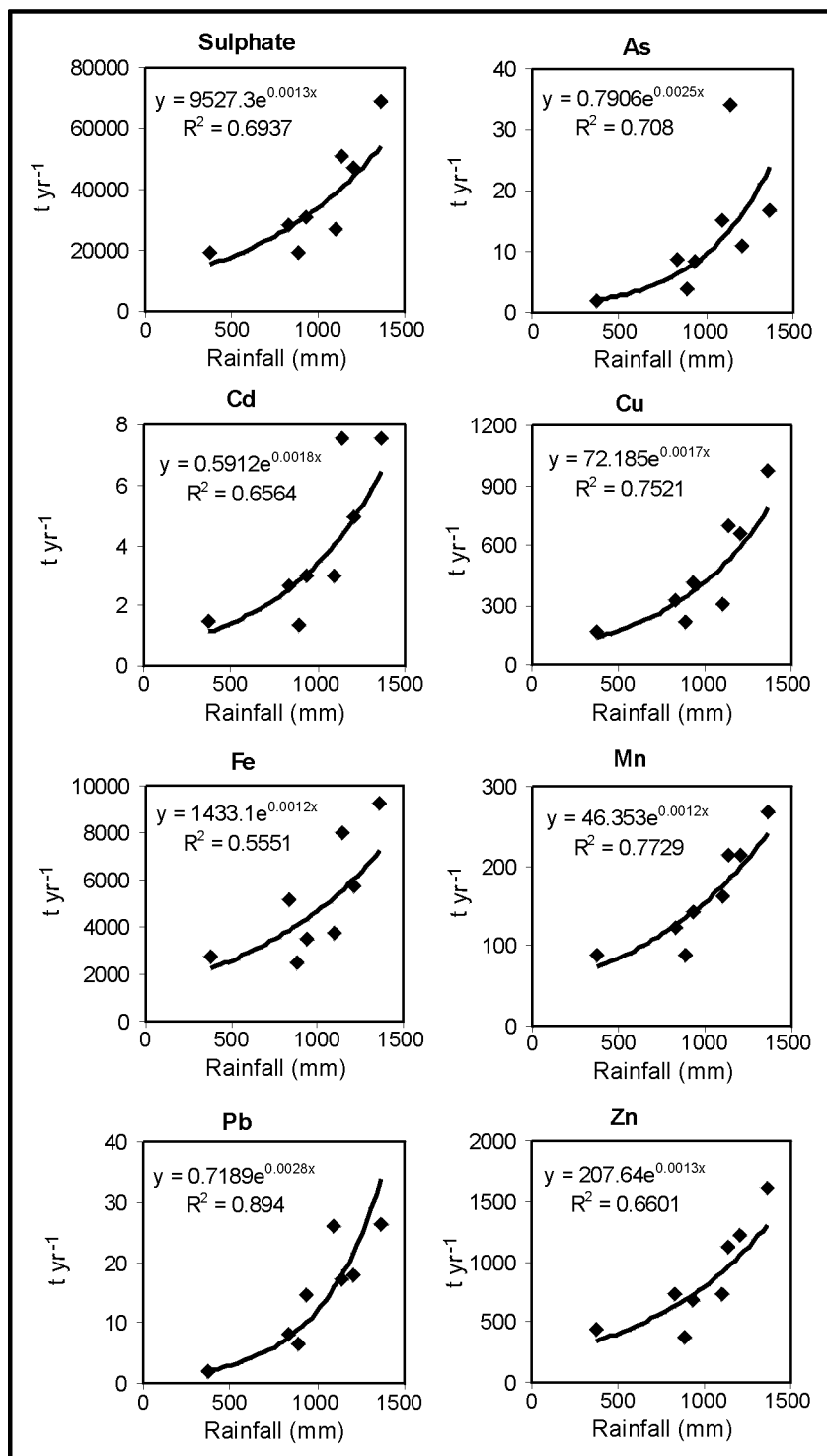


Figure 8

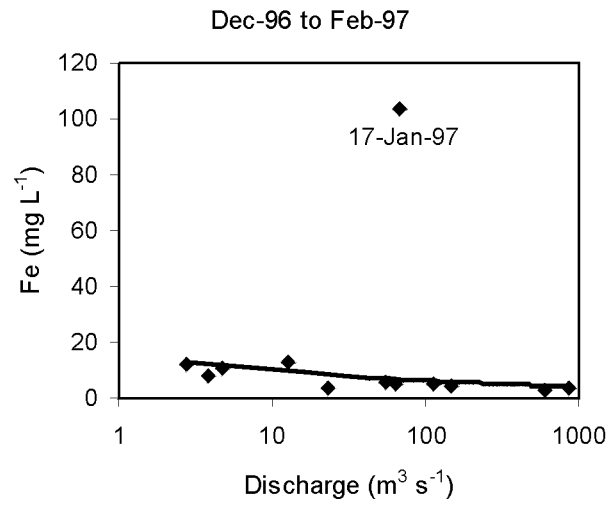


Figure 9

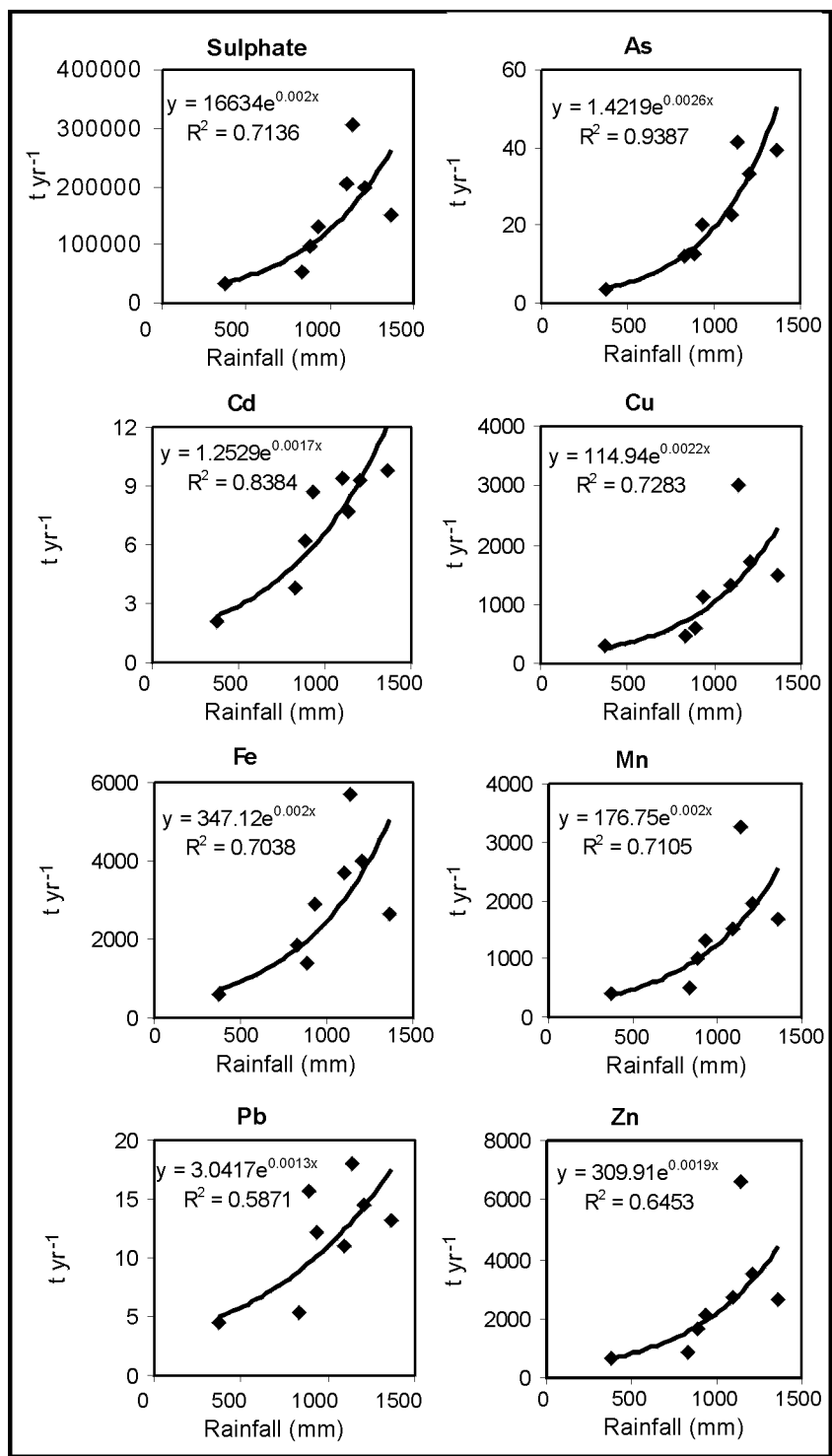


Figure 10