

# Characterisation of heavy metal discharge into the Ria of Huelva

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## Abstract

The Ria of Huelva estuary, in SW Spain, is known to be one of the most heavy metal contaminated estuaries in the world. River contribution to the estuary of dissolved Cu, Zn, Mn, Cr, Ni, Cd, and As were analysed for the period 1988–2001. The obtained mean values show that this contribution, both because of the magnitude of total metals (895.1 kg/h), composition, toxicity (8.7 kg/h of As + Cd + Pb) and persistence, is an incomparable case in heavy metal contamination of estuaries. The amount and typology of heavy metal discharge to the Ria of Huelva are related to freshwater flow (and, consequently, to rainfall); as a result, two different types of heavy metal discharge can be distinguished in the estuary: during low water (50% of the days), with only 19.3 kg/h of heavy metals, and during high water or flood (17% of the days), where daily maximum discharge of 72,475 kg of heavy metals were recorded, from which 1481 kg were of As, 470 kg of Pb, and 170 kg of Cd. In the most frequent situation (77% of the days), the Odiel River discharges from 90% to 100% of the freshwater received by the estuary. Despite this, the high concentration of heavy metals in the Tinto River water causes this river to discharge into the Ria of Huelva 12.5% of fluvial total dissolved metal load received by the estuary.

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## 1. Introduction

The Ria of Huelva, in Southwestern Spain, has been world-famous as one of the most heavy metal contaminated estuaries in the world (Stenner and Nicless, 1975; Tomás et al., 1983; Nelson and Lamothe, 1993; Sáinz et al., 2002; Sainz et al., 2003a,b; Grande et al., 2003a). From the late 1960s, this estuary began undergoing a progressive process of environmental damage. Its waters became increasingly more acidic until they reached pH values lower than four (Cortés and Varela, 1992). Water and sediments of the estuary and its coast of influence experienced serious contamination by copper, zinc, manganese, cadmium and arsenic; and molluscs held important accumulations of copper and cadmium (Stenner and Nicless, 1975; Tomás et al., 1983; AMA, 1989; Borrego et al., 2002). Two causes were responsible for this contamination: river inflow of the Tinto and Odiel rivers, and effluents from the chemical industry located along the estuary banks. In 1988, the

Andalusian (regional) Environmental Agency (AMA) set in motion its Remediation Plan to remove the  $20 \times 10^6$  kg of heavy metals dumped into the estuary by industrial disposal. Once these effluents disappeared, the Tinto and Odiel rivers are nowadays the main channels of heavy metal entrance to the estuary.

As a result of individual (Pérez et al., 1991; Nelson and Lamothe, 1993; Sainz et al., 2003a) or multidisciplinary team research, such as the TOROS project (Tinto-Odiel-River-Ocean Study), numerous works on the characterisation of the estuary environmental deficit appear. Although they all point out the great importance of these rivers' inflows in the estuarine and coastal contaminating process (Cortés and Varela, 1992; Elbaz-Poulichet and Leblanc, 1996; Elbaz-Poulichet et al., 2001a,b; Grande et al., 2000, 2003a,b,c; Van Geen et al., 1997), there are, however, no specific studies to characterise them. Tinto-Odiel-River-Ocean Study (TOROS) has been studying the biogeochemical processes which control metals and nutrients cycling in the mixing zone of the Tinto and Odiel rivers (SW Spain) and has established the fate of metals in the Gulf of Cadiz in relation to hydrodynamics and biological activity. A large plume of metal-rich water

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due to the Tinto and Odiel discharges occurs along the coast in the Gulf of Cadiz. This plume affects seasonally the Atlantic inflow through the Strait of Gibraltar (Elbaz-Poulichet et al., 2001b).

There is a double influence of the Tinto and Odiel rivers on the estuary environmental conditions. Firstly, the freshwater inflow contributed by them has an influence on salinity gradient, estuarine circulation, biota, etc., as what happens to other estuaries (Kurup et al., 1998; Pierson et al., 2001; Vieira and Bordalo, 2000; Wilber and Bass, 1998). Secondly, acid mine drainage (AMD) contamination carried by these rivers is an entrance of toxic or potentially toxic pollutants to the estuary (Wright and Welbourn, 2002).

On this line, the present study focuses on fluvial input of dissolved heavy metals received by the Ria of Huelva. Our goal is to make a general holistic approach to the phenomenon of heavy metal inputs received by the estuary, and its characterisation by analysing several of its aspects: amount, composition, ways of occurrence, contribution of each river, etc.

In studies of fluvial contamination, a referential hydrological framework is necessary in order to be able to interpret the analyses of water quality or contaminant load (Sáinz, 1999). As a result, daily inflows of the Tinto and Odiel rivers to the estuary during the recording period were studied, as well as precipitation in different rainfall stations along their drainage basins. With these data, a comparative study of inflows between the two rivers was carried out, and an inflow frequency analysis was made for each river, studying the seasonal and yearly variation and their relationship with yearly rainfall.

## 2. General setting

The Ria of Huelva is an estuary formed by the junction of the Tinto and Odiel rivers, which run together into the Atlantic Ocean. The Tinto River (Fig. 1) rises in Rio Tinto Mines and flows 100 km until its mouth into the estuary, draining a basin of 720 km<sup>2</sup>. The Odiel River springs up in the mountains of Aracena and is 140 km long. Its basin is 2300 km<sup>2</sup> (Fig. 1). Both rivers have a torrential nature and are located in a climatic zone of extremely irregular rainfall. Their hydrological behaviour is very different in the wet and dry seasons. Given the randomness in the occurrence of wet years, mean values of their yearly water inflows vary remarkably depending on the studied period. According to the official hydrological series for 1967–1980, values of 460.10<sup>6</sup> and 90.10<sup>6</sup> m<sup>3</sup>/year are cited as yearly average inflows for the Odiel and Tinto rivers. However, the subsequent construction of reservoirs has progressively reduced the true values of river inflows. Thus, in the Tinto River, the progressive regulation of 64% of its runoff has turned this river into an ephemeral water flow, permanently dry and with sporadic discharge.

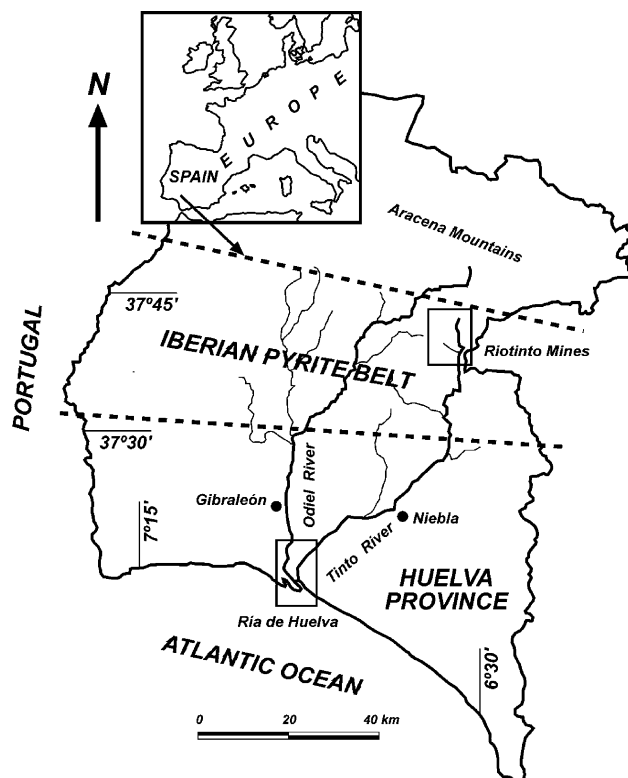


Fig. 1. Location map.

The serious contamination by acid mine drainage (AMD) undergone by the Tinto and Odiel rivers is due to the fact that the Iberian Pyrite Belt crosses their drainage basins (Fig. 1). This 230-km-long and average 50-km-wide geological formation is one of the biggest sulphide deposits in the world (Leistel et al., 1998). Its metallogenic richness has been the cause of its exploitation for 5000 years (Davis et al., 2000). As a consequence of such a large mining activity, more than 100 abandoned mines and over 200 × 10<sup>6</sup> m<sup>3</sup> of waste distributed in 70 mine dumps and 14 deposits have remained in the Tinto and Odiel drainage basins. Runoff from these sources is an everlasting polluting machinery carrying sulphates and heavy metals into these two rivers (Sainz et al., 2003b). Described as ‘dump rivers’ (Pinedo, 1963), their extremely high contamination was the reason why in 1987 the Ministry responsible for the environment in Spain classified the Tinto and Odiel rivers as ‘industrial rivers’, allowing any kind of waste disposal into their beds (MOPU, 1987).

## 3. Methods

During the period 1988–2001, fluvial inputs of dissolved Cu, Zn, Mn, Cr, Ni, Cd, Pb and As to the estuary were analysed. Data used in this study come from the Andalusian Environmental Agency (Spain) (AMA, 1989–2002).

Three variables have been analysed to characterise the behaviour of contaminant inputs of fluvial origin to the estuary: inputs and the two factors causing them—river inflow and heavy metal concentration in water. The choice of contaminants was made according to two criteria: contamination found in the water and sediments of the estuary and the coast of influence, and impact of these contaminants on human health and environment (USEPA, 1994, 1999). Water pH and river inflows at the moment of the sample taking were also observed.

Sampling sites were at the lowest points of the Tinto and Odiel rivers, before their entrance into the estuary (Fig. 1) (Grande et al., 2003b), that is, upstream beyond the limit of the tidal influence zone.

Methods for sample taking, preservation and analysis were performed according to the procedures established in the Watch Water Plan of the Regional Government Environmental Agency (Usero et al., 2000), which follow the recommendations of the APHA, AWWA, and WPCF (1992), regarding the standard methods for the analysis of drinking and waste waters. Water samples were transported using polyethylene bottles. Samples for the determination of Cu, Cd, Pb, Ni, and Zn were previously filtered, adding HNO<sub>3</sub> up to pH <2 as a preservation agent to the filtered liquid, kept in the dark and refrigerated at 4 °C. Samples for the determination of arsenic, after being filtered, were added 2 ml/l of HCl. Copper, zinc, manganese, nickel, chromium, cadmium, lead and iron were analysed by atomic absorption spectrophotometry, after being extracted with APDC/MIBC (SM 311C). Arsenic was analysed by hydride generation atomic absorption spectrophotometry (SM 3114B). pH was analysed in situ and inflow was calculated by entering float gauge readings recorded during the sampling in the discharge curves. At each gauging station, stage was sensed for automatic recording by a float in stilling web. A water-stage recorder produces a graphic record of the rise and fall of a water surface with respect to time.

For each sample, total dissolved heavy metal load (TdML) is made up by the sum of individual inputs of each type of the selected heavy metals (Cu, Zn, Mn, etc.). Given that the value of this sum, as well as the rates relating the augends, can change considerably with temporal and seasonal variations of the inflow (Gray, 1998; Sainz, 1999; Wirt et al., 1999), it is necessary to obtain metal input values in a wide range of inflows. The great randomness of rainfall in the area of study and the need to sample wet years have forced to increase the number of years of the sampling period to 14, from 1988 to 2001, limiting to a maximum of four samples each year. Metal input of each contaminant for a specific sample and river was calculated by multiplying its concentration in water by the river inflow at the sampling site and moment. Total fluvial input of each metal to the Ria of Huelva estuary was calculated adding individual inputs of both rivers.

The techniques used were univariate analysis and time analysis. Finally, the influence of these river inflow varia-

tions on inputs and concentrations was studied by means of regressive analysis.

#### 4. Results and discussion

The hydrological characteristics of the Tinto and Odiel rivers are determined in the behavioural patterns of contaminant inputs to the estuary. In the data obtained from the corresponding basin organism, we observe an average annual input value of  $5.5 \times 10^6 \text{ m}^3$  in the Tinto River and  $79 \times 10^6 \text{ m}^3$  in the Odiel River during dry years (rain <400 mm/year) in the period of study (1988–2001). In wet years (rain >1200 mm/year) mean values were of  $99 \times 10^6 \text{ m}^3$  in the Tinto and  $1670 \times 10^6 \text{ m}^3$  in the Odiel. Daily inflows are characterised by having long persistent low water periods. This characteristic is even more stressed in dry years: in the Odiel River, low water (flow <2.5 m<sup>3</sup>/s) is 3 months long in a wet year and over half a year in a drought year. In the Tinto River, low water (flow <0.2 m<sup>3</sup>/s) lasts over 6 months in a wet year and over 11 months in dry years, breaking with this event only 10 or 20 days a year. It turns evident that yearly inflows are concentrated in a few short-lasting floods.

Regarding the analysis of dissolved heavy metal load (TdML) of fluvial origin to the estuary during the period of study, four aspects are remarkable and will be individually analysed: magnitude and composition of total fluvial inputs of heavy metals to the estuary, uninterrupted persistence of these inputs, their sampling variability, and finally, each river input contribution to the estuary.

#### 5. Magnitude and composition

Main values of location (average, median) and dispersion characteristics (standard deviation, range or minimum–maximum, coefficient of variation) for joint inputs (Tinto River+Odiel River) of heavy metals to the estuary for the observed period (1988–2001) are shown in Table 1.

Table 1  
Location and variability characteristic data for fluvial input of dissolved heavy metals to the Ria of Huelva estuary, 1988–2001

Fluvial input	Average	Median	Standard deviation	Minimum	Maximum	Coefficient variation
Cu (kg/h)	191.4	107.0	232.4	5.0	998.1	121.2
Zn (kg/h)	468.7	323.0	436.6	9.9	1603.6	92.2
Mn (kg/h)	220.7	166.6	190.6	4.2	753.8	86.3
Ni (kg/h)	4.4	3.0	4.0	0.08	17.5	91.6
Cr (kg/h)	1.2	0.5	1.6	0.01	7.0	136.0
Cd (kg/h)	1.8	1.3	1.6	0.04	7.1	91.4
Pb (kg/h)	3.4	2.0	3.9	0.05	19.6	115.6
As (kg/h)	3.5	0.2	9.7	0.002	61.7	276.1
TdML (kg/h)	895.1	639.6	848.5	19.3	3019.8	94.8
Fresh-water flow (m <sup>3</sup> /s)	11.1	3.7	21.0	0.06	93.2	189.5

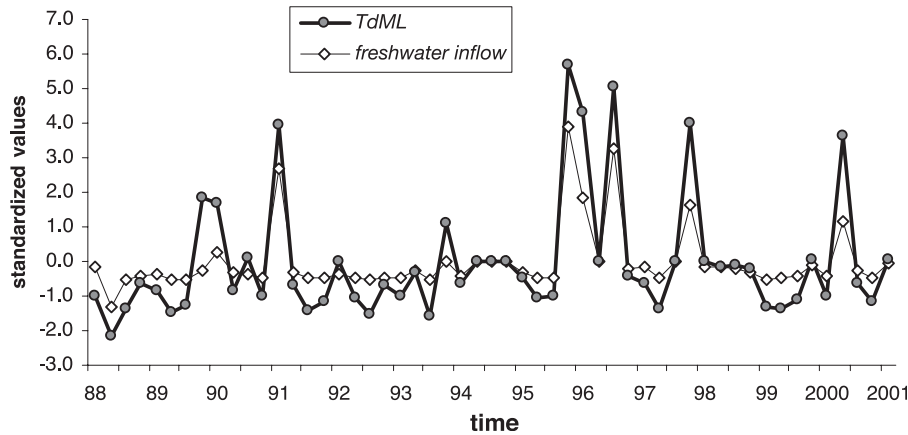


Fig. 2. Comparison between standardised values for freshwater and dissolved metal load (Cu+Zn+Mn+Cd+Cr+Ni+Pb+As) entered in the estuary during the different samplings.

According to the results, the Tinto and Odiel rivers, coming from the mining basin, discharge a yearly average input of  $7.84 \times 10^6$  kg of dissolved heavy metals (Cu+Zn+Mn+Ni+Cr+Cd+Pb+As) to the estuary. This amount is lower than that initially calculated by the Andalusian Environmental Agency for the period 1987–1989 (Sáinz, 1992) and than the input of major heavy metals (copper, zinc and manganese) calculated for the period 1987–1995 (Sáinz, 1999). Compared to other rivers in the world (Vink et al., 1999), a mass input of 895 kg/h, generated by the drainage of 3020 km<sup>2</sup> and carried by only 11.1 m<sup>3</sup>/s of freshwater, is unusually high. The first remarkable characteristic of the achieved data is the high value of average total input and of individual averages and, therefore, the great magnitude of total heavy metal contamination received by the estuary as a result of the fluvial input from these two rivers. The importance of these values can be illustrated comparing the results in Table 1 to those published for other European rivers contaminated by heavy metals (Vink et al., 1999): joint inputs from the Tinto–Odiel are the same order of magnitude (As) or higher (Cd, Pb, Cu) than the inputs from the Elbe River, ‘the most contaminated river in Europe’ (Vink et al., 1999). Moreover, the Tinto–Odiel rivers discharge more cadmium into the Ria of Huelva than the Rhine River into the North Sea, being the Elbe and Rhine drainage areas 44 and 53 times larger, respectively, than those of the Tinto + Odiel, and their average inflows, 65 and 197 times more abundant, respectively (Vink et al., 1999; Behrendt and Boehme, 1994).

Within total input, each heavy metal input follows an order of importance similar to the existing in the content of these metals in the pyritic mineral. Major contaminants are zinc, with 52.4% of total, followed by manganese (24.7%), and copper (21.4%). As secondary or minor elements, there appear nickel, arsenic, lead, cadmium and chromium, summing up 1.5% of the total input. Despite the little quantitative importance of these minor inputs, their environmental relevance is outstanding, as the individual or

joint toxicity of metals such as cadmium, arsenic or lead (Campain et al., 2000; Goyer, 1997; ATSDR, 1999a,b, 2000) is not irrelevant.

## 6. Input persistence

Seriousness of AMD contamination of a river does not only lie in its potentiality to destroy aquatic ecosystems downstream, but also in the fact that it can continue indefinitely (Beverly, 1995; Taylor et al., 2002). As a result, we must emphasize the chronic, and therefore, uninterrupted nature of the contamination carried by the Tinto and Odiel rivers into the Ria of Huelva. Even after a 3-year long drought, in samples taken during a month in the dry period (September, 1993), the estuary continued receiving fluvial inputs with their corresponding heavy metal mass load, though just 436 kg/day. Heavy metal persistence in the environment (Nebel and Wriqth, 1999) makes it necessary to calibrate not only the contamination entered in the estuary in a given time, but also the accumulated contamination. In this respect, the present study proves how the continuous

Table 2

Regressions for fluvial inputs of heavy metals to the estuary with respect to freshwater flow into the Ria of Huelva

Pollutant	Equation	Correlation coefficient
Cu	$Y = 43.8X^{0.70}$	0.94
Zn	$Y = 134.3X^{0.63}$	0.90
Mn	$Y = 66.0X^{0.63}$	0.89
Cd	$Y = 0.54X^{0.63}$	0.93
Cd	$Y = 0.24X^{0.66}$	0.78
Ni	$Y = 1.22X^{0.66}$	0.92
Pb	$Y = 0.85X^{0.62}$	0.77
As	$Y = 0.13X^{0.71}$	0.40
TdML	$Y = 250.7X^{0.64}$	0.90

Y = dissolved metal load (kg/h); X = freshwater inflow (m<sup>3</sup>/s).

machinery of AMD release has caused the estuary to receive, only for the period of study (1988–2001),  $430 \times 10^3$  kg of arsenic,  $221 \times 10^3$  kg of cadmium,  $417 \times 10^3$  kg of lead,  $23.4 \times 10^6$  kg of copper,  $27.1 \times 10^6$  kg of manganese and  $57.5 \times 10^6$  kg of zinc as dissolved elements. However, contrary to what happens with environmental

accidents, the chronic nature of this phenomenon itself turns it into an ordinary event and removes its real seriousness (Behrendt and Boehme, 1994). In April 1998, just a few kilometres from the zone of study, a world-known environmental disaster occurred in Aznalcóllar. According to the data provided by the regional Environmental Department,

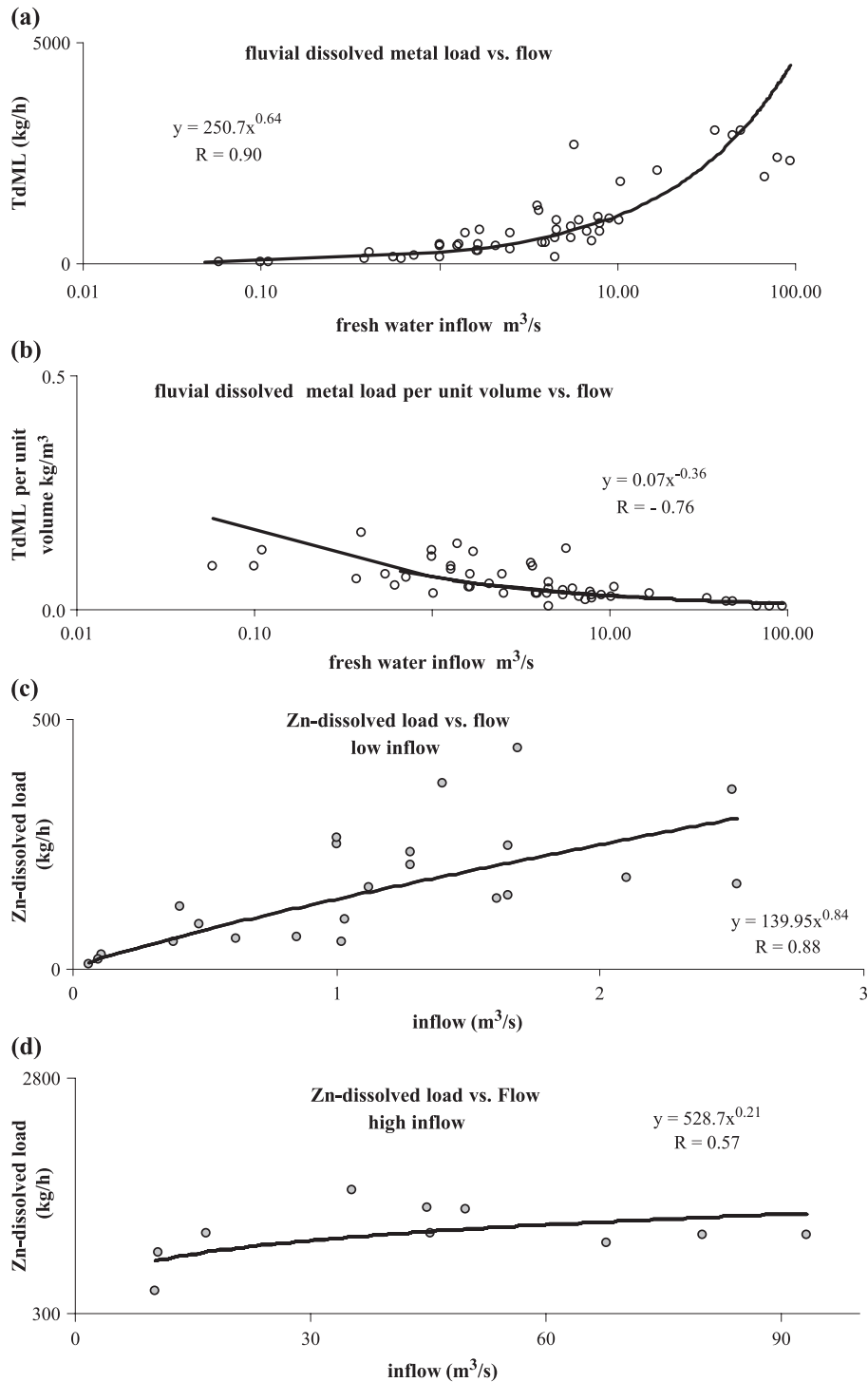


Fig. 3. (a) Ratio of total dissolved metal load to freshwater inflow in the Ria of Huelva. (b) Total dissolved metal load discharged into the estuary per freshwater unity of volume. (c) Total dissolved metal load (TdML) for freshwater low inflow (d) Zn dissolved load to the estuary during high inflow.

the effluent spilled in the Guadiamar River caused by the breakdown of Boliden's mining dam, discharged dissolved metal inputs of  $1.1 \times 10^3$  kg of arsenic,  $3.4 \times 10^3$  kg of cadmium,  $0.12 \times 10^3$  kg of total chromium,  $4.4 \times 10^3$  kg of nickel and  $14.4 \times 10^3$  kg of lead. Comparing these figures to those calculated in this work, we observe how for the period of study the Aznalcóllar disaster has occurred 65 times with respect to cadmium and some 391 times regarding arsenic. These figures will unceasingly rise with the passage of time.

## 7. Variability

### 7.1. Input variability

Variability found in inputs to the estuary during the period of study is extremely high (Table 1). Thus, standard deviation for the total dissolved heavy metal load (TdML) is 848.5 kg/h, similar to the average 895.1 kg/h. By single metals, standard deviation value is, in general, similar to its corresponding average—slightly lower in Mn, Cd, Ni, and Zn, and slightly higher in Pb, Cu, and Cr. It is clearly higher for As. To compare variabilities of the different inputs with each other, the variation coefficient (VC) has been calculated, which relates the standard deviation value with its average (Table 1). It must be noted that VC value for freshwater flow is higher than that of TdML.

In the analysis of variations found in the inputs, there were two fundamental causes for this variability: freshwater total amount received by the estuary, and absolute and relative contributions of each river (Tinto/Odiel) to this amount.

In an initial analysis, we observe (Fig. 2) the relationship between TdML to the Ria of Huelva and total freshwater amount entered in the estuary. Finally, the relationship between TdML and freshwater inflow was verified by means of regressive analyses. The results (Table 2) show that sampling values for TdML and the associated inflow adjust very well (regression coefficient  $R=0.90$ ) to a potential equation  $\text{TdML (kg/h)} = 250.7X^{0.64}$ . From the analysis of this relationship (Fig. 3a), we can deduce that by increasing the amount of freshwater inflow into the estuary, also TdML entered in the Ria of Huelva increases, although with different intensities. For low inflow, small increases of

inflow result in great increases of inputs, whereas for high inflow, the same increases of inflow result in subsequent every time smaller input increases (Fig. 3a) (freshwater inflow  $\text{m}^3/\text{s}$ ). The corresponding regression curves have also been obtained for each type of metal. The resulting equations (Table 2) are very similar to the previous one, with a very good adjustment of the sampling values to the curve, except for arsenic.

In the detailed analysis of these curves, two regions corresponding to two different water regimes can be distinguished: low inflow, with freshwater flows into the estuary lower than  $2.5 \text{ m}^3/\text{s}$ , and high inflow, with inputs higher than  $10 \text{ m}^3/\text{s}$ . Sampling values for TdML and the associated inflow adjust very well in low inflow (Fig. 3c) whereas the relationship is worse in high inflow (Fig. 3d).

#### 7.1.1. Low inflow

It is the most frequent event recorded in the Ria of Huelva, with almost 50% of the observed period. During this kind of regime, despite the high values reached by concentrations of heavy metals in the waters entering the estuary, low inflow are moments of low contamination for the estuary. In fact, waters entering the estuary in low inflow regime present a lower dilution rate, the discharge of dissolved heavy metals per unity of volume being  $75.19 \text{ g/m}^3$  (Table 3). However, in these events, freshwater inflows into the estuary are very scarce, around  $1.1 \text{ m}^3/\text{s}$ . Consequently, the input of dissolved heavy metals to the Ria of Huelva during the days this regime occurs, is very small,  $304.4 \text{ kg/h}$  (34% of yearly average). Also, the observed variability is very low, with a coefficient of variation of only 55%. Though small, these inputs are never null, the total entered in the estuary for the whole low inflow period being 15.6% of yearly total.

#### 7.1.2. High inflow

It is an unusual event in the Ria of Huelva, with only 17% of the observed period. When it occurs, the estuary receives a great amount of freshwater (average  $45.4 \text{ m}^3/\text{s}$ ), and with it, very high inputs of dissolved heavy metals,  $5 \times 10^3 \text{ kg/h}$ . However, contamination entering the estuary is very diluted—the load per unity of volume being only  $13.97 \text{ g/m}^3$  (Table 3).

The existence of these freshwater inflow regimes ( $Q > 10 \text{ m}^3/\text{s}$ ) can be observed in an exploratory analysis (Fig. 2).

Table 3

Average characteristics of heavy metal inputs to the estuary during low inflow and high inflow regimes

Regime	F.I. ( $\text{m}^3/\text{s}$ )	Dissolved metal inputs	Cu	Zn	Mn	Ni	Cr	Cd	Pb	As	TdML
High flow	45.4	kg/h	581.7	1154.6	513.6	11.2	2.9	4.7	6.2	7.4	2282.3
		$\text{g/m}^3$	3.56	7.07	3.14	0.07	0.02	0.03	0.04	0.05	13.97
Low inflow	1.1	kg/h	48.2	164.6	87.3	1.6	0.3	0.6	1.1	0.7	304.4
		$\text{g/m}^3$	11.91	40.67	21.56	0.39	0.07	0.15	0.27	0.16	75.19

F.I. = freshwater inflow; TdML = total dissolved metal load.

Table 4  
Percentage composition of inputs to the Ria of Huelva according to regime

Input	Regime		
	Low inflow	Average	High inflow
Cu	15.84	21.38	25.49
Zn	54.09	52.37	50.59
Mn	28.66	24.66	22.51
Ni	0.52	0.49	0.50
Cr	0.09	0.13	0.13
Cd	0.21	0.20	0.21
Pb	0.36	0.38	0.27
As	0.22	0.39	0.32
TdML	100.0	100.0	100.0

TdML = total dissolved metal load.

The corresponding associated TdML also present an extremely high value with respect to the sampling average, spacing it out from the median. These regimes are the cause for the average value for TdML to be higher than its median (Table 1) in the statistical values. Also, they are responsible for the fact that the average value is always higher than the median for heavy metals, sometimes 3 times higher and even 17 times higher (As). These moments of high inflow are absolutely determining the characteristics of fluvial inflow regime into the Ria of Huelva, affecting the estuary circulation and water quality. According to the results, during a maximum registered in the sampling period, the Ria of Huelva received in a day over  $8 \times 10^3$  m<sup>3</sup> of freshwater carrying  $82 \times 10^3$  kg of dissolved heavy metals to the estuary:  $34 \times 10^3$  kg of zinc,  $15 \times 10^3$  kg of copper and  $15 \times 10^3$  kg of manganese, and more than a ton of arsenic, nickel, chromium, cadmium and lead (Table 1). Despite their low time frequency (just 14% of the samples taken), these high inflow events mean 74% of the variation found in TdML and over 53% of its average.

High and low inflows differ not only in the total input of heavy metals to the estuary (Table 3), but also in the fact that the relative importance varies for some type of metal in the TdML. Comparing the results in Table 4, we observe that Cu rate increases (from 15.84% to 25.49%) when shifting from a low water regime to a flood regime, whereas rates for the other metals, mainly Zn (from 54.09% to 50.59%) and Mn (from 28.66% to 22.51%), decrease slightly. Cd does not undergo any variation; and As seems not to depend on the flow.

During drought years, the scarce rainfall produces small runoff, increasing the frequency of low inflow events. On the

Table 6  
Mean values for dissolved heavy metal concentrations and inputs of the Tinto and Odiel river mouths to the estuary

Input	Dissolved heavy metal concentration (mg/l)		Ratio pollutant load* (%)	
	Odiel river	Tinto river	Odiel river	Tinto river
Cu	9.7	39.6	83.1	16.9
Zn	30.6	97.1	85.5	14.5
Mn	16.1	16.4	95.6	4.4
Ni	0.3	0.78	93.0	7.0
Cr	0.07	0.26	86.6	13.4
Cd	0.1	0.5	82.2	17.8
Pb	0.24	0.6	93.8	6.2
As	0.18	1.8	69.1	30.9
Td.ML**	57.3	155.2	87.5	12.5

\*Ratio pollutant load = for each metal, fluvial input with respect to total input to the estuary.

\*\*Td.ML = concentration of total dissolved metals.

Period 1988–2001.

contrary, high inflow events increase in wet years. During the period of study, the driest year was from 1992 to 1993, with only 359 mm/year, whereas the year from 1995 to 1996 was the most wet, with 1360 mm/year (Table 5).

## 8. Fluvial inputs composition

The two main components of the freshwater that enters the estuary are the waters from the Tinto and Odiel rivers. Despite geographical proximity and climatic similarity of both drainage basins, their inputs have different characteristics. The Odiel River has a larger flow than the Tinto, but a lower heavy metal concentration in its waters. On the contrary, the Tinto River is almost permanently in low flow regime (73% of the sampled days it had a flow lower than 0.2 m<sup>3</sup>/s and 21% of the days it was totally dry). Despite of it, the acidity (pH = 2.5) and concentration of dissolved heavy metals in its waters (TdML = 155.2 mg/l) are extraordinarily high. From the analysis of TdML that each river discharges into the Ria of Huelva (Table 6) and of their temporal evolution (Fig. 4b), it can be deduced that the Odiel River is the main contaminant of the estuary; this river discharges 87.47% of total heavy metals of fluvial origin into the Ria of Huelva compared to only 12.52% of the Tinto River. Table 6 shows the composition of individual inputs from each river to the estuary. It can also be observed that the Tinto inputs of major (Cu, Zn, Mn) or minor (Ni, Cr,

Table 5  
Freshwater inflow (m<sup>3</sup>/s) and hourly average inputs (kg/h) to the Ria of Huelva for a dry year (1992–1993) and a wet year (1995–1996)

Year type	F.I. (m <sup>3</sup> /s)	Cu (kg/h)	Zn (kg/h)	Mn (kg/h)	Ni (kg/h)	Cr (kg/h)	Cd (kg/h)	Pb (kg/h)	As (kg/h)	TdML (kg/h)
Dry year	2.66	115.6	351.6	182.4	3.18	0.52	1.36	4.34	0.30	659.3
Wet year	72.9	628	1123	608	10.7	3.8	5.2	5.2	7.2	2391.4

F.I. = freshwater inflow; TdML = total dissolved metal load.

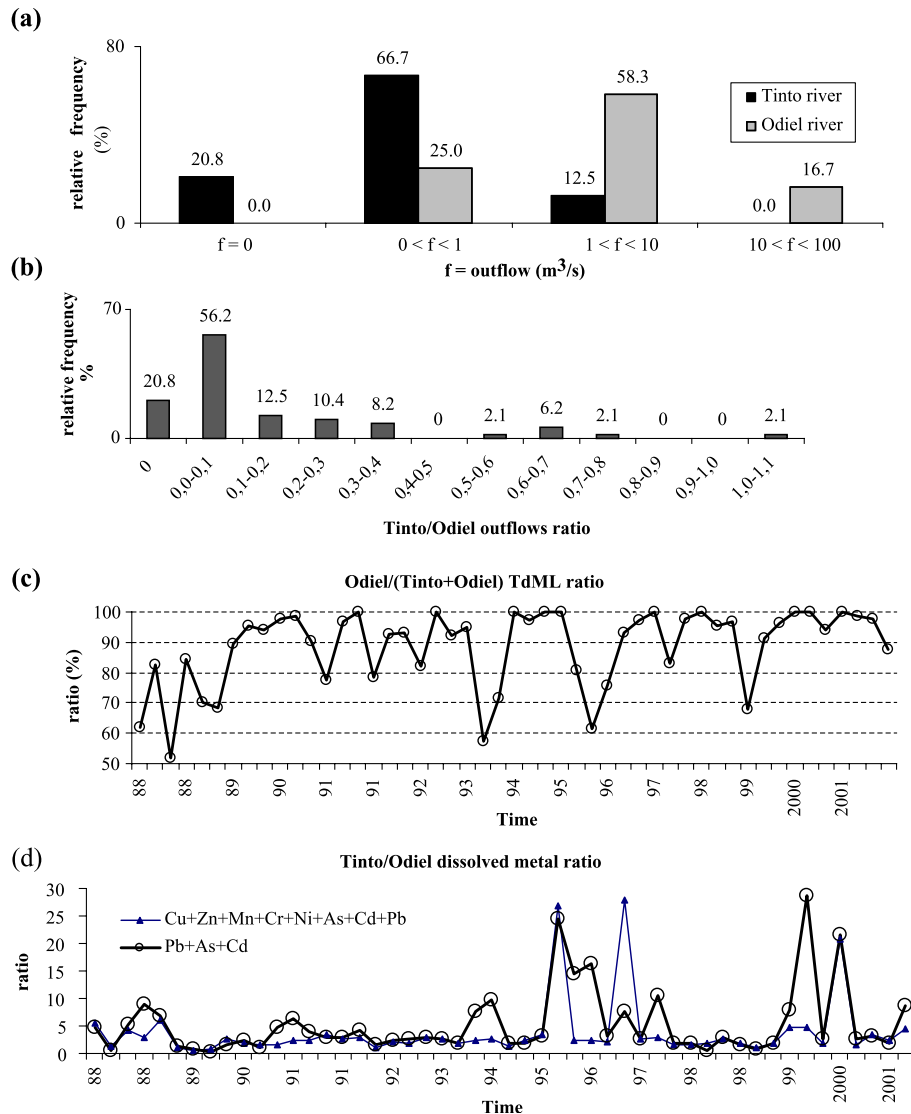


Fig. 4. (a) Relative frequencies of ratios found during sampling of the Tinto and Odiel river flows. (b) Relative frequencies of Tinto and Odiel outflows into the Ria of Huelva. (c) Time series of Odiel River input in the total dissolved metal load discharged by the rivers Tinto and Odiel to the estuary. (d) Time series of the relation between dissolved metal concentrations in the Tinto and Odiel rivers at the entrance of the estuary.

Cd, Pb, As) heavy metals are much lower than those from the Odiel (Fig. 4d). From this study's results we have concluded that there is little importance in the estuarine contamination of the Tinto river inputs not only of certain major elements (4% of total manganese input), but also of highly toxic elements (18.5% of total As + Cd + Pb input).

## 9. Conclusions

1. In general, fluvial inputs of dissolved heavy metals to the Ria of Huelva are, for their amount, composition and persistence, a unique case in estuarine contamination by heavy metals. The exceptional nature of this contamination increases when considering the size of the rivers that originate it.
2. Because of their environmental toxicity, it must be emphasized that an average of 84 kg of arsenic, 82 kg of lead, and 43 kg of cadmium enter the estuary in 1 day, reaching even maximums of 1481 kg of As, 470 kg of Pb, and 170 kg of Cd.
3. The amount of heavy metals discharged into the Ria of Huelva is directly related to the freshwater inflow ( $Y = 250.7X^{0.64}$ ). Given that this flow increases with rainfall, contamination discharged into the estuary by these rivers increases in wet years. This contamination can be almost eight times higher than in drought years.
4. According to typology, two possible forms of heavy metal discharge into the estuary can be distinguished, depending on freshwater inflow to the Ria of Huelva—in low freshwater regime and in high water regime or flood. The former is the most frequent (50% of the days), when

the estuary receives around 1.1 m<sup>3</sup>/s of highly contaminated freshwater (175.2 g/m<sup>3</sup> of dissolved heavy metals). However, the total input received by the Ria of Huelva in those days is only 15.6% of average yearly total. The latter is less frequent in the estuary (17% of the days), but during those few days, the Ria of Huelva receives more than 53% of the average yearly total. During floods, the estuary receives between 10 and 100 m<sup>3</sup>/s of freshwater with 'low' concentration of dissolved heavy metals (13.97 g/m<sup>3</sup>). The characteristics of fluvial inputs to the estuary in a given moment are within these two limits, getting closer to one or the other according to the magnitude of freshwater received by the estuary.

- The most frequent situation observed (77% of the days) is that 90% to 100% of the freshwater inputs received by the estuary come from the Odiel River. Despite this, the extremely high concentration of heavy metals in the Tinto River waters causes this river to discharge almost 32% of total fluvial input of dissolved heavy metals to the estuary. The Odiel River discharges 81.5% of the most toxic heavy metals (As + Cd + Pb) entering the Ria of Huelva estuary.

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