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# Trace metal partitioning over a tidal cycle in an estuary affected by acid mine drainage (Tinto estuary, SW Spain)

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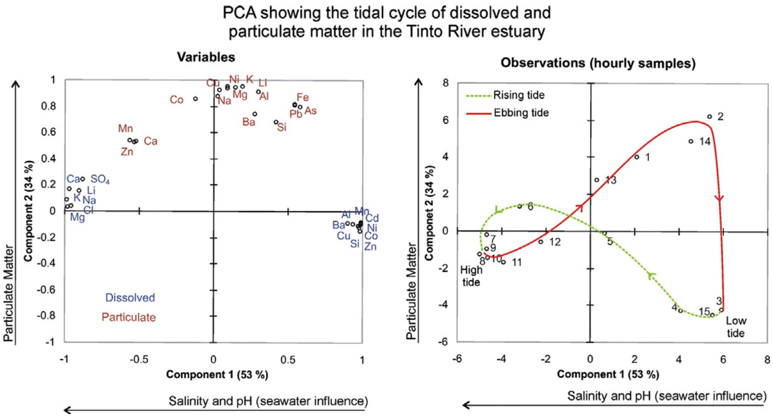
## HIGHLIGHTS

- The Tinto estuary shows strong pH gradients and high trace elements concentrations.
- PM has a hysteretic relationship with tides and high contents of Fe, Al, As and Pb.
- Co and Mn are controlled by river and sea water mixing and sorption processes.
- Sorption processes strongly affect Cu below pH 6, above this value Cu is desorpted.
- Cadmium behaves conservatively along the pH range studied (4.4–6.9).

## GRAPHICAL ABSTRACT



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## ABSTRACT

The Tinto River estuary is highly polluted with the acid lixiviates from old sulphide mines. In this work the behaviour of dissolved and particulate trace metals under strong chemical gradients during a tidal cycle is studied. The pH values range from 4.4 with low tide to 6.9 with high tide. Precipitation of Fe and Al is intense during rising tides and As and Pb are almost exclusively found in the particulate matter (PM). Sorption processes are very important in controlling the mobility (and hence bioavailability) of some metals and particularly affect Cu below pH 6. Above pH ~ 6 Cu is desorbed, probably by the formation of Cu(I)–chloride complexes. Although less pronounced than Cu, also Zn desorption above pH 6.5 seems to occur. Mn and Co are affected by sorption processes at pH higher than ca. 6. Cd behaves conservatively and Ni is slightly affected by sorption processes.

## 1. Introduction

Estuaries are complex systems governed by tidal action and river flow. The mixing zone of salt and fresh water constitutes a complex and dynamic environment because of strong longitudinal gradients in

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physico-chemical parameters such as salinity, pH, and temperature (Benoit et al., 1994). Dissolved elements can behave conservatively in estuaries. Salinity is typically a conservative constituent of water and can be used to trace the mixing of water masses (Liu et al., 1998; Turner et al., 1998; Stedmon et al., 2003). Dissolved trace elements, however, are often non-conservative as they are affected by processes of sorption/desorption, precipitation and co-precipitation, transfer at the sediment–water interface, etc. (Zhou et al., 2003).

Metal pollution by acid mine drainage (AMD) because of coal and sulphide mining is one of the biggest environmental impacts that aquatic systems are facing across the globe (Equeenuddin et al., 2013). AMD results from the oxidation of sulphide minerals, mainly pyrite, and is characterised by low pH values and high dissolved concentrations of sulphates, metals and metalloids. AMD is responsible for the pollution of groundwaters, streams, rivers and whole river basins, such as the Odiel and Tinto watersheds (Olías et al., 2004; Cánovas et al., 2007; Sarmiento et al., 2009). These rivers flow across the Iberian Pyrite Belt (IPB) in South-West Spain, one of the most famous sulphide mining regions in the world. Although today there is almost no active mining at the IPB because of the longevity of these processes the pollution continues to increase (Younger, 1997), transporting high concentrations of sulphates, metals and metalloids to the estuary formed by the two rivers (Sáinz et al., 2004; Cánovas et al., 2007; Nieto et al., 2007). The average quantities transported by both rivers annually are (in tonnes): 7900 of Fe, 5800 of Al, 3500 of Zn and very high amounts of other toxic elements (Olías et al., 2006).

Besides the well-documented AMD sources of metal contamination, since the 1960s this estuary has included a heavily industrialised area (with phosphate fertiliser plants, oil refinery, power plants, other chemical industries and phosphogypsum piles). This activity has generated a huge volume of effluents in the estuary which have contributed to large quantities of toxic elements and nutrients, making this one of the most polluted estuarine systems in Western Europe (Grande et al., 2000; Borrego et al., 2002; Ruiz et al., 2008). More recently, the main industrial effluents have been reduced thanks to the environmental controls imposed by the European Union as well as local regulatory organisations (Pérez-López et al., 2011).

There have been several studies on the longitudinal distribution of metals from the Tinto and Odiel rivers to the sea (e.g. Elbaz-Poulichet et al., 1999; Braungardt et al., 2003; Grande et al., 2003; Borrego et al., 2012), but they do not consider certain aspects of the behaviour of trace elements, such as variations in particulate matter and kinetic effects in sorption/desorption processes (Balls et al., 1994). We carried out sampling during a full tidal cycle from a fixed point in the Tinto River estuary, with the objective of investigating the behaviour of trace elements and water–particle interactions under strong chemical gradients during the mixing of acidic river water and seawater.

## 2. Methodology

### 2.1. Study area

The Tinto and Odiel Rivers flow into the Atlantic Ocean at the North-West of the Gulf of Cádiz, forming an estuarine system known as Ría of Huelva (Fig. 1). This estuary is located along a mixed-energy mesotidal coast, with a mean tidal range of 2.1 m (0.5 m during neap tides and up to 4.0 m during spring tides; Borrego et al., 2002). The volumes of water transferred between the estuary and the open sea (tidal prism) during a tidal half-cycle (6 h) range from 37 $hm^3$ during a mean neap tide to 82 $hm^3$ in a mean spring tide (Grande et al., 2003). The Tinto River has a length of 100 km with a drainage basin of 1646 $km^2$ (Olías et al., 2004; Ruiz et al., 2008). Its average flow is 1.5 $m^3\ s^{-1}$, although this value is extremely variable because of the irregular rainfall, ranging between 0.2 and 4.4 $m^3\ s^{-1}$ (Cánovas et al., 2007). In its upper course it crosses the Iberian Pyrite Belt (IPB), one of the largest sulphide metallogenic provinces in the world, in which intense mining activity occurred from the second half of the nineteenth century to the end of the twentieth century (van Geen et al., 1997). The legacy of such activity is several hundred kilometres of adits, a multitude of open pits and enormous volumes of uncontrolled waste dumps which generate large amounts of acid lixiviates with high contents of sulphates and metals which are transported to the Huelva estuary (López-González et al., 2006; Cánovas et al., 2008; Cánovas et al., 2010).

In addition, at the industrial complex of Huelva there are five plants dedicated to the phosphoric acid production. The phosphate rock used as a raw material come mainly from Morocco, with high concentrations of $^{238}U$ (~1500 Bq $kg^{-1}$; Más et al., 2006; Villa et al., 2009). The production process generates annually about 2.5 to 3 million tonnes of a solid waste byproduct known as phosphogypsum (PG), which is mainly composed of gypsum ($CaSO_4 \cdot 2H_2O$) but also has strong acidity (pH around 1.5) and high levels of impurities such as fluorine, toxic metals and U-series radionuclides (Pérez-López et al., 2007; Bolivar et al., 2009). The PG piles currently cover an area of approximately 1200 ha (Fig. 1) containing about 100 Mt of wastes. Since December 2010, the production plants have been closed and subsequently the PG production stopped. Nevertheless, there still are some inputs of very polluted acid water from PG stacks to the Tinto River (Hierro et al., 2014).

### 2.2. Sampling

A total of 15 water samples were collected at a central sampling point in the Tinto estuary (Fig. 1) on 11 March 2009. During the sampling there was a spring tide with an extreme tidal range (3.3 m). Conversely, the fluvial inputs were low because there was no rainfall in the Tinto basin in the preceding days. Samples were taken hourly from a bridge using a hose connected to a GRUNDFOSS DIN W-Nr 14401 stainless steel pump activated by a generator set and stored in 5 L polyethylene containers. The system extracted surface water from a depth of 50 to 60 cm. Polyethylene bottles were washed in 5% (*v*/*v*) nitric acid and then with milli-Q water (18.2 MΩ) prior to sampling. The pumping line was also cleaned following the same procedure.

As sea level was recorded at the junction of the two estuaries at a distance of 3 km from the sampling point (Fig. 1), a tide delay of 20 min was applied to obtain the sea level value during the sampling (Hierro et al., 2013). As Fig. 2 reflects, samples 3 and 15 were taken at low tide, whereas high tide occurred between samples 8 and 9.

The main physico-chemical parameters were determined in situ. Temperature, pH and electrical conductivity (EC) were measured with a portable MX 300 metre (Mettler Toledo) and the redox potential using a HANNA metre with Pt and Ag/AgCl electrode (Crison). The instruments were calibrated before the readings and the measured potential was corrected for temperature and converted to potential vs. the standard hydrogen electrode (Eh).

### 2.3. Pretreatments and analytical determinations

After being collected, water samples were filtered with polycarbonate filter discs (0.45 μm Millipore). Subsequently, two filtered aliquots of each sample (100 mL) were obtained. The first one contained no chemical preservative and was used for determination of anions. The second aliquot was reserved for measurement of dissolved metals, and therefore acidified to pH ~ 2 with $HNO_3$. All aliquots were stored at 4 °C in the dark until analysis. For each sample a volume of about 4 L was filtered by cellulose nitrate filters (0.45 μm), in order to obtain the particulate matter (PM) content. The filters were dried and weighed, and the mass of suspended matter was calculated by subtracting the mass of the blank filter. The filters and the PM contained in them were dissolved by means of strong $HNO_3$ and aqua regia (3 HCl:1 $HNO_3$).

All analyses were performed at the Central Research Services of Huelva University. Anions ($Cl^-$, $F^-$, $Br^-$, $SO_4^-$ and $PO_4^-$) were determined by