



Major hydrogeochemical processes in an Acid Mine Drainage affected estuary



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ABSTRACT

This study provides geochemical data with the aim of identifying and quantifying the main processes occurring in an Acid Mine Drainage (AMD) affected estuary. With that purpose, water samples of the Huelva estuary were collected during a tidal half-cycle and ion–ion plots and geochemical modeling were performed to obtain a general conceptual model. Modeling results indicated that the main processes responsible for the hydrochemical evolution of the waters are: (i) the mixing of acid fluvial water with alkaline ocean water; (ii) precipitation of Fe oxyhydroxysulfates (schwertmannite) and hydroxides (ferrihydrite); (iii) precipitation of Al hydroxysulfates (jurbanite) and hydroxides (amorphous Al(OH)₃); (iv) dissolution of calcite; and (v) dissolution of gypsum. All these processes, thermodynamically feasible in the light of their calculated saturation states, were quantified by mass-balance calculations and validated by reaction-path calculations. In addition, sorption processes were deduced by the non-conservative behavior of some elements (e.g., Cu and Zn).

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1. Introduction

Oceans are mainly impacted by the supply of anthropogenic and natural trace elements from atmospheric and riverine inputs. Human activities, such as mining or industry, cause important global environmental changes because of the release of significant concentrations of metals to rivers that finally flow into the oceans.

Estuarine systems, which represent transition zones between freshwater and seawater, regulate the flux of major and minor elements entering the coastal areas and ultimately the deep ocean. In estuaries with important salinity gradients, ionic composition and redox condition changes occur diurnally due to the tidal cycles (Liang and Wong, 2003). During the seawater–freshwater mixing some elements are removed from the solution due to mineral precipitation or to their sorption onto newly-formed solid phases; whereas, other elements could be released to the solution, increasing their concentration in the estuarine waters, due to dissolution, desorption, and transformation and migration across the sediment/water interface (Morris et al., 1986; Bewers and Yeats, 1989; Baeyens et al., 1998; Zhou et al., 2003; Hierro et al., 2014a). Hence, understanding the geochemical processes occurring in estuaries is

highly important because of the influence they exert on the metal transport to the oceans.

The estuary of Huelva is formed by the confluence of the Tinto and Odiel rivers (Fig. 1). Both rivers drain almost entirely the Central Domain of the South Portuguese Zone (SW Iberian Peninsula), crossing the Devonian–Carboniferous materials of the Iberian Pyrite Belt (IPB). The IPB is one of the most important mining areas in the world, with about 1700 million tons of original reserves of polymetallic massive sulfide (Sáez et al., 1999). The mining activity in this region dates back to 5000 years (Nocete et al., 2005), being especially intense from the middle of the 19th century (Oliás and Nieto, 2012). The uncontrolled exploitation of sulfide-bearing ore deposits has caused the exposure of large amounts of mining wastes, which undergo oxidation in the presence of atmospheric oxygen and water, leading to the generation of large discharges of acidic leachates known as Acid Mine Drainage (AMD), with very high concentrations of toxic metals and sulfates. Consequently, the Tinto and Odiel rivers are an outstanding example of contamination by AMD worldwide.

The absence of rocks capable of buffering the acidity within the IPB materials makes the Tinto and Odiel rivers maintain low pH (approx. 2.5 and 3.5 respectively) and high pollutant load throughout their fluvial courses. Near the mouth of the estuary, however, the area is characterized by a Tertiary succession of basal gray-blue marlstone and upper fine sands and gray-yellow silt

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(López-González et al., 2006). Although these carbonate-rich sediments can provide a potential source of alkalinity through some minor tributaries (Cánovas et al., 2005), this alkalinity is quickly consumed due to the extreme acidity of both rivers. Therefore, the Tinto and Odiel rivers flow into the Atlantic ocean transporting to the estuarine system acid waters ($\text{pH} < 3$) with high concentrations of metals (Zn, Cu, Cd, Ni, Pb, Cr, As, etc.) as dissolved species and colloidal particles (Nelson and Lamothe, 1993; Sáinz et al., 2004; Sanchez-España et al., 2005; Nieto et al., 2013). Indeed, these rivers contribute significantly to the total metal transfer from continents to the oceans. For example, Olías et al. (2006) calculated the fluvial metal contribution to the estuary between 1995 and 2003, showing that mean contaminants discharge is 7900, 5800, 3500, 1700 and 1600 t/y of Fe, Al, Zn, Cu and Mn, respectively. These values represent 60% of the global gross flux of dissolved Zn transported by rivers into the ocean, and 17% of the global gross flux of dissolved Cu. Owing to the huge impact that this heavily-polluted environment could have on the water and sediments of the Gulf of Cadiz area (Van Geen et al., 1997) many previous researches have been focused on the study of the trace elements in the estuary of Huelva (Elbaz-Poulichet et al., 1999, 2000; Braungardt et al., 2003; Carro et al., 2011; Hierro et al., 2014a,b). However, despite the valuable insights into trace metal geochemistry in the estuarine waters provided by these earlier studies, the quantification and the simulation of the main geochemical processes in the Huelva estuary is still in its infancy. Considering that the metal behavior and, at the end, their flow into the ocean water, will be strongly influenced by the geochemical processes that take place in the estuary, it is of paramount importance to understand them

in order to evaluate the total metal transfer from continent to the ocean.

Therefore, the major objective of this study is to quantify the main geochemical reactions occurring in the estuarine waters, which could significantly affect the riverine flux of elements to the ocean. With that aim, classical geochemical calculations (including speciation-solubility calculations and forward and inverse modeling) were performed with the PHREEQC code (Parkhurst and Appelo, 1999). These calculations allowed us to evaluate the conservative or non-conservative behavior of the dissolved elements, depending on whether their distribution is mainly controlled by physical mixing of different end-members or by more complex processes, as well as to identify additional processes that occur in the Huelva estuary.

2. Geological setting

As stated above, owing to the intense mining activity the Tinto and Odiel rivers are currently two of the most polluted rivers in Spain and in the world (Olías et al., 2004; Nieto et al., 2007; Sarmiento et al., 2009). As a result, the Tinto-Odiel estuary shows high pollutant load and an extreme range of chemical conditions (from highly-acidic fluvial environments ($\text{pH} 2\text{--}3$) to typical seawater values ($\text{pH} = 8$)) that will determine most of the geochemical processes occurring in this system.

The estuary of Huelva is a partially-mixed estuary with tidal range of 2–3 m and a tidal prism between 37 and 82 hm^3 during a tidal half-cycle (6 h) (Grande et al., 2000). The acidic river discharge originates two processes of water mixing in the estuary

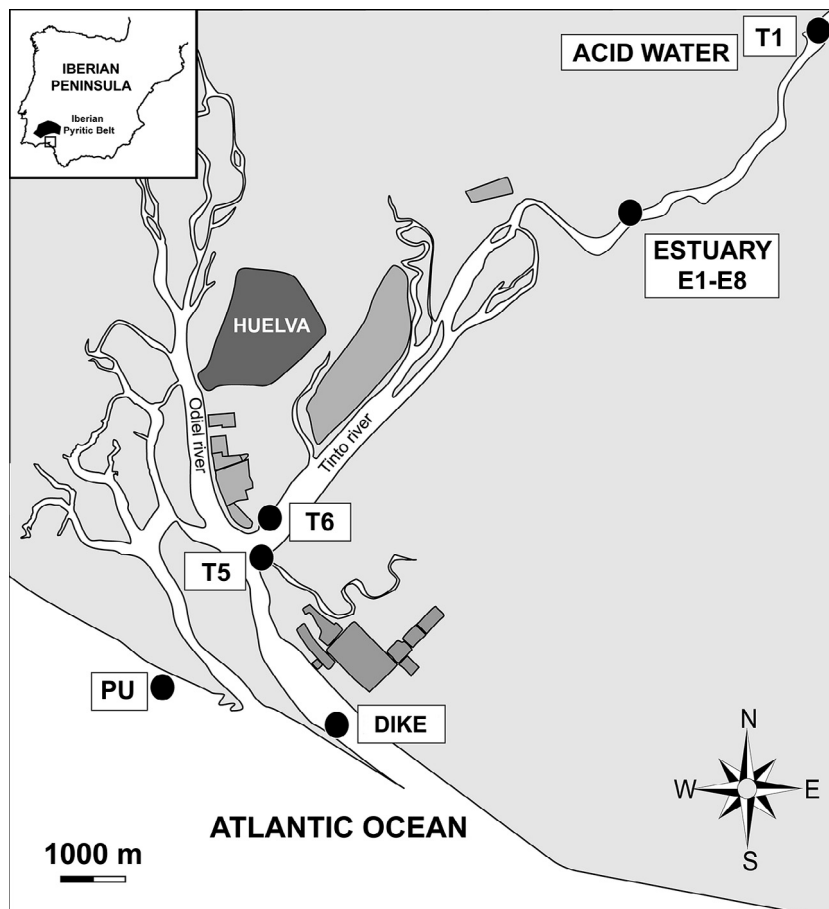


Fig. 1. Site map and sampling points in the Huelva estuary and mixing end-members: Tinto River (T1) and Atlantic Ocean (PU).

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