

Mobility and contribution of contaminants to oceans through an Acid Mine Drainage affected estuary – the Ría de Huelva (SW Spain)

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INTRODUCTION

The Tinto and Odiel rivers drain the Iberian Pyrite Belt, one of the largest sulfide deposits in the world exploited since ancient times. Oxidation of the residues from the abandoned mining activity has caused intense contamination of both rivers by Acid Mine Drainage (AMD) (Nieto et al., 2013). Both rivers converge in the estuary of the Ría de Huelva, where the mixing of acidic river water and alkaline seawater leads to a series of geochemical reactions that control the residence time of pollutants along the estuarine transition. During the neutralization, it takes place the flocculation of particulate material (schwertmannite and basaluminite) by chemical precipitation. Both newly-formed precipitates are poorly-crystalline and metastable minerals that play an important role in scavenging contaminants. The mobility of contaminants in the Estuary of Huelva during the mixing has been observed in several hydrochemical studies (e.g., Asta et al., 2015). However, the set of geochemical processes that affect the particulate material controlling such mobility is still unclear. Elucidating these processes is crucial to assessing pollution's actual transfer to the Atlantic Ocean. This research focuses on elucidating the role of particulate matter in the mobility and contribution of pollutants within the estuary to develop a geochemical model for predicting pollutant mobility in the face of future sea level oscillations.

METHODOLOGY

The geochemical processes that occur during the interaction of AMD and estuarine water have been evaluated by two types of laboratory experiments. The first one consisted of titration experiments by dropwise addition of seawater to an initial volume of AMD throughout the rise in pH up to values of 7-7.5. The second one consisted of adding different amounts of schwertmannite to 40 mL of seawater in centrifuge tubes to carry out sets of experiments at different ratios: 1:40, 1:200, and 1:400. In turn, for each ratio, the interaction between schwertmannite-seawater was maintained for different times (0-336 h). To provide a complete picture of the geochemical processes, a field study was carried out with water samples from the estuary Ría de Huelva from the fluvial section to the marine domain. In both experiments and field samplings, dissolved contaminants were analysed by ICP-MS/OES, and solids were characterized by SEM-EDS and XRD.

RESULTS AND DISCUSSION

As pH increases during the mixing between AMD and seawater, two buffer zones related to the formation of two mineral phases are observed. The first buffer (pH 2.5-4.0) corresponds to precipitation of schwertmannite which removes Fe(III) and As from solution. The second buffer (pH 4.5-6.0) corresponds to precipitation of basaluminite, which removes Al from solution, as well as part of Cu, REE and Y. In the water mixing zone, the increase in pH is accompanied by a decrease in dissolved [Fe] by precipitation. [As] first tends to decrease along with the decrease in [Fe] by adsorption. However, at pH values above 5-6, [As] increases again in solution until it reaches 100% in the dissolved fraction. This increase in [As] has been associated with changes in the surface properties of schwertmannite in the marine environment related to the zero point charge (ZPC). The schwertmannite surface becomes positively charged at pH below 4.6 in seawater; whereas the main aqueous As species is an anion (H_2AsO_4).

Both features explain the high affinity of As for schwertmannite through an adsorption process. At higher pH values, the surface of schwertmannite becomes negatively charged, and desorption of As is expected. In addition, schwertmannite also controls the mobility of other elements such as Cr, V, Mo, or Sb which occur as oxyanions as the main species in solution. Other contaminants such as Zn, Cd, Co, and Ni show a conservative behavior, i.e. they do not precipitate during estuarine mixing and most of the total concentration is in the dissolved fraction. Consequently, they may pass through the estuary giving rise to a metal-rich plume in the coastal waters of the Gulf of Cádiz and increasing metal exposure to living organisms (e.g., Cánovas et al., 2020).

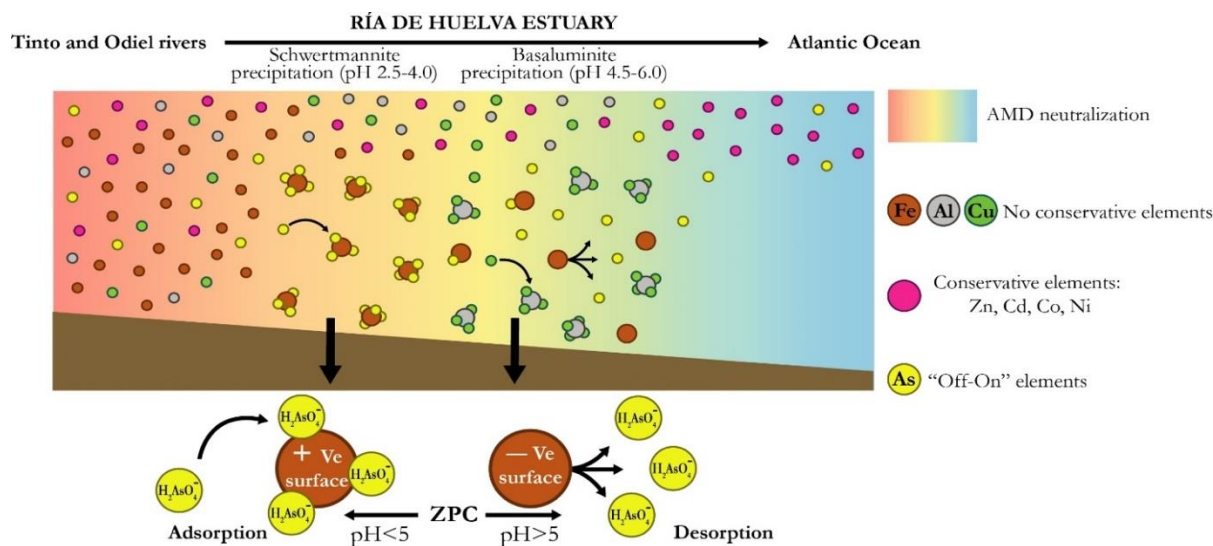


Fig 1. Conceptual model of the processes that affect particulate matter in the Ría de Huelva Estuary.

CONCLUSIONS

The present research has shed light on the geochemical processes that are triggered during the neutralization of river discharges affected by AMD in the Estuary Ría de Huelva. During the mixing of acidic water with seawater, Fe and Al precipitate as schwertmannite and basaluminite along with other metals, mainly As and Cu, respectively, acting as sinks of pollution. Nevertheless, As seems to have an “Off-On” behavior. The schwertmannite that flocculates in the estuary adsorbs As (Off) below a pH value close to 5.0, however, the As would be desorbed (On), passing again to solution, when these precipitates reach the estuarine zones with pH values above 5.0; that is when the zero point charge is surpassed. Special attention should be paid to conservative elements such as Cd, Zn, Co, or Ni since the total amount discharged by both rivers would practically reach the oceans.

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