Influence of tidal coefficient and river regime on pollutant dynamics in the Estuary of Huelva

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Palabras Clave: Estuario, Carga contaminante, Aguas ácidas. **Key Words:** Estuary, Pollutant load, Mine waters.

INTRODUCTION

The abandoned mining districts of the Iberian Pyrite Belt (IPB) in the Tinto and Odiel river basins are long-lived sources of acidity, sulfates and metal(loid)s transported to the Estuary of Huelva by Acid Mine Drainage (AMD) processes. The discharges of pollutants from rivers to the estuary present average values of 7900, 5800, 3500, 1700 and 1600 ton/year of Fe, Al, Zn, Cu and Mn, respectively, which represent more than 50% of Zn and 10% of Cu of the total metals transferred on a global scale from the continents to the oceans (Olías et al., 2006). This study focuses on the behavior of contaminants in the estuary, highlighting the role of tidal dynamics.

METHODOLOGY

The behavior of contaminants during mixing between AMD-affected rivers and seawater was evaluated: (1) spatially, by collecting samples by boat through the estuary and (2) temporally, using autosamplers in high estuarine sections. The samples for the dissolved fraction were filtered (0.45 µm) and acidified with suprapure HNO_3, while those for the total fraction (dissolved + particulate fractions) were only acidified without filtering, to be later analyzed with ICP-OES/MS. The difference between both fractions is the fraction associated with the particulate matter.

RESULTS AND DISCUSSION

In the estuary, there is an increase in the pH from acidic river values (~ 2.5 and 3.5 in the Tinto and Odiel rivers, respectively) to alkaline values typical of seawater (~ 8). Associated with this increase in pH, the pollutants exhibit a behavior through the estuary that can be grouped into: non-conservative, conservative and ON-OFF (Fig. 1).

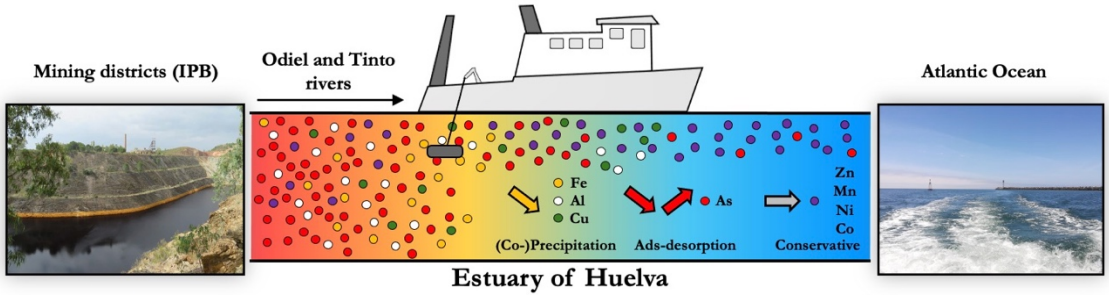

Fig. 1 *Conceptual model of the pollutant behavior from flocculation to sedimentation in the Estuary of Huelva. The pH gradient is represented by colors, from red (approx. 2.5) to blue (approx. 8.0) (also in Fig. 2).*

Non-conservative elements, mainly Fe, Al and Cu, are those that are removed from water by mineral precipitation during the neutralization of AMD, i.e. these elements tend to form part of the particulate material that is then deposited in the bottom sediments (Pérez-López et al., 2023). As the pH increases, the sequential precipitation of Fe phases occurs initially, followed by those of Al, schwertmannite and basaluminite, respectively. Schwertmannite removes Fe(III) from water (orange arrows in Figs. 1 and 2), while basaluminite removes Al and part of Cu. Meanwhile, the conservative elements, mainly Zn, Mn, Cd, Ni and Co, are those that remain in solution through the estuary, ultimately reaching the Atlantic Ocean. Finally, elements with an ON-OFF behavior (red arrows in Figs. 1 and 2), notably As, are first retained by mineral sorption (OFF) and subsequently become dissolved again (ON), also reaching the ocean along with the conservative elements.

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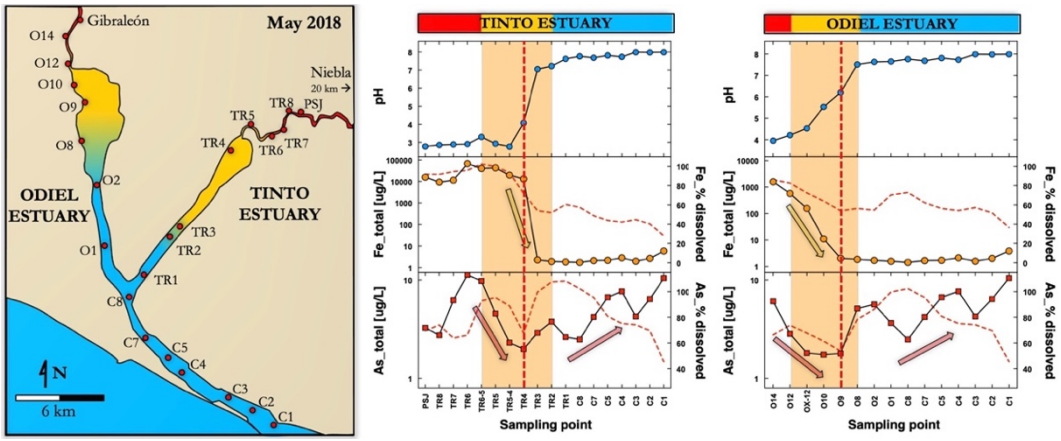

Fig. 2 *Map of the Estuary of Huelva showing sampling points. Spatial evolution of pH and total concentrations (dashed lines) and dissolved percentages (dotted lines) of Fe and As along the Tinto and Odiel estuaries.*

The ON-OFF behavior of As observed in the autosampler samplings in the upper estuary seems to vary depending on the tidal coefficient (Fig. 3). When the tidal coefficient is high (>70), the pH values oscillate from 4.0 at low tide to 8.0 at high tide. Arsenic is removed from the water along with Fe by sorption on schwertmannite at the beginning of the tidal rise; however, at pH above 6.5, an increase in As in solution is observed until reaching proportions in the dissolved phase close to 100%. In contrast, when the tidal coefficient is low (<50), the high tide in the upper estuary reaches pH values that do not exceed 6.5. Under these conditions, As is removed alongside with Fe at the outset of the rising tide, but it is not later released to the water by desorption. The desorption of As occurs when the particulate material reaches the marine domain of the estuary. Therefore, the tidal coefficient appears to control the form and bioavailability of As to ecosystems. Other oxyanions (Cr, Mo, Sb and V) also exhibit an ON-OFF behavior, analogous to As, influenced by the tidal coefficient (Fig. 3).

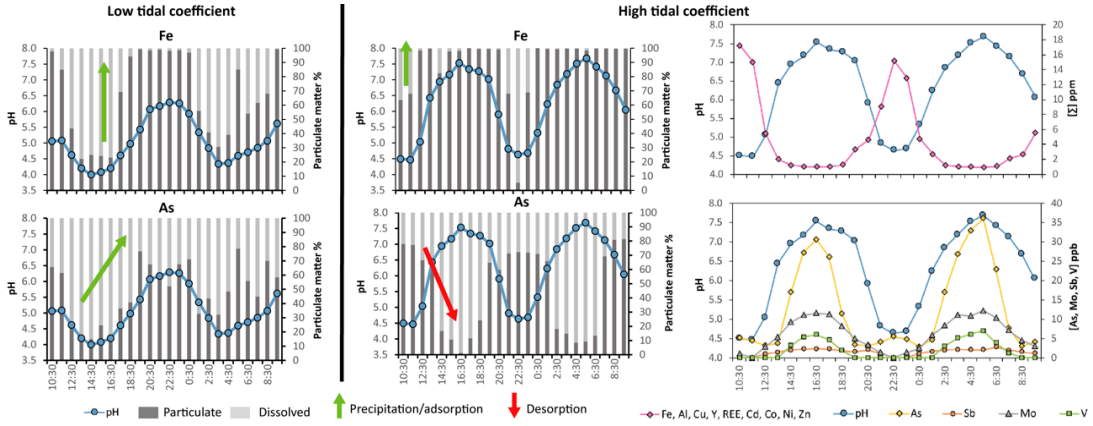

Fig. 3 *Temporal evolution of pH and particulate/dissolved percentages of Fe and As in the upper Tinto Estuary during two tidal cycles in low and high tidal coefficient. The antagonistic behavior of cationic metals (above) compared to oxyanions (below) is included for high tidal coefficient. pH is positively correlated with sea level variation.*

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