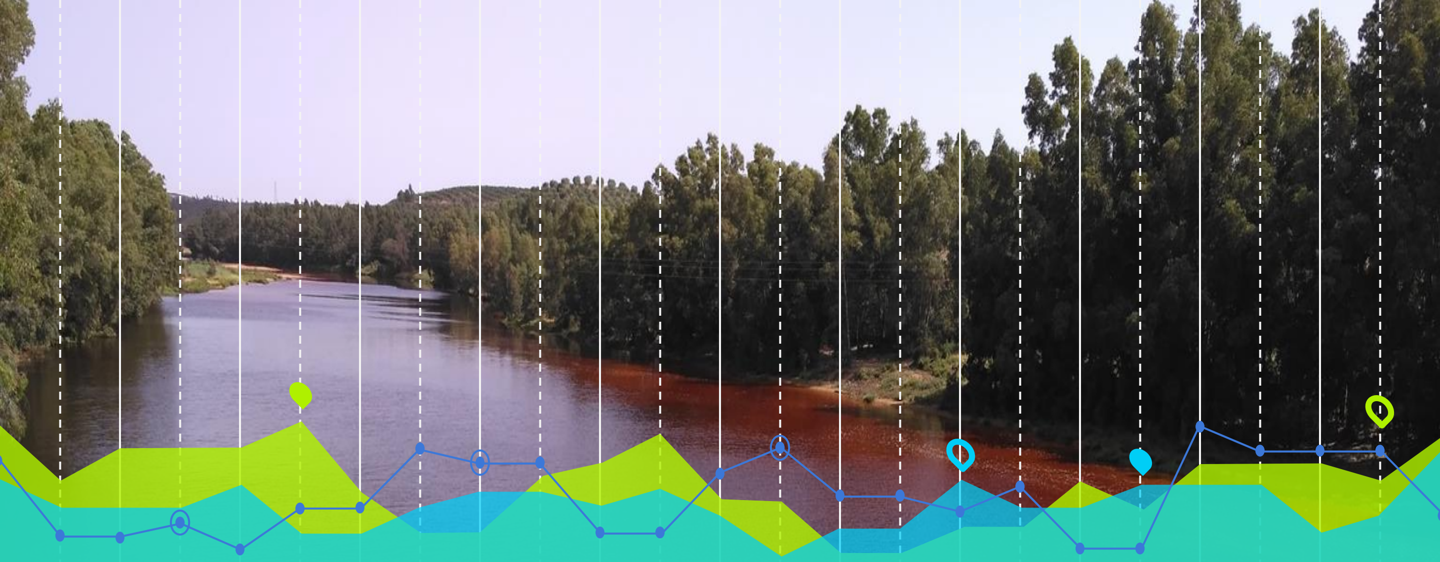

Mobility of Rare Earth Elements (REE) in AMD-Impacted Estuarine Environments

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EIT RawMaterials Connecting matters

Industrial and Mine Wastes as a Source of Technology Critical Elements
Workshop of EIT Morecovery Proyect
5th May 2020

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RENSMA Centro de Investigación en Recursos Naturales Salud y Medio Ambiente

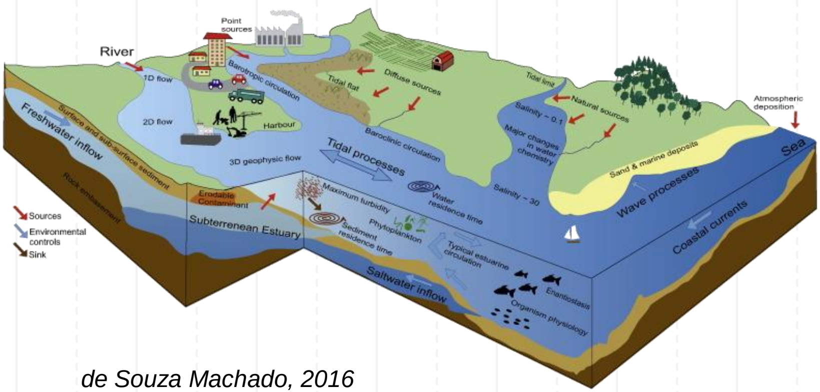
Universidad de Huelva

Outline

- REE in seawater environments
- Factors controlling REE incoming in the Ria of Huelva estuary
- REE Distribution and final deposition
- Ecotoxicological implications

Introduction

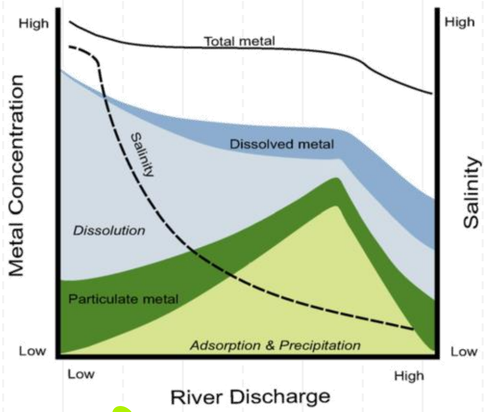
- Metal/loid pollution in estuaries represents a serious environmental challenge, especially in areas affected by industrial and mining activities.
- Rising production and emissions of technology metals

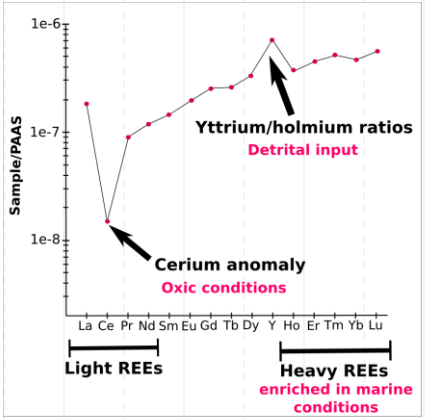


de Souza Machado, 2016

Introduction

- Dissolved REE are strongly removed when river water mixes with seawater at the low salinity zone, leading to the typical marine REY pattern.





Typical open marine REE pattern

Iberian Pyrite Belt ----->Ría de Huelva

Mining legacy;

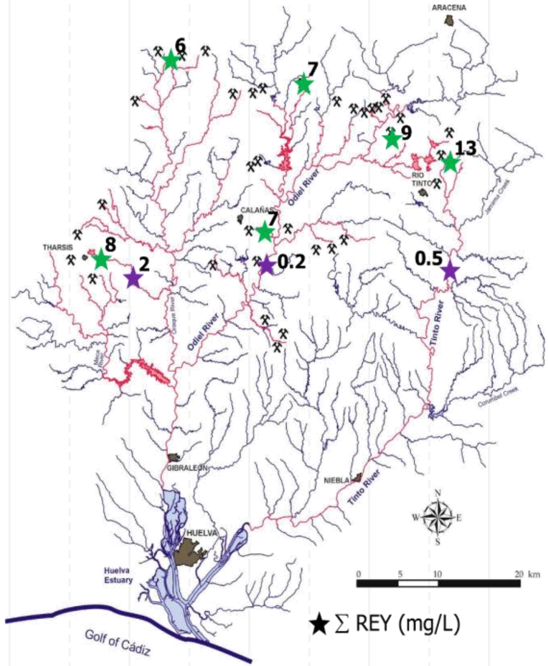
- Last 150 years ≈ 90 abandoned mines
- > 4800 ha affected by pyritic wastes and mining infrastructures
- > 200 millions of m^3 accumulated sulfide-rich wastes.

Absence of control measures

Odiel and Tinto Rivers Water Quality Degradation

Iberian Pyrite Belt ----->Ría de Huelva

- The high acidity released during sulfide oxidation also causes the **dissolution of host rocks**, which leads to increased concentrations of elements commonly enclosed in such as Al, Ca, Mg, Na and **REE**.



Iberian Pyrite Belt ----->Ría de Huelva

ODIEL

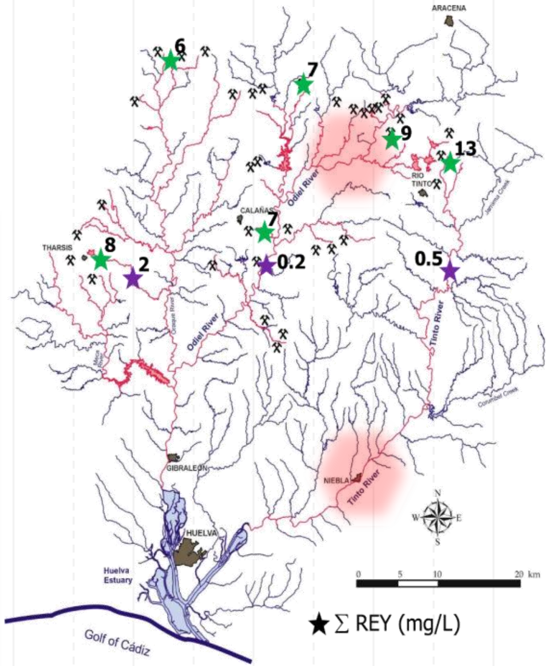
ΣREE ≈ 4.6 mg/L;

1170 mg/L of Al;

628 mg/L of Fe (highest values observed from the Agrio River)

pH 2.41

(November 2016)



TINTO

ΣREE ≈ 1.02 mg/L;

453 mg/L of Al;

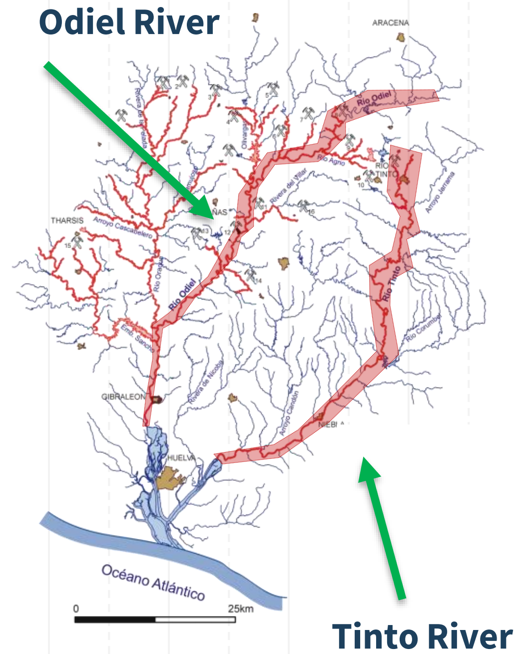
1172 mg/L of Fe

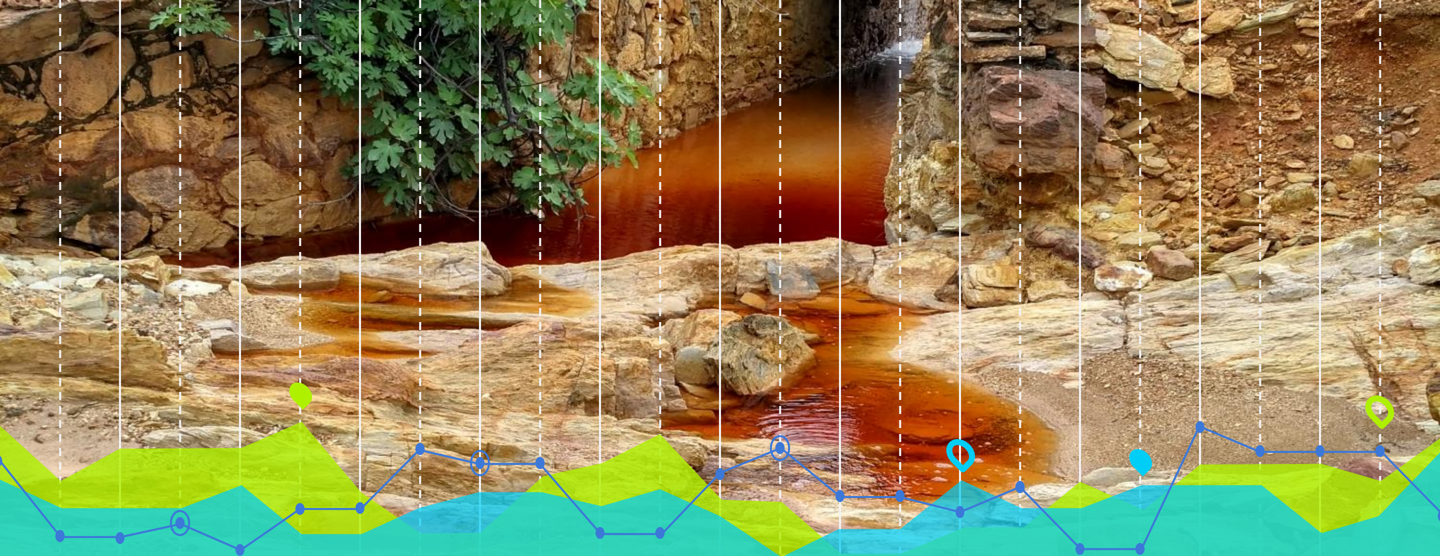
pH 2.3

(November 2017)

Iberian Pyrite Belt ----->Ría de Huelva

- ~ 37% of the Odiel drainage network and 100% of the Tinto affected by AMD
- At pH < 3 almost 100% of the ΣREE is transported in the dissolved phase
- At acid pH values and higher sulfate concentrations prevail sulfate complexes (REE (SO4)+)



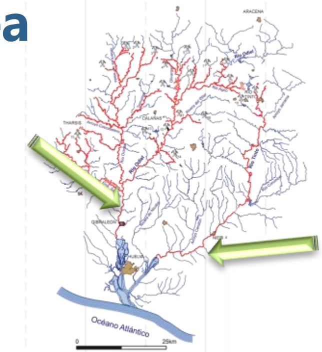


Factors controlling REE incoming in the Ria of Huelva estuary

Mediterranean climate in the area

- Mild winters and hot summers (average temperature of 16.5° C)
- High variability of river flows which feed the estuary
  - **High flow conditions (winter; 30-60m^3/s) and lower metal concentrations**
  - **Low flow conditions (summer; < 100 L/s) and very high metal concentrations**

Mediterranean climate in the area



	Odiel River Gibraleón		Tinto River Puente San Juan	
	High-river Flow (March)	Low-river Flow (May)	High-river Flow (March)	Low-river Flow (May)
pH	4.52	3.21	3.9	2.77
Al (mg/L)	3.4	45	10.3	25
Fe (mg/L)	1.1	10	3.1	19
ΣREE (µg/L)	27	300	23	107

Other Factors

- Washing of evaporitic salt formed

Other Factors

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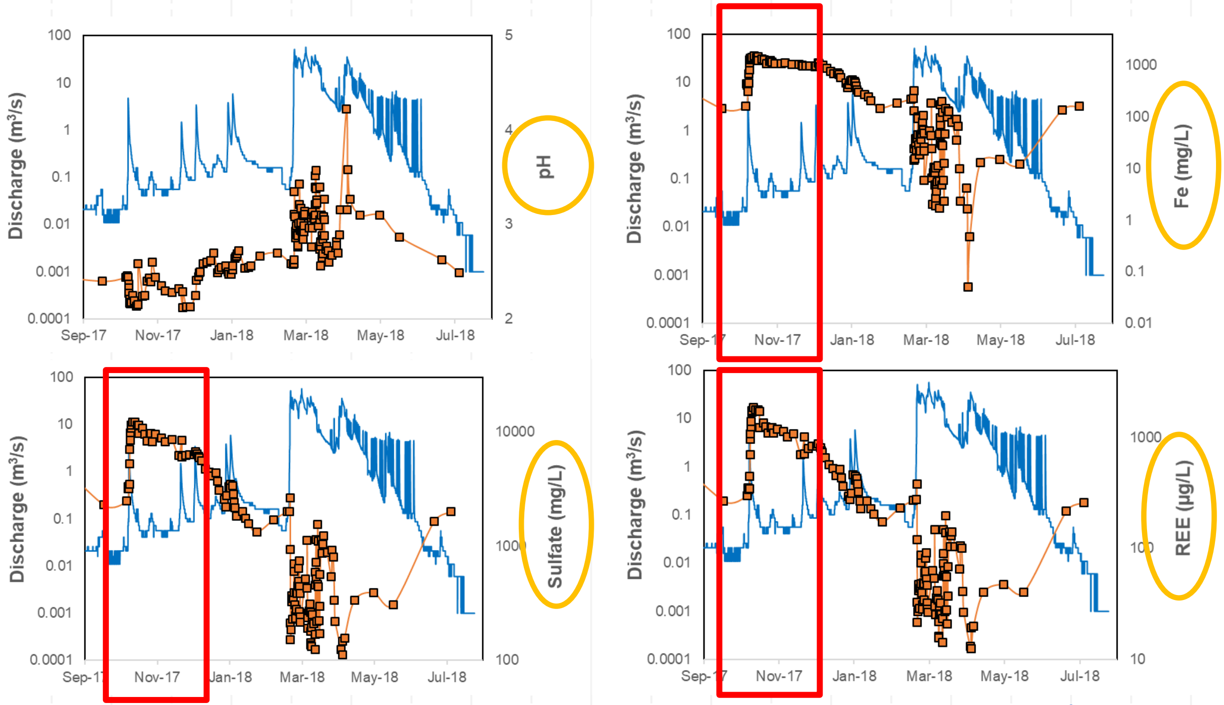
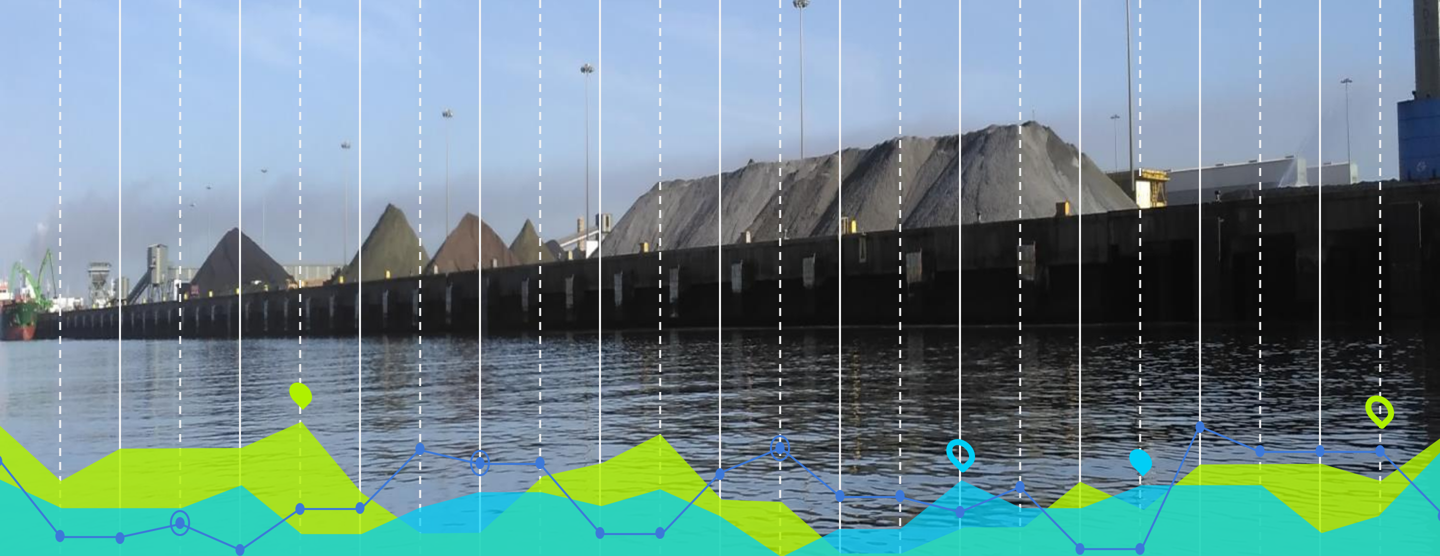


Other Factors

- Accidental acid mine water spill

- May 2017
- 270.000 m^3 AMD
- 80 % reached the Odiel river
- 53 km of the Odiel River main course affected



REE Distribution and final deposition

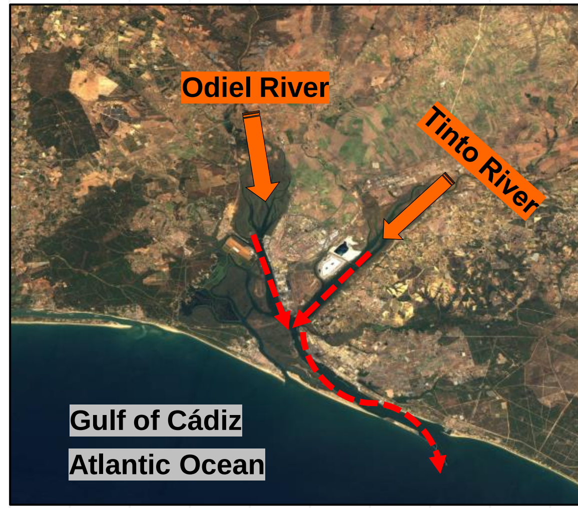
REE Distribution

- Transition zone between the fluvial inputs and the Atlantic Ocean

Rivers water → ← Marine water

- pH gradient: 3 (fluvial domain) – 8 (marine water)
- Mixing and AMD-neutralization processes
- Metals Precipitation

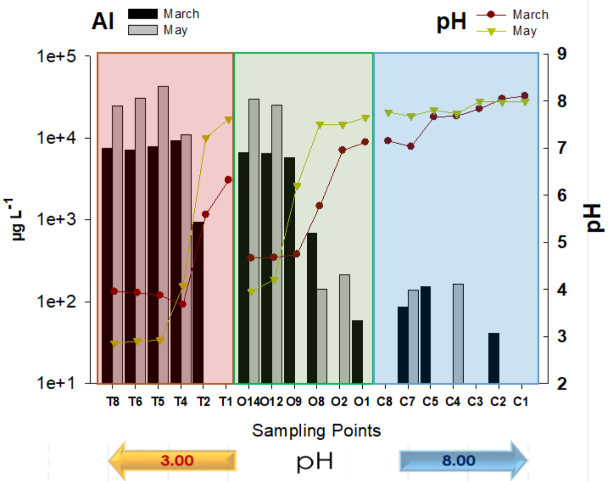
Dissolved elements → suspended material → element sediment deposition

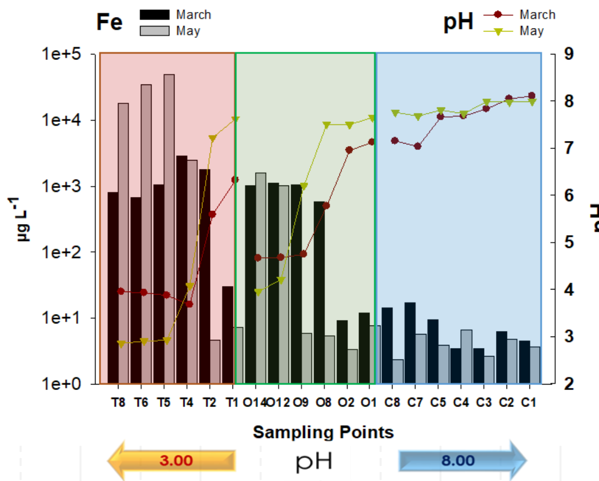


Important elements contributor to the litoral

Water

AMD + Alkaline waters → buffer Fe and Al → pH ranges between 2-4 and 4.5-6, respectively (e.g. Nordstrom 2011; Carrero et al., 2015) ⇒ Similar processes in estuarine systems affected by AMD

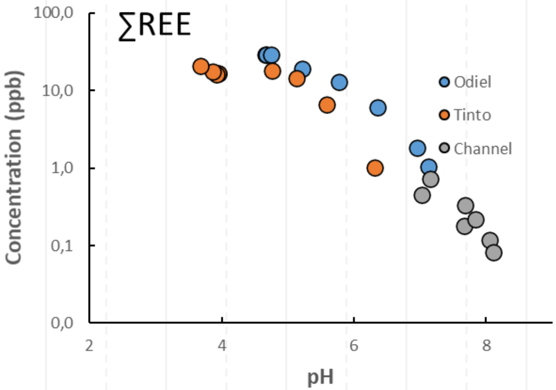




- Fe and Al precipitation also affect to other trace metals and REE→ e.g., Cu, Pb, Zn, Co, Ni, Cd. high correlations (R2 0.66-0.96)

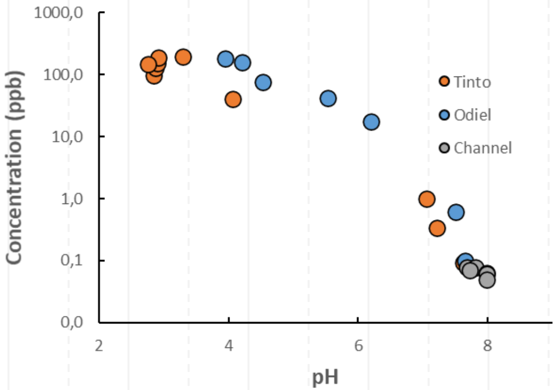
Estuary Dissolved REE Concentrations

March



29 - < 0.1 ppb

May

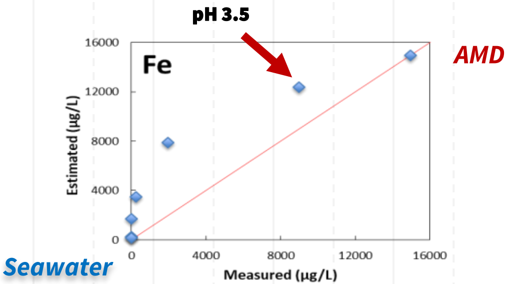


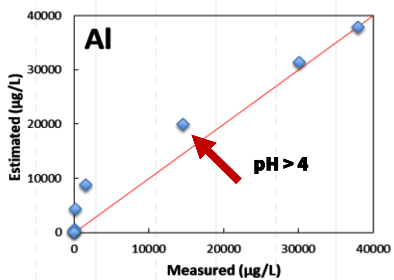
180 – 0.05 ppb

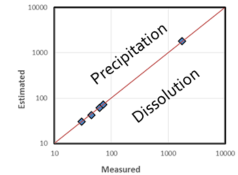
$R^2 \geq 0.9$ Fe/Al and REE

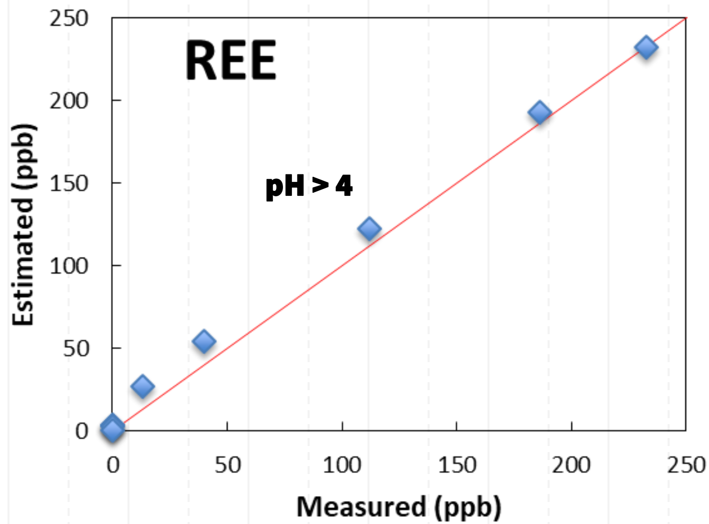
Estuary Dissolved REE Concentrations

Precipitation to particulate matter



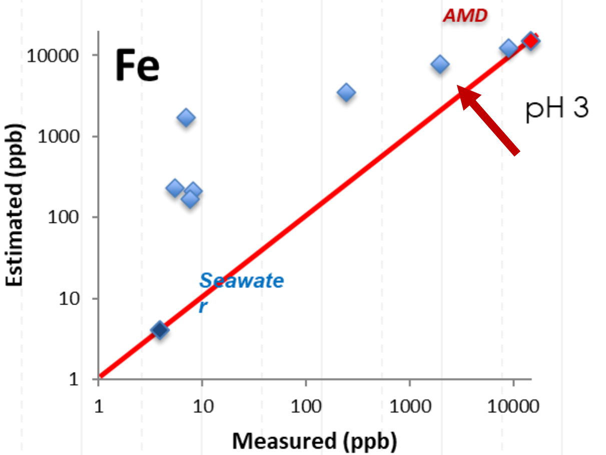


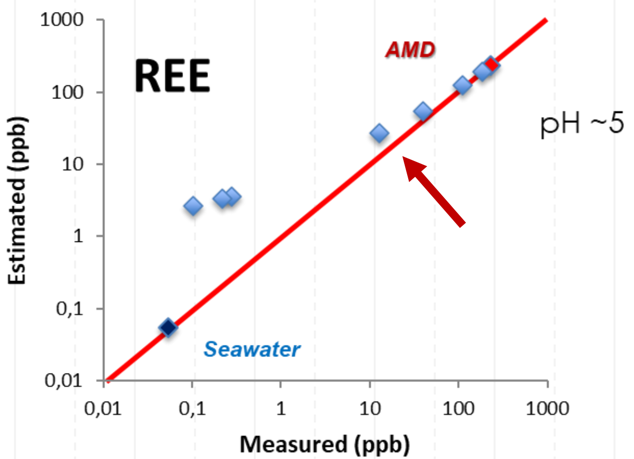




Mixing Model along the estuary (conservative elements i.e. Cl, Na, Li)

Estuary Dissolved REE Concentrations

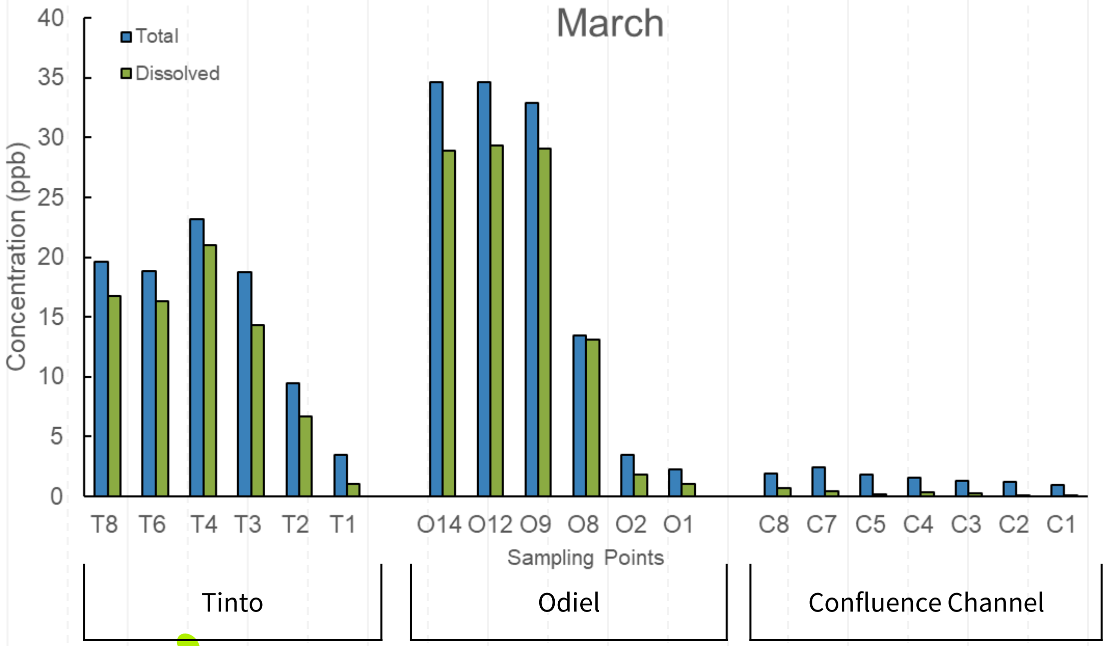




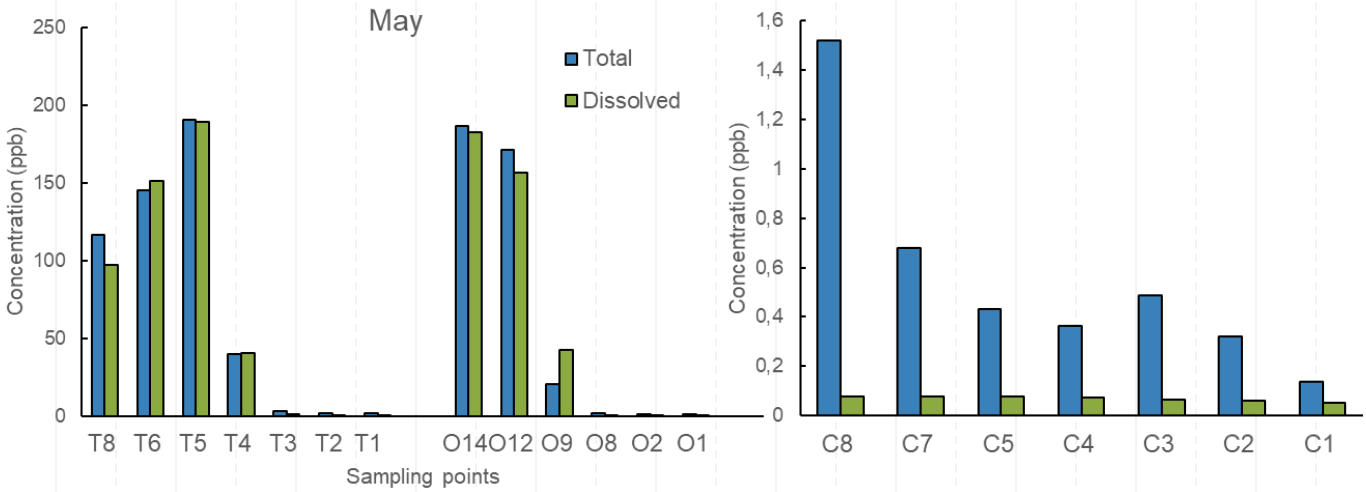
Accidental acid mine water spill – Low river flow conditions

Mixing Model along the estuary (conservative elements i.e. Cl, Na, Li)

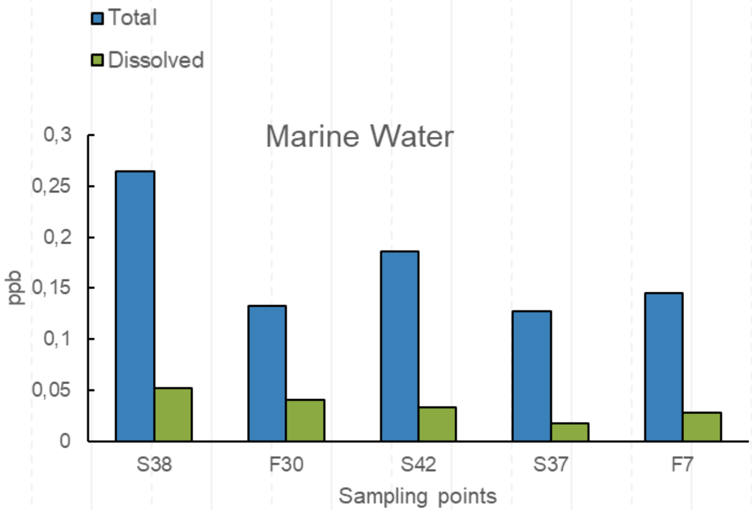
REE partitioning Total - Dissolved



REE partitioning Total - Dissolved

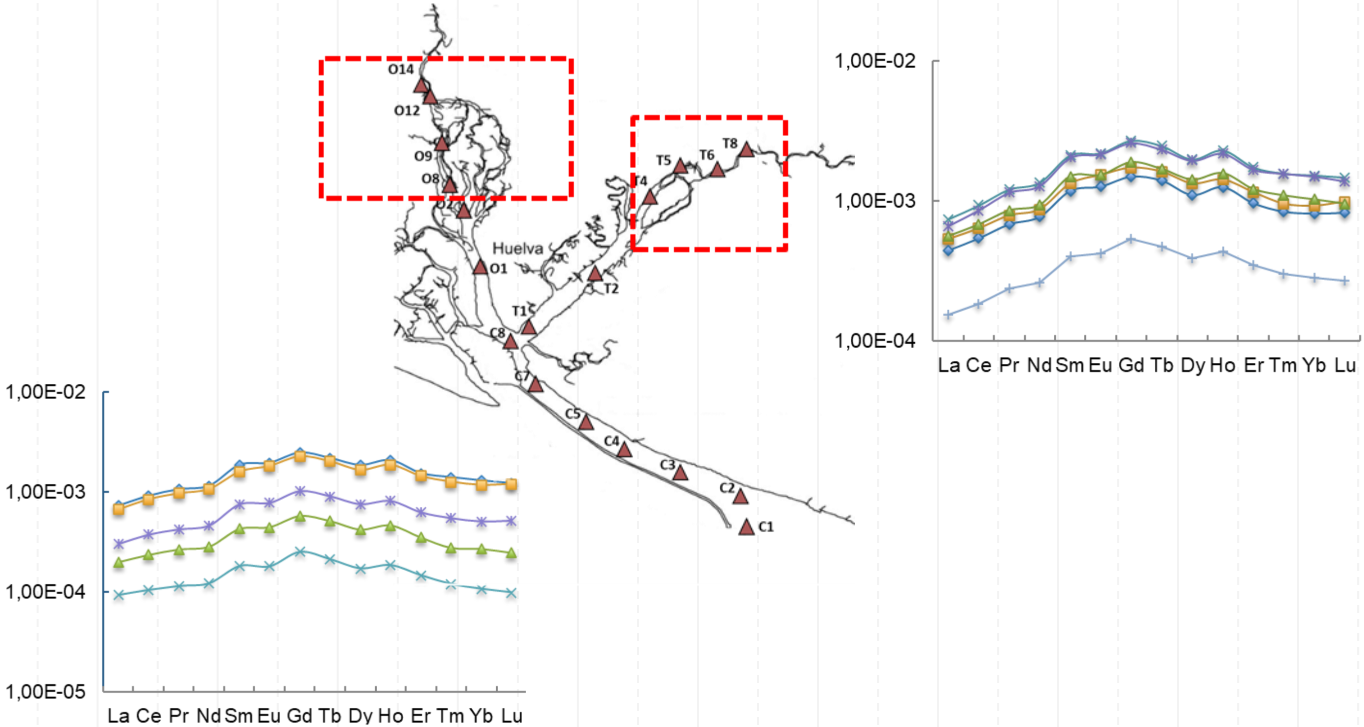


REE partitioning Total - Dissolved

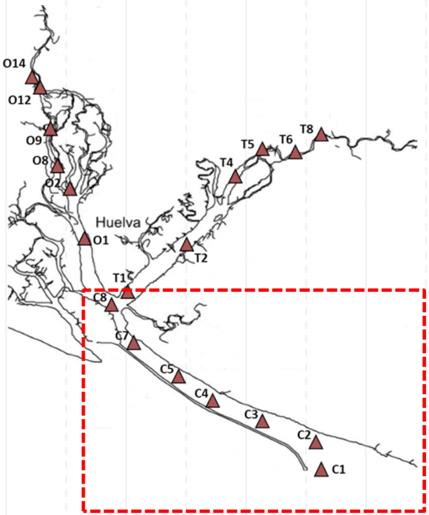


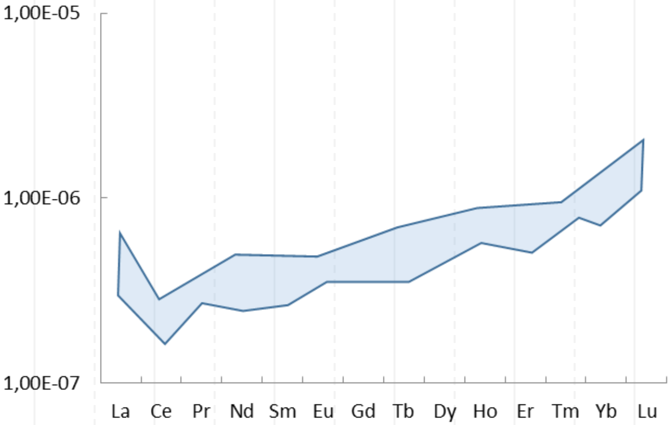
High-river Flow
(March)

NASC-Normalization pattern



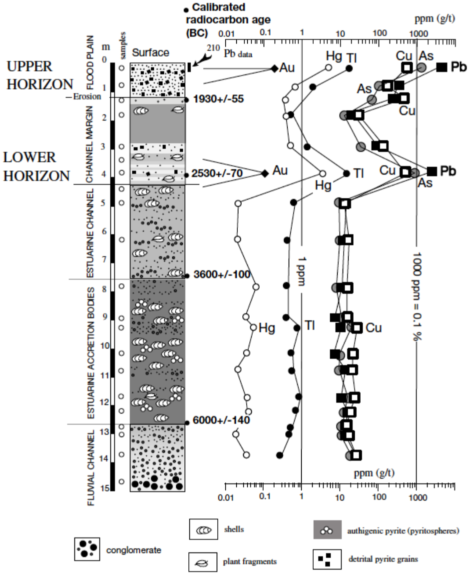
NASC-Normalization pattern

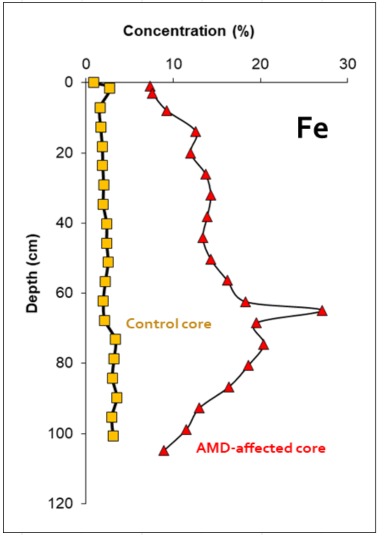




Accumulation in estuarine sediments

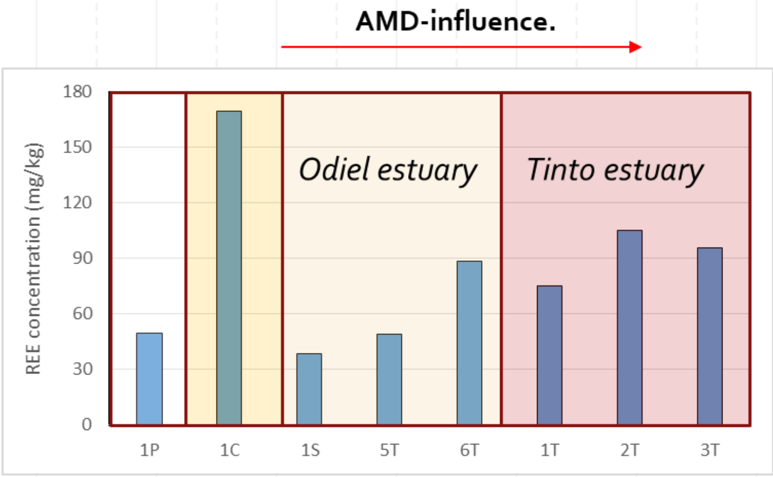
Metals concentration in Tinto river-estuarine sediments

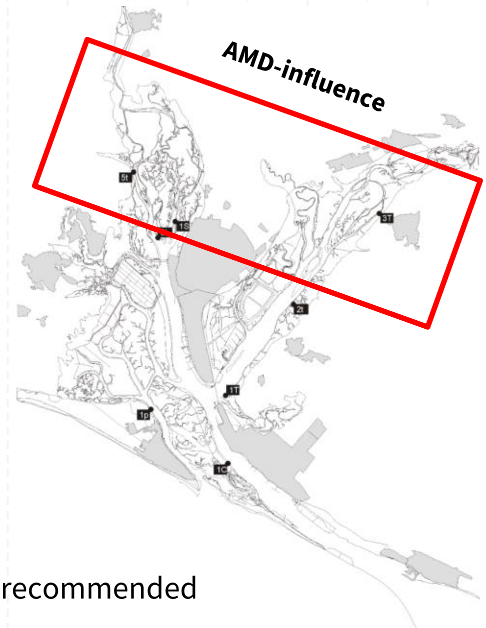




Leblanc et al. 2000

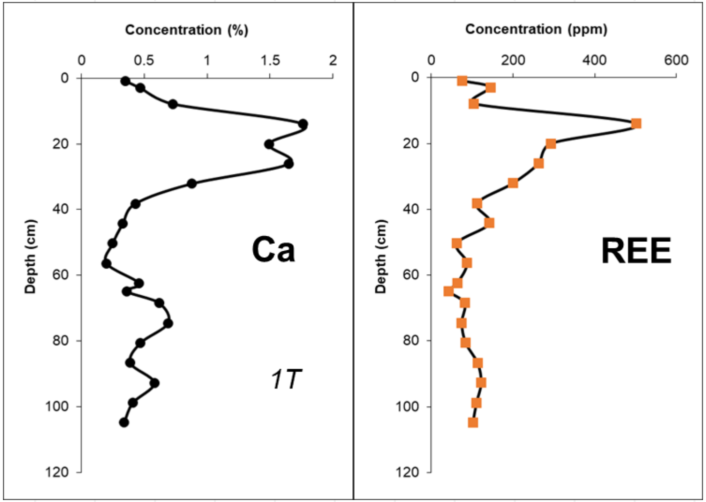
Accumulation in estuarine sediments



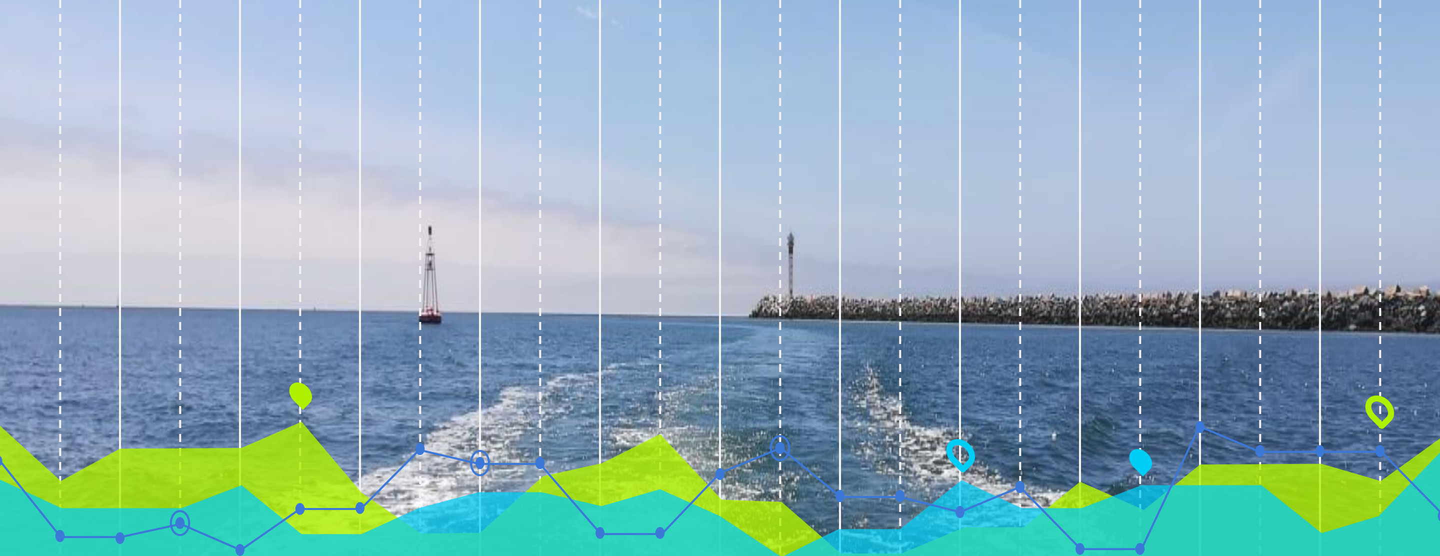


- REE concentrations mainly below 200 mg/kg
- Total REE concentrations in sediments did not exceed the recommended values for toxicity in organisms

Accumulation in estuarine sediments



Anomalous concentrations of REE linked to a phosphogypsum deposited accumulated since 1960



Ecotoxicological implications

Ecotoxicological implications

- The knowledge about the toxicity/bioavailability of REE as well as other technological elements (e.g., Ag, Tl, U, Cs and Y) is still limited.
- Dissolved concentrations of REE in the channel or the confluence zone between rivers and seawater are in the same order of magnitude than those reported in other estuaries worldwide. However, upper sections of the estuary show higher dissolved elements concentrations than other estuaries worldwide
- The concentration of particulate REE (and Y) is noticeably higher than dissolved

Ecotoxicological implications

- Diffusive gradient in thin-films (DGTs), which provide reliable and sensitive measurements of DGT-labile metal species ——> mimic the metal absorption by biological membrane

  - The retention in the DGT for each element was mainly related to the concentration in the water column.
  - This relationship between chemical properties and absorption by biological membranes is also observed for REE (and Y), which exhibited a high correlation.

LET'S Conclude

Conclusions

- ✓ The distribution of the contaminants in the estuary is highly controlled by the ratio of river water and seawater in the mixing zones.
- ✓ Most elements (Al, Fe, REE) are transferred from the dissolved to the particulate phase due to pH and salinity gradients.
- ✓ Intense precipitation zone can be identified in the fluvial domain of the estuary, for both Odiel and Tinto systems. However, this zone shifts spatially along the estuary depending on the hydrological conditions.
- ✓ The Tinto-Odiel rivers constitute a significant contribution of metals to the ocean, both dissolved and particulate.
- ✓ Despite the retention mechanisms during the mixing process, a fraction is transported through the estuary, reaching the littoral waters.

Conclusions

- ✓ AMD formation leads to the release of significant quantities of REE into the watercourses, however, in circumneutral waters like those found in the studied reach, a predominant transference from the dissolved to the particulate phase takes place, limiting the ecotoxicological risk.
- ✓ The role of the REE concentrations in ecological effects is not clear because of the presence of other toxic metal/loids in the water such as As, Cu, U, Cd, etc., which must contribute to the ecotoxicity problems, masking the influence of REE

THANK YOU FOR YOUR ATTENTION!

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