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Rare earth elements distribution in the Gulf of Cádiz (SW Spain): geogenic vs. anthropogenic influence

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There is a current interest in the study of the geochemical behavior of the rare earth elements (REE) in aquatic systems since their identification as potential microcontaminants in natural waters. In this context, here we report the concentrations and patterns of dissolved REE (dREE) in the waters of the Gulf of Cádiz (GoC) and its major estuaries (Guadiana, Tinto-Odiel and Guadalquivir). Contamination in this area by metals has been extensively reported, linked to acid-mine inputs resulting from the mineralization of the Iberian Pyrite Belt, discharged mainly to the Tinto-Odiel river. However, the impact of these inputs on the concentrations and distribution of the dREE in the coastal waters of the GoC has not been addressed yet. Accordingly, elevated concentrations of dREE were obtained in the Tinto-Odiel estuary compared to the Guadiana and Guadalquivir, reflecting the impact of acid-mine drainage on this system. Only a significant fraction of anthropogenic gadolium (Gd) was observed in the Guadalquivir estuary, as a result of the input from major urban areas, where anthropogenic Gd fractions higher than 70% over the total dissolved pool were obtained for the freshwater end-member. Regarding the surface waters of the GoC, typical NE Atlantic distribution patterns of dREEs were obtained, but modified by two different end-members within this region. Accordingly, and despite the low water discharge of the Tinto-Odiel river, its elevated concentrations lead to an increase in the concentrations of dREEs in the nearshore waters of the GoC and producing a distinctive signature as observed for the MREE anomalies and HREE/LREE ratios. At the easternmost stations, close to the Strait of Gibraltar, these signals are also impacted by the inflow of Mediterranean waters and also by the discharge of the Guadalquivir river.

Introduction

Current interest on the geochemical behavior of the rare earth elements (REE) from an environmental perspective has arisen since their identification as potential microcontaminants in aquatic systems (Kulaksız and Bau, 2007; 2011). The REE are a group of seventeen chemical elements consisting of yttrium and the 15 lanthanide elements (lanthanum, cerium, praseodymium, neodymium, promethium, samarium, europium, gadolinium, terbium, dysprosium, holmium, erbium, thulium, ytterbium, and lutetium); scandium is also generally classified as a rare earth element as it is commonly found in REE deposits (King, 2023). They are a group of chemically similar metallic elements with a gradual decrease in their ionic radii with increasing atomic number. Based on their separability and ionic radii, rare earth elements can be subdivided into light REE (LREE: La, Ce, Pr, Nd, Sm), medium REE (MREE: Eu, Gd, Tb, Dy), and heavy REE (HREE: Ho, Er, Tm, Yb, Lu). All REE occur in the trivalent state in nature, with the exception of Eu and Ce, which can also display +2 and +4 valences, respectively. REE are geochemically fractionated in the environment in a subtle and predictable manner and are thus suitable for their application as tracers of natural processes (Andrade et al., 2020; Neira et al., 2022). The use of REEs in current high-tech applications – e.g. computer memories, rechargeable batteries (including those in electric vehicles), cell phones, catalytic converters, magnets or fluorescent lighting, among others – has led to a marked increase in their production in the last decade. Accordingly, whereas during the period 2005-2017 the production remained relatively constant at around 120,000 metric tons per year (as rare earth oxide equivalent), it has continuously increased in the recent years reaching a production of 300,000 metric tons per year in 2022 (King, 2023). Despite of the anthropogenic uses of the REE, a widespread contamination has only been observed for gadolinium (Gd). The observation of these Gd anthropogenic anomalies has been demonstrated to be linked to the use of this metal in contrasting agents for magnetic resonance imaging (MRI), and are especially relevant in aquatic systems receiving effluents from densely populated areas with developed medical and healthcare systems (Kulaksız and Bau, 2007; 2011). These anthropogenic Gd anomalies can then be used as a pseudo-natural tracer of water discharge from wastewater treatment plants since the Gd organic complex used for medical purposes is not removed by common sewage treatment technologies (Andrade et al., 2020).

Elevated dissolved metal concentrations have been historically reported in estuarine and coastal waters of the Gulf of Cádiz (GoC; South Spain). These elevated concentrations have been claimed to be the result of the mineralization of the Iberian pyrite belt, which is one of the most important sulphide deposits in the World, and whose acidic and metal rich drainage discharge is transported by the Tinto-Odiel river. Accordingly, highest dissolved metal concentrations in the GoC are generally found at the mouth of the Tinto-Odiel river (Elbaz-Poulichet et al., 2001; González-Ortegón et al., 2019). On the other hand, the Guadalquivir river has also been identified as another significant source of metals into

GoC; despite having typical lower concentrations than the Tinto-Odiel, its greater discharge (>2000 hm^3 year^{-1} vs. 100–473 hm^3 year^{-1} of the Tinto-Odiel; Elbaz-Poulichet et al., 2001) results in a higher flux of certain metals (e.g., Cu, Ni; González-Ortegón et al., 2019) into the continental shelf than that derived from the Tinto-Odiel. Both main sources result in the presence of a metal-enriched water mass that seasonally impacts the Atlantic inflow through the Strait of Gibraltar (Elbaz-Poulichet et al., 2001).

However, there is still little information to date on the impact of these inputs on the geochemistry of dissolved Rare Earth Elements (dREEs) in the GoC. Available studies are restricted to the Tinto-Odiel river and its estuary, where concentrations exceeding 10 mg L^{-1} are found in the upper, acidic (pH<2) reaches of the river decreasing downstream as the water pH increases and upon mixing within the estuary (Lecomte et al., 2017; Olías et al., 2018; Cánovas et al., 2020). Concentrations and patterns of dREEs in the other major freshwater inputs to this coastal area, the Guadiana and Guadalquivir estuaries, are unknown at present, as well as for the coastal waters of the GoC. In this study we present the results of the distribution of dREEs in the outer part the major estuarine areas of the GoC (Guadiana, Tinto-Odiel and Guadalquivir) as well as in the surface coastal waters of the GoC, with the aim of (i) provide an assessment of the concentrations and patterns of dREEs in the estuarine areas of the GoC, (ii) evaluate the geogenic and anthropogenic impacts on their distributions, and (iii) determine the major sources controlling the distribution of dREEs in the GoC coastal waters.

Materials and methods

Study area

The Gulf of Cádiz (GoC) in southwest Spain is a partially enclosed area where the movement of water is primarily influenced by interactions between different environmental basins: the Mediterranean and Atlantic basins, as well as the coastal system (Sánchez-Leal et al., 2017). The GoC receives freshwater input from three major rivers: the Guadiana, Tinto-Odiel, and Guadalquivir (Figure 1). In the semiarid environment surrounding these rivers, the flow of freshwater into the Guadiana, Tinto-Odiel, and Guadalquivir estuaries is completely regulated by dams. Both the Guadiana and Guadalquivir rivers have a higher freshwater input (>2000 hm^3 year^{-1}) compared to the Tinto-Odiel estuary (100–473 hm^3 year^{-1}) (Elbaz-Poulichet et al., 2001).

The estuary formed by the confluence of the Odiel and Tinto rivers stretches along the southwestern coast of the Guadalquivir sedimentary basin. Historically, the Tinto-Odiel river drained the world's largest sulphide deposit that have been mined for over 4500 years, making it one of the oldest mining regions globally (Olías and Nieto, 2015). Due to natural changes in these sulphide deposits and mining activities, the Tinto-Odiel river has become severely contaminated, with extremely low pH levels (<2) in their upper reaches and extremely elevated concentrations of metals (Grande et al., 2000). Previous studies conducted in the Tinto-Odiel estuary found that it serves as a source of certain metals (such as Cu, Zn,
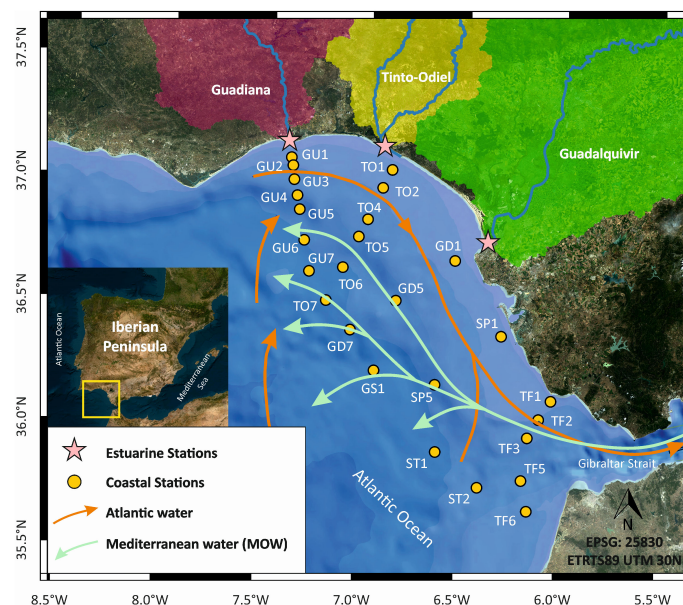
FIGURE 1
Map showing the stations in the continental shelf of the Gulf of Cádiz and the fixed stations in the estuaries of the Guadiana, Tinto-Odiel and Gudalquivir rivers. Also indicated the dominant surface currents in the area.

and Cd) to the GoC (Elbaz-Poulichet et al., 2001; Beckers et al., 2007). The high levels of dissolved metals and metalloids, coupled with low pH values indicates that this river can be a significant source on the influx of metals into the Mediterranean through the Strait of Gibraltar (Elbaz-Poulichet et al., 2001).

The Guadiana estuary is characterized by its rocky shoreline (Garel and Ferreira, 2013), and contamination from acidic mine drainage enters the river system through leachate seepage from a small number of active mines (Delgado et al., 2009) with additional inputs of contaminants in the estuarine area derived from port activities in the estuarine area, tourism developments and the irrigation of intensive crops in the lands adjacent to the estuary introduce significant quantities of contaminants and nutrients (González-Ortegón et al., 2019). The Guadalquivir estuary exhibits a high sediment load, resulting in increased water turbidity (González-Ortegón et al., 2015). The Guadalquivir river basin, with its intensive agriculture in former marshlands and large population centers, experiences a significant influx of nutrients into its waters (González-Ortegón and Drake, 2012). Despite the historic presence of mines in the Guadalquivir basin, metal contamination has not been detected in its estuary, even after the Aznalcóllar toxic spill into two of its lower tributaries in 1998 (Tornero et al., 2014).

Sampling

A detailed description of the sampling protocols can be found in González-Ortegón et al. (2019). Briefly, estuarine samples were collected at a fixed station, following a 24-h sampling cycle in order to evaluate the variation of water composition during a tidal cycle, on

24th–25th February 2016 in the Guadalquivir Estuary (lat. 36.7923 N; long. −6.35623 W) and Tinto-Odiel Estuary (lat. 37.13271 N; long. −6.8426 W) and 17th March 2016 in the Guadiana Estuary (lat. 37.1989 N, long −7.4095 W) for the wet season. For the dry season, samples were collected during 5th-9th July 2016. A peristaltic pump with acid-cleaned Teflon tubing coupled to a C-flex tubing at the pump head, filtered in-line through an acid-cleaned polypropylene cartridge filter (0.22 μm; MSI, Calyx$^{®}$) was used. Coastal surface water samples in the Gulf of Cádiz (GoC) were collected during 3rd–8th March 2016 using a Teflon towfish system deployed from the research vessel. Seawater was pumped into a class-100 HEPA laminar flow hood through acid-cleaned Teflon tubing coupled to C-flex tubing using a Teflon diaphragm pump, filtered online (0.22 μm). For both estuarine and coastal locations, filtered samples were collected in 0.5 L LDPE bottles and acidified at the onshore lab to pH<2 with ultrapure grade HCl (Merck) in a class-100 HEPA laminar and stored double-bagged (ziplock) pending analysis.

Analysis of dissolved REEs

The determination of dissolved REEs was attained by the use of a seaFAST (Elemental Scientific) preconcentration module coupled on-line to an ICP-MS (7900, Agilent) (Romero-Freire et al., 2020). In order to produce narrower peaks and lower the analysis time, a 2 cm-long mini-column of 27 μL of volume (Global FIA) was used instead of the original default seaFAST 200 μL column. The mini-column was packed with a chelate resin modified with carboxymethylated polyethylenimine (Fujifilm Wako, Presep$^{®}$ PolyChelate) (Cobelo-García et al., 2021), which was used as the

solid phase material for REEs preconcentration in the seaFAST module. The on-line preconcentration method consisted in a 10-mL sample loop; the loaded acidified sample was buffered using 2M ammonium acetate (pH 6.0) and then passed through the column. After preconcentration, the column was rinsed with the buffer solution in order to remove remaining salts and then eluted on-line using 1.5M HNO_3, obtaining a chromatographic signal for the target masses. The following isotopes were used for REEs determination: ^{139}La, ^{140}Ce, ^{141}Pr, ^{146}Nd, ^{147}Sm, ^{153}Eu, ^{157}Gd, ^{159}Tb, ^{163}Dy, ^{165}Ho, ^{166}Er, ^{169}Tm, ^{172}Yb, and ^{175}Lu. There was no need to correct for the typical interference of Ba ($^{137}Ba^{16}O^+$, $^{136}Ba^{16}O^1H^+$) on ^{153}Eu, as alkaline earth elements are not retained in the column at the working pH. Potential interferences on certain REEs due to the formation of oxides of lighter REEs during the ICP-MS determination was assessed and accounted for – when necessary – following a similar approach of that given by Babechuk et al. (2020). Accordingly, typical interferences were observed for ^{157}Gd ($^{141}Pr^{16}O^+$, $^{140}Ce^{16}O^1H^+$), ^{159}Tb ($^{143}Nd^{16}O^+$, $^{142}Ce^{16}O^1H^+$), ^{163}Dy ($^{147}Sm^{16}O^+$, $^{146}Nd^{16}O^1H^+$), ^{165}Ho ($^{149}Sm^{16}O^+$, $^{148}Nd^{16}O^1H^+$), ^{166}Er ($^{150}Nd^{16}O^+$, $^{150}Sm^{16}O^+$), ^{169}Tm ($^{152}Sm^{16}O^1H^+$, $^{153}Eu^{16}O^+$), ^{172}Yb ($^{156}Gd^{16}O^+$), ^{175}Lu ($^{159}Tb^{16}O^+$). In general, interferences accounted from ~0.1% (^{163}Dy, ^{165}Ho) to ~3% (^{157}Gd). All the samples were analyzed in duplicate, with a relative standard deviation for both determinations lower than 4%; average concentrations are presented. Detection limits, expressed as three times the standard deviation of the blanks, ranged from 0.02 to 0.001 ng L^{-1} depending on the given analyte, making the methodology appropriate for the determination of REEs in natural waters. The reference materials CASS-4 and CASS-6 (Coastal Sea Water, National Research Council, Canada) were analyzed following the same analytical procedures, obtaining values in agreement with previously reported concentrations (Supplementary Tables S1, S2, Supporting Information).

Normalization of REEs concentrations and calculation of Ce, Eu and Gd anomalies

REE concentrations were normalized to European Shale (EUS) as reported by Bau et al. (2018). Calculation of anomalies based on the normalized concentrations, in order to gain insight on fractionation processes (e.g. Ce, Eu) or anthropogenic inputs (e.g. Gd), followed the equations (Lawrence et al., 2006; Rétif et al., 2023):

$$La^* = La_N/[Pr_N \cdot (Pr_N/Nd_N)^2]$$

$$Ce^* = Ce_N/[Pr_N \cdot (Pr_N/Nd_N)]$$

$$Eu^* = Eu_N/(0.67Sm_N + 0.33Tb_N)$$

$$Gd^* = Gd_N/(0.33Sm_N + 0.67Tb_N)$$

where La^*, Ce^*, Eu^* and Gd^* represent the respective anomalies, and the subscript N the normalized concentrations.

Results and discussion

Concentrations and patterns of dissolved REEs in the Guadiana, Tinto-Odiel and Guadalquivir estuaries

Dissolved REEs concentrations were higher in the sampling campaign conducted in the wet season, especially for the Tinto-Odiel Estuary (Table 1) where a 4-fold enrichment was observed compared with the dry season. This estuary also contains the highest concentrations of REEs compared to the Guadiana and Guadalquivir estuaries, as expected for the results of other dissolved trace metals in these systems (e.g. González-Ortegón et al., 2019). The Tinto-Odiel river flow through different materials of the Iberian Pyrite Belt (IPB) and is greatly impacted by its metal-bearing bedrock and historical mining activities, explaining their elevated dissolved REEs concentrations observed in its estuary; accordingly, concentrations above 10^6 ng/L (Lecomte et al., 2017; Olías et al., 2018; Ruiz Cánovas et al., 2021) have been reported in the upper reaches of the watercourse where pHs around or below 2 are commonly found. The Guadiana river is subject, although to a lesser extent, to the impact of the IBP, but the industrial, urban and agricultural activities in the watershed appear to have a greater influence on the levels of trace metals within its estuary (González-Ortegón et al., 2019). The 2-fold higher concentrations obtained for dissolved REEs in the Guadiana estuary compared to the Guadalquivir (Table 1) – which is not impacted by the IBP and only subject to urban and anthropogenic activities – suggests that for REEs the IBP may still be responsible for its higher content in the Guadiana.

With the exception of the Tinto-Odiel estuary in the sampling carried out in the dry season, the normalized patterns (Figure 2) show a typical increase from LREE to HREE as typical for estuarine and coastal waters (e.g. Andrade et al., 2020). Highest LREE/HREE fractionation, as indicated by the Pr_N/Yb_N ratios (Table 1), was found in the Guadalquivir estuary with values even lower than those observed in the GoC coastal waters. The dREE pattern in the Tinto-Odiel estuary in the wet season (Figure 2) was unexpected for a water mass with salinities typical for coastal seawater, and was similar to those reported for upstream waters more influenced by the inputs of the acid mine drainage (AMD), where a bell-shaped distribution with and enrichment in the MREE compared to the LREE and HREE are observed (Olías et al., 2018). This suggests a pulse of AMD in the watercourse of the river that reached the estuary with no time to equilibrate (e.g. estuarine fractionation of the dREEs) to ambient conditions.

Anthropogenic Gd in the estuaries of the GoC

No anthropogenic Gd signal was observed within the Tinto-Odiel estuary (Table 1, Figure 2), which reflects the absence of a significant urban pressure within this system and the 'natural' elevated concentrations that may also lead to an effective dilution

TABLE 1 Average dissolved REE concentrations (ng L^{-1}) in the Tinto-Odiel, Guadiana and Guadalquivir estuaries for sampling campaigns conducted in the dry and wet season.

	Tinto-Odiel Estuary		Guadiana Estuary		Guadalquivir Estuary		Gulf of Cádiz
	Dry (n=5)	Wet (n=10)	Dry (n=6)	Wet (n=4)	Dry (n=6)	Wet (n=11)	n=26
Salinity	35.6-36.3	35.9-36.2	23.7-30.7	29.1-35.2	23.4-33.9	3.9-34.4	35.9-36.4
La	15.8 ± 1.6	45 ± 12	9.8 ± 0.7	13.7 ± 0.7	3.7 ± 0.4	4.5 ± 0.3	3.6 ± 1.0
Ce	15.3 ± 1.4	85 ± 25	10.7 ± 1.9	13.2 ± 1.0	4.9 ± 0.2	6.0 ± 0.5	3.4 ± 1.9
Pr	2.9 ± 0.2	11.3 ± 3.5	1.9 ± 0.1	2.4 ± 0.1	0.69 ± 0.07	0.79 ± 0.05	0.72 ± 0.23
Nd	12.7 ± 1.0	50 ± 15	8.0 ± 0.5	11.6 ± 0.6	3.2 ± 0.2	3.9 ± 0.3	3.3 ± 1.0
Sm	2.7 ± 0.2	10.8 ± 3.5	1.8 ± 0.1	2.6 ± 0.1	0.72 ± 0.06	0.88 ± 0.05	0.72 ± 0.23
Eu	0.66 ± 0.06	2.5 ± 0.8	0.49 ± 0.04	0.72 ± 0.02	0.21 ± 0.02	0.24 ± 0.02	0.19 ± 0.06
Gd	3.5 ± 0.3	12.6 ± 3.6	3.2 ± 0.2	4.1 ± 0.1	3.9 ± 1.6	2.8 ± 1.0	1.06 ± 0.29
Tb	0.55 ± 0.03	1.7 ± 0.5	0.40 ± 0.04	0.56 ± 0.01	0.19 ± 0.02	0.22 ± 0.01	0.16 ± 0.04
Dy	3.8 ± 0.3	10.1 ± 2.8	2.7 ± 0.2	3.7 ± 0.2	1.4 ± 0.1	1.6 ± 0.1	1.2 ± 0.3
Ho	0.88 ± 0.06	2.0 ± 0.5	0.63 ± 0.05	0.87 ± 0.05	0.36 ± 0.02	0.41 ± 0.03	0.32 ± 0.06
Er	2.7 ± 0.2	5.7 ± 1.4	2.0 ± 0.1	2.6 ± 0.1	1.3 ± 0.1	1.4 ± 0.1	1.0 ± 0.2
Tm	0.39 ± 0.02	0.76 ± 0.19	0.26 ± 0.02	0.37 ± 0.02	0.20 ± 0.02	0.22 ± 0.01	0.14 ± 0.03
Yb	2.5 ± 0.2	4.6 ± 1.1	1.7 ± 0.2	2.4 ± 0.1	1.3 ± 0.1	1.6 ± 0.1	0.9 ± 0.2
Lu	0.40 ± 0.04	0.71 ± 0.17	0.29 ± 0.02	0.39 ± 0.01	0.25 ± 0.01	0.29 ± 0.04	0.14 ± 0.03
ΣREE	65 ± 5	242 ± 69	44 ± 4	59 ± 2	22 ± 1	25 ± 1	17 ± 5
Pr$_N$/Yb$_N$	0.35 ± 0.02	0.74 ± 0.06	0.32 ± 0.01	0.30 ± 0.02	0.15 ± 0.01	0.16 ± 0.02	0.25 ± 0.05
La*	1.90 ± 0.17	1.36 ± 0.12	1.72 ± 0.32	2.13 ± 0.16	2.02 ± 0.23	1.76 ± 0.10	1.90 ± 0.17
Ce*	0.77 ± 0.03	1.07 ± 0.05	0.80 ± 0.16	0.82 ± 0.05	1.07 ± 0.06	1.18 ± 0.07	0.67 ± 0.14
Eu*	1.02 ± 0.04	1.07 ± 0.02	1.07 ± 0.07	1.10 ± 0.02	1.08 ± 0.10	1.01 ± 0.05	1.04 ± 0.02
Gd*	1.07 ± 0.02	1.09 ± 0.05	1.40 ± 0.10	1.24 ± 0.05	3.82 ± 1.87	2.24 ± 0.84	1.12 ± 0.03

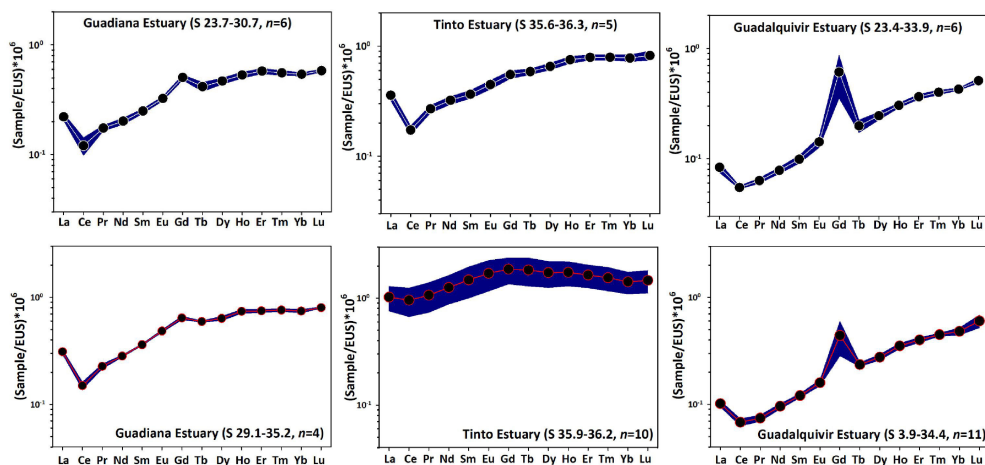Concentrations obtained in the coastal waters of the Gulf of Cádiz are included for comparison.

FIGURE 2
EUS-normalized pattern of dissolved REE in the Guadiana, Tinto-Odiel and Guadalquivir estuaries for the sampling conducted during the dry (upper panel) and wet (lower panel) season. Dots represent the average concentrations obtained, whereas the blue shaded area represents the maximum and minimum concentrations for each element.

effect of any anthropogenic contribution. In the case of the Guadiana estuary, the presence of a minor signal of anthropogenic Gd was observed (Figure 2); accordingly, the values calculated were Gd* = 1.40 ± 0.10 and 1.24 ± 0.05 for the dry and wet season respectively (note that anomalies up to 1.5 are considered within the range of the natural variability; Brünjes and Hofmann, 2020).
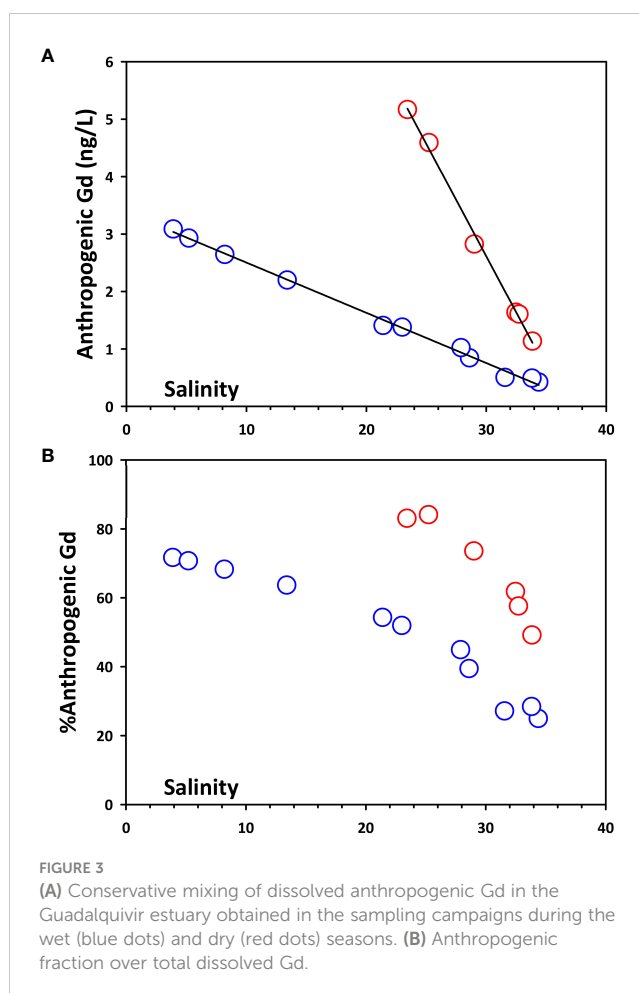
A significant input of anthropogenic Gd was evident in the case of the Guadalquivir estuary (Figure 2). This river flows through major cities (e.g. Córdoba and Seville, with a population of 325,000 and 692,000) and thus is subject to wastewater inputs that are behind this anthropogenic source. The calculated concentration of anthropogenic (Gd_{ant}), expressed as $Gd_{ant} = (Gd_N - Gd_N/Gd^*) \cdot Gd_{EUS}$ where Gd_{EUS} is the Gd concentrations in the European Shale (Bau et al., 2018), follows a conservative mixing within the estuary (Figure 3), as expected by the unreactive Gd-complexes used as a contrast agent for magnetic resonance imaging (MRI), which is the major contamination source of this element (Neira et al., 2022). The fraction of Gd_{ant} over total dissolved Gd was higher during the dry season, accounting for a greater dilution during the periods of elevated water discharge in the wet season. Nevertheless, Gd_{ant} represented a significant fraction in both sampling campaigns (Figure 3), increasing above 70% as salinity decreases, which indicates that, at the freshwater end-member, the anthropogenic inputs dominate the total dissolved concentrations of Gd in the Guadalquivir river.

Dissolved REE distribution in the GoC

The highest surface total dREEs in the GoC were obtained in the near-shore area between the outflow of the Tinto-Odiel and Guadalquivir rivers (Figure 4), responding to the inputs of elevated concentrations of dREEs by the Tinto-Odiel which are then transported eastwards by the surface coastal currents (Figure 1). The fractionation of dREEs, regarding the LREE/HREE and MREE/HREE ratios (expressed as Pr_N/Yb_N and Gd_N/Yb_N, respectively; Figure 4), display the highest values in the area of the influence of the Tinto-Odiel discharge, with values decreasing southeastwards to the Strait of Gibraltar. A similar distribution pattern showing a distinctive signal due to this freshwater source is also observed for the La, Ce and Eu anomalies (La*, Ce*, Eu*; Figure 4).

Sources of REEs to the GoC

Estuarine fluxes of dREEs to the GoC, estimated from the average concentrations obtained for each estuary and the freshwater discharge at the sampling date, are given in Table 2. Highest fluxes of LREE were derived from the Tinto-Odiel estuary during the wet season; during the dry season, the Guadiana and Guadalquivir were a higher source of LREE to the GoC. A higher flux for the heavier REE were obtained for the Guadiana and/or the Guadalquivir estuaries compared to the Tinto-Odiel.

FIGURE 3
(A) Conservative mixing of dissolved anthropogenic Gd in the Guadalquivir estuary obtained in the sampling campaigns during the wet (blue dots) and dry (red dots) seasons. (B) Anthropogenic fraction over total dissolved Gd.

In order to constrain the impact of these continental sources of dREEs on their distribution in the GoC, the relative differences in EUS-normalized concentrations presented as the MREE anomaly vs. the HREE/LREE ratio (Figure 5) were used (Crocket et al., 2018). Note that, in order to avoid the inference of Gd_{ant} in the calculation of the MREE anomaly, the Gd concentrations were not used in the calculations (see caption of Figure 5). In the water samples of the GoC (Figure 5, left), results show a trend of increasing MREE/MREE* values as the HREE/LREE decreases. The two samples with highest MREE/MREE* (>0.75) correspond to TO1 and GD1 (Figure 1), that is, the two most influenced by the Tinto-Odiel discharge (note that GD1 is affected due to the coastal eastward surface currents in this area; Figure 1), whereas lowest MREE/MREE* ratios (and highest HREE/LREE) occurred at the easternmost stations close to the Strait of Gibraltar. In order to assess the control of the potential sources on the distribution of dREEs in the GoC, the values obtained in the estuaries were also included (Figure 5, right). It can be observed that both the Guadiana and Tinto-Odiel (in the dry season) display a similar REE signature, overlapping with several stations in the GoC. The data from the Tinto-Odiel in the wet season, due to the likely presence of a pulse of non-fractionated AMD within the estuary, results in significantly
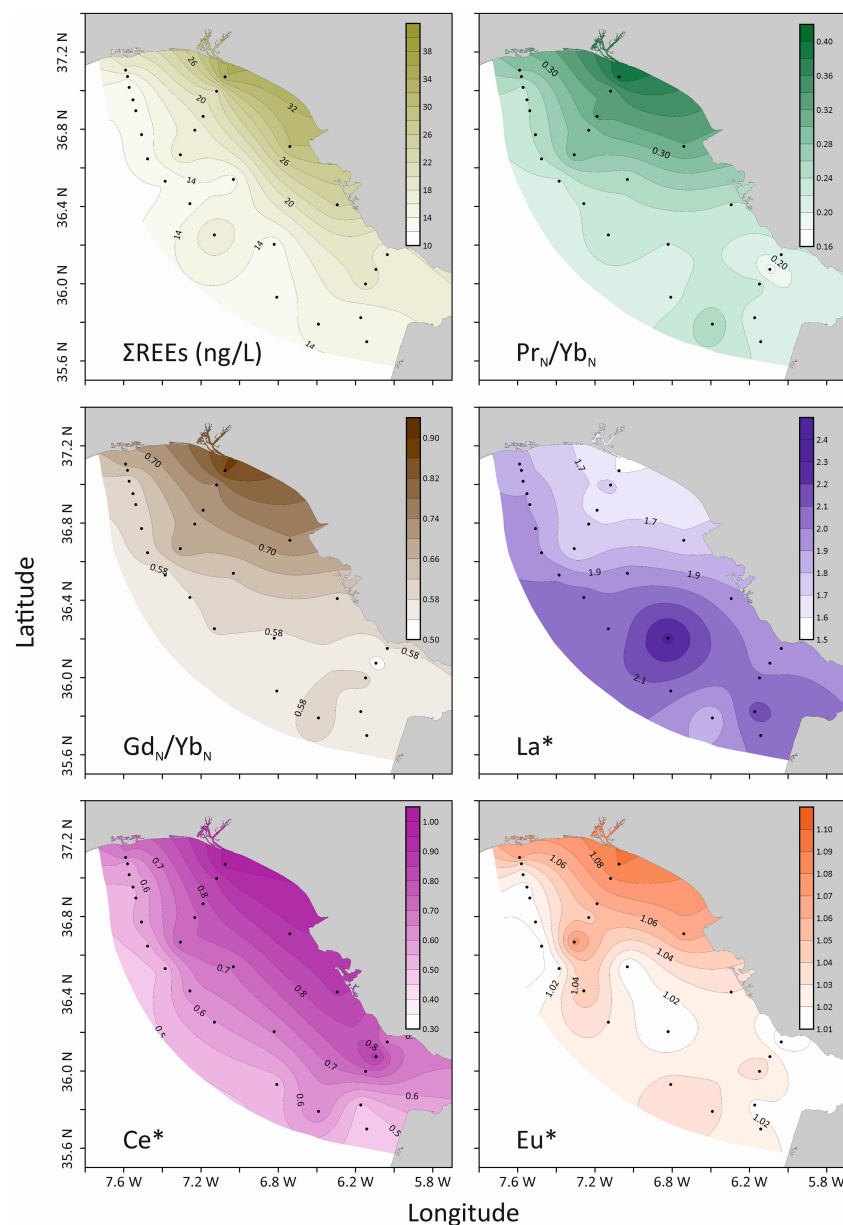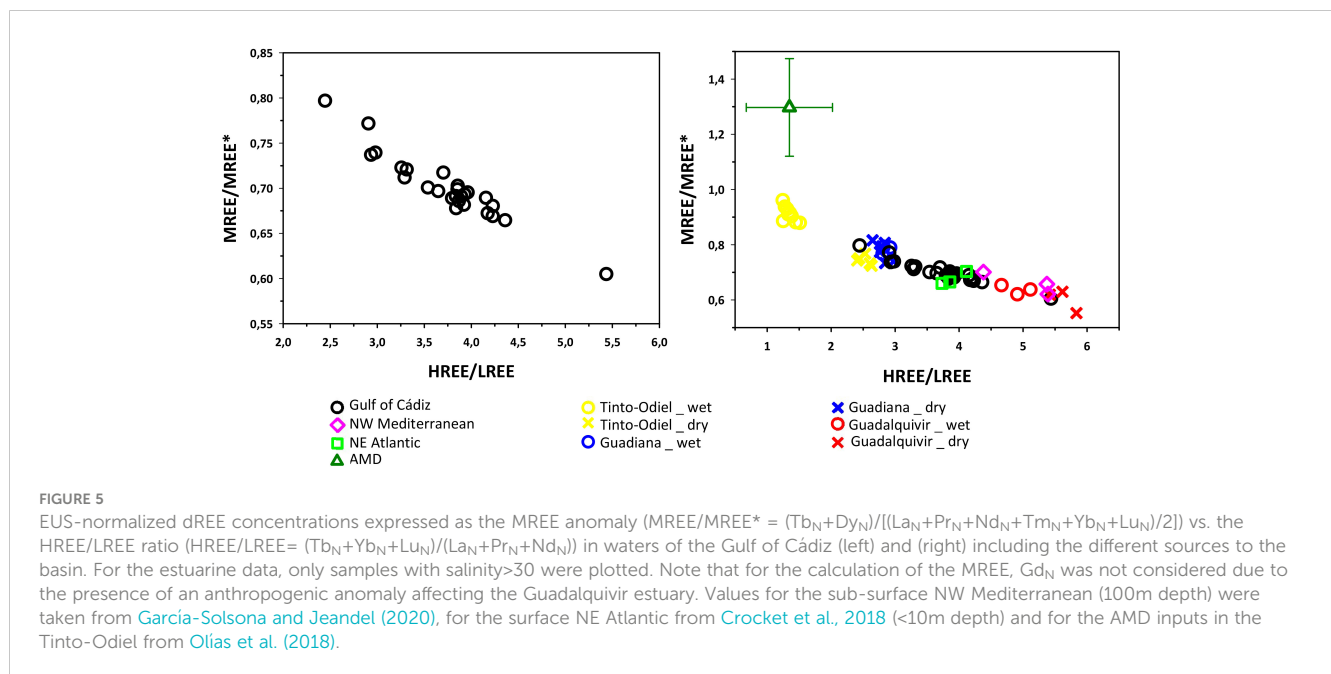
FIGURE 4
Contour plots of the surface spatial distribution of total dREEs, the LREE/HREE (as expressed as Pr_N/Yb_N) and MREE/HREE (expressed as Gd_N/Yb_N) ratios, and the anomalies of La (La*), Ce (Ce*) and Eu (Eu*) in the continental shelf of the Gulf of Cádiz. Dots indicated the location of the sampling stations.

higher values for MREE/MREE* and lower for HREE/LREE, but maintaining the continuum in the trend; this increase in MREE/MREE* for the AMD-impacted estuarine waters in the Tinto-Odiel estuary are in agreement with the elevated values reported for the AMD end-member (Olías et al., 2018; Figure 5). Data of the Guadalquivir estuary provides a distinctive end-member, with the lowest MREE/MREE* ratios (and highest HREE/LREE), and are within the typical ratios reported for the NW Mediterranean (García-Solsona and Jeandel, 2020; Figure 5). The majority of

ratios in the open waters of the GoC are, however, typical of those for surface NE Atlantic waters (shown in Figure 5 the data of the easternmost stations of the Extended Ellett Line in Crocket et al., 2018), indicating that the typical signature of NE atlantic surface waters in the GoC is altered by two different end-members, i.e., the Tinto-Odiel signal leading to high MREE/MREE* and low HREE/LREE ratios, and the Mediterranean and Guadalquivir inputs resulting in lower MREE anomalies and higher HREE/LREE ratios.

TABLE 2 Fluxes of dREEs to the Gulf of Cádiz (in µg/s) from the Tinto-Odiel, Guadiana and Guadalquivir estuaries for the sampling campaigns conducted in the dry and wet seasons (d-w).

	Tinto-Odiel	Guadiana	Guadalquivir
La	101-338	126-294	109-115
Ce	98-639	137-238	144-153
Pr	19-85	24-52	21-20
Nd	81-376	102-249	94-99
Sm	17-81	23-56	21-22
Eu	4.2-19	6.3-15	6.2-6.1
Gd	22-95	41-88	115-71
Tb	3.5-13	5.1-12	5.6-5.6
Dy	24-76	35-79	41-41
Ho	5.6-15	8.1-19	11-10
Er	17-43	26-56	38-36
Tm	2.5-5.7	3.3-8.0	5.9-5.6
Yb	16-35	22-52	38-41
Lu	2.6-5.3	3.7-8.4	7.4-7.4

FIGURE 5
EUS-normalized dREE concentrations expressed as the MREE anomaly (MREE/MREE* = $(Tb_N+Dy_N)/[(La_N+Pr_N+Nd_N+Tm_N+Yb_N+Lu_N)/2]$) vs. the HREE/LREE ratio (HREE/LREE= $(Tb_N+Yb_N+Lu_N)/(La_N+Pr_N+Nd_N)$) in waters of the Gulf of Cádiz (left) and (right) including the different sources to the basin. For the estuarine data, only samples with salinity>30 were plotted. Note that for the calculation of the MREE, Gd_N was not considered due to the presence of an anthropogenic anomaly affecting the Guadalquivir estuary. Values for the sub-surface NW Mediterranean (100m depth) were taken from García-Solsona and Jeandel (2020), for the surface NE Atlantic from Crocket et al., 2018 (<10m depth) and for the AMD inputs in the Tinto-Odiel from Olías et al. (2018).

Conclusions

Elevated dissolved metal concentrations have been previously reported in estuarine and coastal waters of the GoC, as a result of the mineralization of the Iberian pyrite belt, and whose acidic and metal rich drainage discharge is transported by the Tinto-Odiel river. However, this impact on the concentrations and distribution of dREEs in this coastal area has not been addressed yet. Here, we have observed that surface waters of the GoC display typical NE Atlantic distribution patterns of dREEs, which are modified by two different end-members within this region. Accordingly, and despite the low water discharge of the Tinto-Odiel river, its elevated concentrations lead to an increase in the concentrations of dREEs in the nearshore waters of the GoC and producing a distinctive signature as observed for the MREE anomalies and HREE/LREE ratios. At the easternmost stations, close to the Strait of Gibraltar, these signals are also impacted by the inflow of Mediterranean waters and also by the discharge of the Guadalquivir river.

The presence of anthropogenic Gd in the estuaries was significant in the Guadalquivir estuary, likely due to the wastewater discharge from large cities (e.g. Córdoba, Seville) to this river, representing a major fraction of total dissolved Gd (>70%) in the freshwater end-member. In the case of the Guadiana estuary, a slight Gd anomaly was detected but was within the typical values of natural variability, whereas in the Tinto-Odiel no anomaly was observed.

Data availability statement

The raw data supporting the conclusions of this article will be made available by the authors, without undue reservation.

Author contributions

AC: Conceptualization, Data curation, Formal analysis, Methodology, Writing – original draft, Writing – review & editing. PB: Data curation, Formal analysis, Writing – review & editing. CM: Formal analysis, Writing – review & editing. EG: Writing – original draft. DS: Writing – review & editing. RS: Writing – review & editing. AT: Funding acquisition, Supervision, Writing – review & editing.

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Conflict of interest

The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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Supplementary material

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