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3 **Pollutant pathways from a phosphogypsum disposal area to an estuarine**
4 **environment: An insight from geochemical signatures**
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23 Version to be submitted to Science of the Total Environment, December 2, 2015
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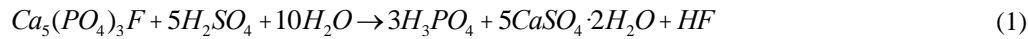
ABSTRACT

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4 This paper reports about the contamination potential of the phosphogypsum stack from fertilizer industry on
5 the Estuary of Huelva (SW Spain). Inside the waste pile (ca. 1200 ha and 100 Mt), highly polluted acid pore-
6 waters flows up to the edge of the stack, emerging as small fluvial courses, known as edge outflows, which
7 discharge directly into the estuary. The disposal area is divided into four zones; two unrestored zones with
8 surface ponds of industrial process water and two a priori already-restored zones. Preliminary restoration actions
9 and those planned for the future prioritize removal of ponded process water and cover of the phosphogypsum
10 with artificial topsoil. These actions presuppose that the ponded process water percolates through the porous
11 medium towards the edge up to reach the estuary. Accordingly, the already-restored zones would not produce
12 pollution on the ecological receptors. However, this study reveals by using geochemical tracers such as rare earth
13 elements (REE) and Cl/Br ratios that this statement is far from reality. An extensive sampling of edge outflows
14 conducted in the perimeter of the four phosphogypsum zones demonstrates the high potential of contamination
15 of the whole stack, including those zones that were supposedly restored. These solutions are characterized, on
16 average, by a pH value of 1.94 and concentrations of 6111 mg/L for P, 1967 mg/L for S, 617 mg/L for F, 205
17 mg/L for NH_4^+ , 125 mg/L for Fe, 28.5 mg/L for Zn, 16.6 mg/L for As, 9.52 mg/L for U, 7.02 mg/L for Cr, 4.27
18 mg/L for Cu, 3.62 mg/L for Cd, among others. These findings should lead to an immediate change of future
19 restoration plans and improve the preliminary already taken mitigation measures.
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38 **Keywords:** phosphogypsum stack; acid leachates; contaminant; restoration; Estuary of Huelva
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1. INTRODUCTION

The production of phosphoric acid (H_3PO_4) by fertilizer industry following the wet chemical digestion of phosphate rock (fluorapatite, $Ca_5(PO_4)_3F$) with sulfuric acid (H_2SO_4) generates huge amounts of a waste known as phosphogypsum (gypsum, $CaSO_4 \cdot 2H_2O$). The overall reaction is (Eq. 1):



The phosphate rock is commonly concentrated by flotation prior to phosphoric acid manufacturing. The flotation process is enhanced by the addition of chemical reagents such as ammonium hydroxide or amine (Lottermoser, 2010). The final phosphogypsum is soaked with the chemical reactants used and the products obtained in the industrial process, which leads to the existence of interstitial acidic solutions containing high concentrations of mainly phosphate, but also of sulfate, fluoride and often ammonium. Phosphate corresponds to the fraction of residual phosphoric acid obtained as product that cannot be effectively separated in the industrial process for sale. On the other hand, phosphate rocks also contain metal and radionuclides as impurities that are released during the industrial process and finally concentrated in the reaction products (Rutherford et al., 1994).

In the vicinity of Huelva city (SW Spain) there is a phosphate fertilizer factory located at the estuary formed by the confluence of the Tinto and Odiel Rivers, the so-called Ría of Huelva estuary. Around 2 Mt of phosphate rocks were annually processed leading to the generation of 2.5 Mt of phosphogypsum. Between 85 and 95% of most toxic elements, including U and Th, are transferred from the phosphate rock to the phosphoric acid (Bolívar et al., 2009; Pérez-López et al., 2010). Thus, the residual phosphoric acid trapped in the interstices of phosphogypsum particles explains the acidic nature and the high contaminant release potential under leaching conditions of this waste. On the other hand, Ra is transferred to gypsum due to its strong affinity with Ca (Bolívar et al., 2009). The high content in these impurities limits the commercial use of the phosphogypsum.

Since the beginning of the phosphate fertilizer production in 1968 until 1997, phosphogypsum was transported with seawater and deposited over the Tinto River salt-marshes in several decantation zones that reached up to 10 m in height on average. The whole disposal area covered around 1200 ha of maritime-terrestrial public domain ceded to the industry at less than 300 m of the city. After decantation, seawater used for transport along with the remaining 20% of phosphogypsum was directly released to the estuary without any treatment despite showing high acidity and pollutant concentration loads. These direct releases together with other

1 industrial effluents in the area caused a severe damage to the estuarine water and sediments (Bolívar et al.,
2 2002).

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4 The enforcement of more strict environmental regulations in 1997 compelled the factory to avoid any direct
5 discharge to the estuary according to the OSPAR convention (OSPAR, 2002; 2007). The new waste
6 management plan proposed two main measures to fulfil this goal; on the one hand, the deposit of
7 phosphogypsum in a large pyramidal pile over a single, previously-used zone; and on the other hand, the
8 implementation of a closed-circuit system for transport and settling of phosphogypsum using freshwater instead
9 of seawater. The closed-circuit system, also known as process water circuit, included the existence of ponds to
10 store water in the central part of the stacks and different perimeter channels collecting all lixiviates from the piles
11 and returning them to the closed-loop. The implementation of these measures caused a drastic reduction of
12 pollution in the estuary (Villa et al., 2009).
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22 However, phosphogypsum stack is still a source of indirect pollution due to the presence of the residual
23 phosphoric acid trapped into the interstices of the gypsum particles. The presence of these acidic pore-solutions
24 makes the piles behave as an unconfined aquifer, clearly distinguishing a vadose zone and a saturated zone with
25 contaminated groundwater flow. The piles are directly settled on bare marshland soils without any type of
26 isolation, which act as an impermeable barrier that withholds groundwater in depth and forces the water to flow
27 laterally. When the groundwater reaches the edge of the stack, polluted water emerges forming superficial
28 drainages, known as edge outflows, which release a high load of contaminants into the estuary (Gázquez et al.,
29 2014; Pérez-López et al., 2015). Therefore, despite the improvement obtained from the implementation of the
30 new waste management system, the leakages from the phosphogypsum stacks continue to pose a potential risk to
31 the ecological receptors. The fertilizer plant ceased dumping of phosphogypsum over salt-marshes in December
32 2010 under a decision of the Spanish National Court.
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49 **2. ENVIRONMENTAL SETTING AND OBJECTIVES**

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52 The disposal of phosphogypsum on the Tinto River salt-marshes has been historically marked by successive
53 changes in environmental regulations which have led to the existence of four different zones or modules within
54 the stack (Fig. 1):
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- Zone 1 (400 ha and 2-3 m in height) was closed and restored in 1992 by adding a 25 cm layer of natural soil and vegetation over the bare phosphogypsum. Phosphogypsum is not visually observed and there are not perimeter channels or process water ponded on the top part.
 - Zone 2 (240 ha and up to 30 m in height) is the large pyramidal pile of phosphogypsum deposited after 1997 with the new waste management plan. This zone has been active until discharge cessation in 2010. Restoration measures have not been adopted and, hence, this module is currently exposed to weathering. Ponds with process water are located on the surface, which are surrounded by a network of perimeter channels in order to collect the acidic lixiviates. According to some restoration guidelines included in a report from the regional government (Junta de Andalucía, 2009), these channels collect most of infiltrating waters and, although the existence of some diffuse drainages cannot be dismissed, the impact of this zone on the estuarine environment is supposedly minimal.
 - Zone 3 (200 ha and 8-12 m in height) is a sector where phosphogypsum were deposited until 1997. Since then, this zone has been subject to weathering and no preventive measures have been adopted to minimize the environmental impact (e.g. covers to avoid leaching). In fact, numerous edge outflows draining the pile and reaching the estuary have been previously reported (Pérez-López et al., 2015). This zone was used since 1997 to store process water in surface ponds.
 - Zone 4 (280 ha and 8-10 m in height) is a sector where phosphogypsum were also disposed of before 1997. This zone has been also restored by the addition of a cover over the bare phosphogypsum to prevent weathering. This cover is more complex than that of zone 1 and comprises the following layers (in ascending order): a 1 m layer of building wastes, a 2 m layer of theoretically inert industrial wastes and 30-50 cm layer of topsoil. As in zone 1, zone 4 has not ponded process water and the phosphogypsum is not visible.

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The total amount of phosphogypsum stockpiled on the salt-marshes is approx. 100 Mt. The Spanish National Court obliged the fertilizer factory to elaborate an environmental restoration plan of the affected marshland. This plan was presented in 2014 and is based on the removal of process water ponds and the cover of zones 2 and 3 to limit water infiltration. These measures are in agreement with the previous guidelines prioritized by the regional government, which state that the infiltration of process water stored in the ponds through the porous media and its subsequent emergence as edge outflows is the main pathway of pollutant dispersion to the estuarine system (Junta de Andalucía, 2009). This action plan omits any measure in zones 1 and

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4 based on the assumption that the previous restoration (elimination of process water and the installation of covers) successfully eliminated all discharges into the estuary.

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However, Pérez-López et al. (2015) recently studied by geochemical tracers the weathering process in the zone 3 of the phosphogypsum stack. The main results of this work strongly disagree with the pollutant dispersion pathway assumed by both the regional government and the fertilizer factory, which is the base of the restoration plan. These authors reveal the absence of chemical connection between process water ponded on the surface of the stack and edge outflows reaching the estuary, at least for zone 3. On this basis it is essential to verify the current state of zone 2 as potential source of pollutants into the estuary, as well as to compare the unrestored zones 2 and 3 with already-restored zones 1 and 4. The assessment of the efficiency of restoration measures of zones 1 and 4 based on the elimination of process waters and the implementation of covers to avoid the pollutant leakages is of paramount importance to optimize future restoration criteria for the whole phosphogypsum stack.

3. METHODOLOGY

3.1. Sampling of edge outflow water

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The perimeter of the four zones of the phosphogypsum stack was inspected in May-June 2014 in order to locate possible edge outflows and collect the corresponding samples (Fig. 1). In addition, some samples of process water contained in perimeter channels of zones 2 and 3 were taken. For a better understanding of the study area, localization of all sampling points can be seen by Google Earth™ using the Keyhole Markup Language (KML) file available as electronic supplement. The pH, redox potential and electric conductivity (EC) were measured in the field using a portable Multiparametric Crison MM 40+ equipment. Redox potential was corrected in order to obtain the Eh, with respect to the standard hydrogen electrode (Nordstrom and Wilde, 1998). Water samples were filtered with 0.45 µm membrane filters and divided into three aliquots; one unacidified for anion and ammonia determination, one acidified with HNO₃ to pH < 1 for major and trace element analysis, and the other one was buffered to pH 4.5 with an ammonium acetate/acetic acid buffer and Fe(II) complexed with a phenantroline solution for Fe(II)/(III) determination according to the method outlined by Rodier (1996).

3.2. Aqueous chemistry analysis

Concentrations of anions (Br, Cl and F) and ammonia in all the unacidified samples were analyzed by high performance liquid chromatography (HPLC) using a Metrohm 883 basic ion chromatograph (IC) plus equipped with Metrosep columns. The acidified samples were analyzed using Inductively Coupled Plasma-Atomic Emission Spectroscopy (ICP-AES; Jobin Yvon Ultima 2) for determination of major elements (Al, Ca, Fe, K, Mg, Mn, Na, P and S) and Inductively Coupled Plasma-Mass Spectroscopy (ICP-MS; Agilent 7700) for trace elements (As, Cd, Co, Cr, Cu, Ni, Pb, Sb, U, Zn and REE). Detection limits were: 0.2 mg/L for S; 0.1 mg/L for Na; 0.05 mg/L for Fe, K and Mg; 0.02 mg/L for Al, Ca, Mn and P; and 0.1 µg/L for trace elements. Three laboratory standards, prepared with concentrations within the range of the samples, were analyzed with every 10 samples to check for accuracy. Furthermore, dilutions were performed to ensure that the concentration of the samples was within the concentration range of the standards. Blank solutions with the same acid matrix as the samples were also analyzed. The average measurement error was less than 5%. Determination of Fe(II) and total Fe (following reduction with hydroxylamine hydrochloride) in the solutions was immediately undertaken in the laboratory on the same day of the sampling by colorimetry at 510 nm using a SHIMADZU UVmini-1240 spectrophotometer. The detection limit was 0.3 mg/L and precision was better than 5%; Fe(III) was calculated as the difference between total Fe and Fe(II).

3.3. NASC-normalized REE patterns

Rare earth elements (REE) have been widely used as tracers of geochemical processes (Noack et al., 2014). For the study of earth surface processes, such as weathering, REE concentrations are often normalized using the North-American Shale Composite (NASC) values (Gromet et al., 1984). Cerium anomalies $(Ce/Ce^*)_{NASC}$ were calculated from the expression $Ce_{NASC}/\sqrt{[La_{NASC}\cdot Pr_{NASC}]}$. Moreover, the shape of the NASC-normalized REE patterns was described using the NASC-normalized ratios, $(MREE/LREE)_{NASC}$ and $(HREE/MREE)_{NASC}$, which were calculated as the average of all permutations of those inter-element ratios. The LREE included in the ratio calculation were La, Pr, Nd, and Sm; the MREE were Gd, Tb, and Dy; and the HREE were Ho, Er, Tm, Yb, and Lu. Both Ce and Eu were excluded from calculation due to their anomalous redox activity. Stolpe et al. (2013) proposed these normalized ratios to avoid using a single representative of a whole group, which would be not

advisable for the interpretation of REE patterns in the case of exclusive fractionation affecting only one of the elements in the ratio.

4. RESULTS

4.1. Elemental contaminant concentrations

Leachates samples were collected at fifty-three sites around the perimeter of the four zones of the phosphogypsum stack, including those already-restored zones where supposedly leakages should not occur (Fig. 1). Detailed hydrogeochemical information for these samples is compiled in Table S1 (see electronic supplement). All samples have similar characteristics; i.e. extreme acidity and high EC values, which correlates with high dissolved concentrations of anions and cations, some of them potentially toxic. Of the total sampling points, fifty samples strictly correspond to edge outflows whose average values of pH, EC and major anions and cations for each zone of the stack can be seen in Figures 2 and 3. The remaining three samples (2-26, 3-16 and 3-17) are from solutions contained in perimeter channels of zones 2 and 3 and their chemical composition is detailed in Table S1. All edge outflow solutions and some samples of the perimeter channels discharge to the estuarine waters directly or indirectly through secondary tidal channels. However, it is worth noting that the potential contamination risk to the estuarine environment varies significantly from one zone to another. In the following, the geochemical characteristics of the edge outflows of the areas that are being considered for immediate restoration (zones 2 and 3) will be compared with those observed in previously-restored areas (zones 1 and 4).

4.1.1. Unrestored zones

Twenty-six acid leachates were collected at zone 2 of the phosphogypsum stack (Fig. 1; see example in picture (a)). Of these leachates, twenty-five samples strictly correspond to edge outflows reaching the estuarine environment (samples 2-1 to 2-25; Table S1). These edge leachates are by far more acidic and polluting than those found in other zones of the stack; with the lowest pH values (1.83 ± 0.28) and the significantly highest concentrations of P (10630 ± 6328 mg/L), F (793 ± 417 mg/L), NH_4^+ (347 ± 157 mg/L) and metallic impurities such as Fe (137 ± 87.4 mg/L; mainly as Fe(II)), Zn (43.9 ± 21.0 mg/L), As (20.4 ± 8.81 mg/L), U (16.1 ± 9.74 mg/L), Cr

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(11.7±8.17 mg/L), and minor contents of other elements such as Cd, Co, Cu, Ni and Pb (< 10 mg/L) (Figs. 2 and 3). On the contrary, edge outflows of this zone show lower concentrations of Cl (9944±5134 mg/L) and S (1784±214 mg/L) than the rest (Fig. 2). On the other hand, the sample 2-26 corresponds to acid water of the outermost perimeter channel of zone 2 (Fig. 1), which presents acidity and element concentrations that are slightly higher but within the same order of magnitude as the remaining edge outflow samples of this zone, i.e. with a pH value of 1.68 and concentrations of 17556 mg/L for P, 1347 mg/L for F, 555 mg/L for NH₄⁺, 99.1 mg/L for Fe, 65.8 mg/L for Zn, 31.0 mg/L for U, 27.1 mg/L for Cr and 26.1 mg/L for As (Table S1). Chloride/Br ratios can provide information on the origin of the water (Davis et al., 1998). In this sense, both edge outflows and channeled water of zone 2 have Cl/Br ratio values of 143±42.4, on average, and 59, respectively (Table S1).

Seventeen acid leachates were collected at zone 3 of the phosphogypsum stack (Fig. 1), of which fifteen samples are point edge outflows discharging into the estuarine environment (samples 3-1 to 3-15; Table S1). In the edge outflows of zone 3, average values of pH are slightly higher (1.90±0.48) and concentrations of P (1913±607 mg/L), F (498±174 mg/L), NH₄⁺ (56.1±32.9 mg/L) and metallic impurities (e.g. 16.9±6.18 mg/L of As and 13.9±5.52 mg/L of Zn) are significantly lower than in those of zone 2 (Figs. 2 and 3). Instead, these solutions have higher concentrations of Cl (15407±7522 mg/L) and, to a lesser extent, S (1860±370 mg/L) (Fig. 2). As shown in Figure 1, this zone has a perimeter channel exclusively around the ponded process water and another perimeter-stiffening channel at the back of the stack, where samples 3-16 and 3-17 were taken, respectively (see picture (b) in Fig. 1). Acidity and contaminant level in this channeled water is much higher than in the edge outflows (even than in those of zone 2), with values of pH of 1.10 and 1.85 and concentrations of 141 and 69.5 g/L for P, 1824 and 1725 mg/L for NH₄⁺, 833 and 305 mg/L for F, 309 and 93.3 mg/L for Fe, 202 and 170 mg/L for Zn, 106 and 125 mg/L for As, 131 and 34.8 mg/L for Cr, 117 and 40.9 mg/L for U, 34.2 and 31.4 mg/L for Cd, 36.4 and 21.8 mg/L for Cu, and 21.6 and 26.7 mg/L for Ni, among others (< 10 mg/L), for the samples 3-16 and 3-17, respectively (Table S1). Chloride/Br ratios of most edge outflow solutions of zone 3 are higher (average of 300±118) than that of the rear perimeter channel (180) and, especially than that of the perimeter channel surrounding the process water ponded on the surface (40.3) (Table S1).

4.1.2. Already-restored zones

Zones 1 and 4 of the phosphogypsum stack are characterized by having no water in ponds or perimeter channels. One unique acid leachate was found and sampled in zone 1 (Fig. 1; see picture (c)). This sample does

1 not strictly correspond to an edge outflow, but it is likely produced by interaction of seawater with
2 phosphogypsum outcropping in a small tidal channel during the rising tide (sample 1-1; Table S1). After
3 interaction, the resulting solutions during the lowering tide are already acidic. So, because of the cyclic nature of
4 tides, this channel provides a continuous supply of acidity and contaminants to the estuary. Nevertheless, acidity
5 (pH 3.19) and concentrations of P (188 mg/L), NH_4^+ (77.3 mg/L), F (76.7 mg/L) and other metallic impurities (<
6 1.5 mg/L) in this tidal channel are significantly lower than in edge outflows of the other zones of the stack due to
7 the dilution effect exerted by estuarine waters (Figs. 2 and 3).

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13 Finally, zone 4 has acidic and polluting leakages in up to 9 discharging points (Fig. 1; see example in
14 picture (d)). However, sampling could be carried out only in the half of this zone of the stack because there is a
15 protective fence restricting the access to an area with ^{137}Cs -rich wastes from the steel manufacture, which were
16 accidentally deposited in 1998 (Más et al., 2006). Nevertheless, many edge outflows can be observed at a glance
17 through the fence on that restricted parcel of zone 4 (see picture (e) in Fig. 1). All collected samples correspond
18 to edge outflows (samples 4-1 to 4-9; Table S1), which also show acidic pH values (2.21 ± 0.12) but slightly
19 higher than in zones 2 and 3. Concentrations of P (1217 ± 208 mg/L), F (384 ± 152 mg/L), NH_4^+ (73.1 ± 33.9 mg/L)
20 and metals (e.g. 13.2 ± 7.01 mg/L of Zn) are close to those observed in zone 3 and often even lower (Figs. 2 and
21 3). On the contrary, it is to highlight the relatively high concentrations of Fe (133 ± 46.9 mg/L; mainly as Fe(II))
22 and Sb (0.35 ± 0.16 mg/L), even similar to those exhibited by edge outflows of zone 2 (Figs. 2 and 3). Regarding
23 other elements, concentrations of S in zones 1 and 4 (3010 and 2538 ± 580 mg/L, respectively) and those of Cl in
24 zone 1 (38351 mg/L) are the highest of all edge outflows sampled in the whole stack (Fig. 2). In addition, Cl/Br
25 ratio values of 373 for the leachate of zone 1 and of 195 ± 22.5 , on average, for edge outflows of zone 4 were
26 observed (Table S1).

4.2. Rare earth element concentrations

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48 Concentrations of REE in the leachates of the four zones of the phosphogypsum stack are shown in Table
49 S2 (see electronic supplement). Values of ΣREE as well as the values of the Ce anomaly and the normalized
50 $(\text{HREE}/\text{MREE})_{\text{NASC}}$ and $(\text{MREE}/\text{LREE})_{\text{NASC}}$ ratios are also shown in Table S2. Around 30% of samples showed
51 REE element (mainly HREE) concentrations close to the detection limit of ICP-MS and, for this reason, they
52 were not considered in the interpretations based on the REE pattern shape.

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2 In the edge outflow samples, the highest Σ REE concentrations are found by far in zone 2 ($334 \pm 161 \mu\text{g/L}$)
3 followed by zone 3 ($120 \pm 75.2 \mu\text{g/L}$) and then by zone 4 ($40.0 \pm 21.1 \mu\text{g/L}$), which is in accordance with the
4 overall trend observed for pollutants. The only sample of zone 1 shows concentrations of most REE below the
5 detection limit. Concerning the water of the perimeter channels, sample 2-26 of zone 2 presents Σ REE values in
6 the same order of magnitude as the edge outflows of this zone ($387 \mu\text{g/L}$); however, samples 3-16 and 3-17 of
7 zone 3 exhibit concentrations of up to two and one order of magnitude higher (23700 and $2666 \mu\text{g/L}$,
8 respectively) than the remaining samples of the four zones of the stack. All samples of edge outflows and
9 perimeter channels show NASC-normalized REE patterns with a strong negative Ce anomaly, with values of
10 $(\text{Ce}/\text{Ce}^*)_{\text{NASC}}$ ranging between 0.19 and 0.51 (Supplementary Table S2; Fig. 4).
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NASC-normalized REE patterns of edge outflows seem to be similar from one zone to another of the phosphogypsum stack (Fig. 4). However, normalized ratios reveal some differences in the REE distribution. In general, edge outflow waters show clearly higher $(\text{MREE}/\text{LREE})_{\text{NASC}}$ values than unity than those of $(\text{HREE}/\text{MREE})_{\text{NASC}}$, which are closer to unity (Table S2). These ratios indicate that there is an enrichment of MREE with respect to LREE and a flattening of the pattern in the HREE range. This distribution can be observed specially in zone 2 with average values of $(\text{MREE}/\text{LREE})_{\text{NASC}}$ and $(\text{HREE}/\text{MREE})_{\text{NASC}}$ of 1.73 ± 0.19 and 1.01 ± 0.12 , respectively (Fig. 4a). However, average values of $(\text{MREE}/\text{LREE})_{\text{NASC}}$ and $(\text{HREE}/\text{MREE})_{\text{NASC}}$ decrease notably in edge outflows of zone 3 (1.43 ± 0.16 and 0.98 ± 0.11 , respectively; Fig. 4b) and, mainly, of zone 4 (1.33 ± 0.04 and 0.83 ± 0.04 , respectively; Fig. 4c). In fact, edge outflows of zone 4 have patterns where enrichment of MREE with respect to LREE is observed but there is a slight depletion of HREE with respect to MREE (Fig. 4c).

Sample of acid water from the outer perimeter channel of zone 2 shows a NASC-normalized REE pattern with identical distribution to that found in the edge outflows of this zone, with ratios in the same order of magnitude ($(\text{MREE}/\text{LREE})_{\text{NASC}} = 2.03$ and $(\text{HREE}/\text{MREE})_{\text{NASC}} = 0.95$) (Fig. 4a). Instead, waters contained in the perimeter channels of zone 3, samples 3-16 and 3-17, exhibit normalized patterns with a slight increase of the enrichment of MREE with respect to LREE ($(\text{MREE}/\text{LREE})_{\text{NASC}} = 2.23$ and 2.52 , respectively) and, mainly, with a significant enrichment of HREE with respect to MREE ($(\text{HREE}/\text{MREE})_{\text{NASC}} = 1.71$ and 1.84 , respectively) (Table S2). The strong enrichment in the HREE segment of both samples makes that these solutions have completely different REE patterns in comparison with the rest of samples of the phosphogypsum stack (Fig. 4b). In principle, this difference in the NASC-normalized REE distribution could allow investigation of the possible sources of edge outflow waters discharging into the estuary.

5. DISCUSSION

5.1. Source of edge outflow waters

The origin of all polluting solutions related to the phosphogypsum stack located at the Ría of Huelva can be traced using geochemical indicators such as NASC-normalized REE patterns and Cl/Br ratios, based on the methodology proposed by Pérez-López et al. (2015). In this scenario, it is possible to identify two clearly contrasting geochemical environments. On the one hand, Tinto River estuary waters are characterized by REE patterns with an up-convex curvature in the MREE segment, which results in an enrichment of MREE with respect to both LREE ($(\text{MREE/LREE})_{\text{NASC}} = 1.60$) and HREE ($(\text{HREE/MREE})_{\text{NASC}} = 0.83$), according to the pattern reported by Elbaz-Poulichet and Dupuy (1999). In addition, estuarine water must have Cl/Br ratios close to 280, which is the typical value of seawater (Sánchez-Martos et al., 2002). On the other hand, freshwater used in the industrial process since 1997 acquires REE patterns with an upward positive trend of clear enrichment of MREE with respect to LREE ($(\text{MREE/LREE})_{\text{NASC}} = 3.02$) and of HREE with respect to MREE ($(\text{HREE/MREE})_{\text{NASC}} = 2.08$), according to the pattern of the ponded process water in zone 3 reported by Pérez-López et al. (2015). According to this latter work, these solutions also have a Cl/Br ratio of around 45. Both REE pattern and Cl/Br ratio are typical geochemical characteristics of fertilizers derived from phosphate rock (Otero et al., 2005).

Values typical of Tinto estuarine water and process water ponded on the stacks can be used as end-members in plots of $(\text{HREE/MREE})_{\text{NASC}}$ vs. $(\text{MREE/LREE})_{\text{NASC}}$ and Cl vs. Br in order to guess the origin of the solutions (Fig. 5). In this sense, plotting the values of the samples would allow also identifying the weathering agent leading to the production of contamination in each zone of the phosphogypsum stack. Considering the ideal mixing line between end-members, most the edge outflows of the phosphogypsum stack are closer to the estuarine water end-member; although there are significant differences from one zone to another of the stack, as discussed above. Thus, in zone 2 there are more edge outflows with a relatively greater influence for the process water end-member in comparison to the edge outflows of the remaining zones. These samples have patterns with relatively higher enrichment in HREE with respect to MREE and in MREE with respect to LREE, moving slightly away from the estuarine water end-member in the graph of REE (Fig. 5a). The influence of both sources

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2 is best observed by representing Cl/Br ratios, since all edge outflows are perfectly aligned in a wide range of
3 mixing between the two end-members (Fig. 5b).

4 Some contribution of the process water source is also observed, although to a lesser extent, in some of the
5 edge outflows of zone 3. These samples broadly have higher estuarine influence since the enrichment in HREE
6 with respect to MREE is negligible and only an enrichment in MREE with respect to LREE is observed (Fig.
7 5c); in addition, Cl/Br values are closer to those of seawater (Fig. 5d). Finally, all edge outflows of zone 4 are
8 characterized by presenting characteristics that are attributable exclusively to the Tinto estuarine water, with
9 enrichment in MREE with respect to both LREE and HREE and Cl/Br ratios closer to the typical values of
10 seawater as well (Fig. 5e,f). Such marine influence is also seen in the only sample collected in zone 1 according
11 to the Cl/Br ratio, as expected from its location in a tidal channel (Fig. 5f). Values of Cl/Br ratio in the edge
12 outflows of zones 1, 3 and 4, although much closer to typical values of seawater than to those of process water,
13 often do not coincide exactly. However, it should be noted that most of the edge outflows sampled in the stack
14 are in areas with slow-flowing waters where precipitation or dissolution of evaporitic salts, mainly halite, may
15 take place, causing a slight decrease or increase in Cl/Br ratios (Stober and Bucher, 1999; Göb et al., 2013).

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28 These results are consistent with the history of dumping of the four zones of the phosphogypsum stack. The
29 marine influence in the edge outflows is due to the use of estuarine waters for transport and settling of
30 phosphogypsum slurries in the disposal area from 1968 to 1997. This estuarine water dissolves contaminants
31 associated with residual phosphoric acid but a fraction remains in the interstitial space of the waste after
32 decantation, being subsequently released from the edges of the stack to the estuary. During this time period, the
33 circuit system was open and, hence, seawater is used only once and hardly loses its typical imprint of Cl/Br ratio
34 and REE pattern. This stock of contaminated estuarine water fills the pores of the phosphogypsum in the whole
35 depth profile of zones 1, 3 and 4. However, dumping sequence in zone 2 comprises a first filling stage with
36 seawater before 1997 and a second stage with freshwater after 1997 following the change in phosphogypsum
37 management policy. In this second stage, the continuous reuse of freshwater in a closed-loop system yielded a
38 highly acidic and pollutant process water with the characteristic imprint of phosphate fertilizers according to its
39 Cl/Br ratio and REE distribution. Thus, edge outflows of zone 2 mainly show an estuarine origin from the first
40 filling stage, but with a notable contribution of the process water from the second filling stage. This fact explains
41 why edge outflows of zone 2 have higher concentrations of P, NH_4^+ and contaminants than edge outflows from
42 zones 1, 3 and 4. Furthermore, it is likely expected that the contamination level increases over time if the
43 contribution of the second filling stage also increases. On the other hand, the higher marine influence in edge
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1 outflows of zones 1, 3 and 4 also explain the highest concentrations of Cl and S observed in comparison with
2 those of zone 2.

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4 As for samples from perimeter channels, water of the outermost perimeter channel of zone 2 has a REE
5 distribution comparable to the estuarine water end-member but with a slight influence of process water, i.e.
6 values similar to those found in the edge outflows of this zone (Fig. 5a). The geochemical similarity between
7 these solutions suggests that the outer perimeter channel may intercept part of the emerging groundwater lateral
8 flow before discharging to the outside. However, this channel is not at the same elevation as the stack basement
9 but approx. 2 m height above the marsh. This would be also congruent with the lower value of Cl/Br ratio and
10 the higher element concentrations in relation to edge outflows due likely to a larger contribution of the process
11 water from the second filling stage (Fig. 5b). Therefore, it is also possible to suggest that much of the
12 groundwater lateral flow is not intercepted and emerges to the surface up to reach the estuarine environment. In
13 fact, there are numerous edge outflows around the whole perimeter of this zone of the stack; i.e. both towards the
14 main tidal channel in the front part and towards the secondary channel embracing the back part (Fig. 1).

15
16 On the other hand, samples from the two perimeter channels of zone 3 are completely different to the rest of
17 samples as they reveal a clear connection with the process water end-member according to the shape of REE
18 patterns (Fig. 5c). Process water in this zone is not mainly contained in phosphogypsum pores but in surface
19 ponds. The possible infiltration of ponded process water seems to be successfully intercepted by both perimeter
20 channels. This is certainly reasonable since the channels are very close to the surface ponds (Fig. 1). Presently,
21 the ponded process water is subjected to evaporation in order to reduce its volume, which explains the extreme
22 levels of contamination of these samples. It is important to highlight that the rear perimeter channel is on the
23 same level as the marsh surface so it could be effective in collecting edge outflows in this part. However, the
24 front and side parts have not any perimeter channel in the base of the marsh to prevent groundwater flow, which
25 explains the numerous edge outflows observed towards the main tidal channel and the secondary channel
26 surrounding this zone of the stack. Nevertheless, although it may seem surprising, the rear perimeter channel is
27 connected to the secondary tidal channel and the acidic waters go directly to the estuary (see picture (f) in Fig.
28 1). Entry of seawater to this channel could explain the relatively closer REE pattern to the estuarine water end-
29 member (Fig. 5c) and the relatively higher values of Cl/Br ratio with respect to the perimeter channel
30 surrounding the ponded process water (Fig. 5d).

31 32 33 34 35 36 37 38 39 40 41 42 43 44 45 46 47 48 49 50 51 52 53 54 55 56 57 58 **5.2. Evaluation of previous and future restoration actions** 59 60 61 62 63 64 65

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2 This study reports the existence of leakages from the unrestored zones of the phosphogypsum stack, which
3 are currently a source of pollution to the Ría of Huelva. These findings are in disagreement with the previous
4 restoration guidelines established by the regional government at least for zone 2 (Junta de Andalucía, 2009). In
5 fact, this zone 2 exhibits the highest number of edge outflows along its perimeter; despite having numerous
6 perimeter channels in order to collect the acidic leakages. In addition, leachates of zone 2 are the most polluting
7 observed in comparison with those of the remaining zones of the stack.
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12 In zone 3 many sources of pollution had already been previously recognized in the edge (Pérez-López et al.,
13 2015). Nearly no influence of process water on the chemistry of most of these leachates suggests almost
14 nonexistent, or strongly diluted, connection between process water ponded on the surface and edge outflows,
15 which confirms what was pointed out in that latter study. It seems to be that the process water stored on surface
16 only infiltrates up to the perimeter channels due to their proximity but does not reach the front or side edge of the
17 stack. The discharge of contaminants occurs mainly through the seawater contained in the pores of the waste. In
18 addition, Pérez-López et al. (2015) proposed for zone 3 the existence of a possible continuous recharge of
19 seawater in the deeper zone of the phosphogypsum stack according to some evidences observed in previous
20 technical reports (Tragsatec, 2010). The phosphogypsum weathering likely occurs by seawater intrusion in
21 deeper zones of the stack because of its localization within the estuarine tidal prism.
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34 Edge outflows of zone 2 are influenced by process water in a wide range of mixing. However, these
35 solutions still preserve a marine character, which allow us to extend to this zone the interpretations made for
36 zone 3. On the one hand, process water surely comes from a second filling stage, as stated before. Disconnection
37 between process water ponds and edge outflows seems evident since the thickness of phosphogypsum in zone 2
38 is greater than in zone 3 and therefore infiltration from the surface pond to the basement and edges of the stack is
39 highly unlikely. Definitely, the process water of the central ponds in zones 2 and 3 would not act as a source of
40 edge outflows that reach the estuary by infiltration through porous media, which again contradicts previous
41 restoration guidelines provided by the regional government (Junta de Andalucía, 2009). On the other hand, zone
42 2 shows the highest number of edge outflows because the amount of stack-piled phosphogypsum and, therefore,
43 the thickness of the saturated zone as well as the volume of water stored in pores is substantially greater than in
44 the remaining zones. In addition, we cannot ignore a possible contribution from seawater intrusion in deeper
45 zones of the phosphogypsum stack. According to these results, future restoration actions in unrestored zones
46 involving removal of process water ponds and cover of the stack surface with natural soil would not necessarily
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lead to the cessation of edge outflows. This statement can be confirmed by comparison of these zones with already-restored zones.

Regarding already-restored zones, the absence of edge outflows in zone 1 is probably due to the low thickness of phosphogypsum (2-3 m), which determines that whole profile of weathering corresponds to unsaturated zone; i.e. there is not a large stock of water in the deep pores that can flow laterally to emerge superficially at the edges. Thus, capacity of acidity and metal release is unquestionable owing to the nature of wastes; however, pollution production is limited by the availability of weathering agents acting as hydrological drivers.

On the contrary, considering the half that has been not inspected, zone 4 must present a similar number of edge outflows to zone 3. This seems reasonable since both zones have similar thickness of phosphogypsum and, hence, seawater stored in the pores should be also of the same order of magnitude. It is therefore possible to confirm that the absence of process water ponds and presence of a complex artificial-soil cover does not prevent leakages from the stack to the estuary. The only effect observed is the lack of influence of process water in the chemical composition of edge outflows, which are slightly less polluting for some toxic elements. Nevertheless, these solutions have higher concentrations of Fe and Sb than those found in the remaining zones, which could be released from the 2 m industrial waste layer used in the top cover.

The results obtained in zone 4 allow once more the extension of the weathering model of zones 2 and 3 to even already-restored zones of the stack. The implementation of complex surface covers would serve to hide the phosphogypsum and limit the direct dissolution during rainfall episodes, but it would have not any effect as restoration measure on pollution reaching the estuary through the edge outflows. The release of contaminants into the estuary would be only avoided by channeling and treatment of edge outflows before discharge. Therefore, it can be concluded that future restoration measures planned for zones 2 and 3 shall not involve the interruption of indirect leachates to the estuary. These data are in line with the need for an imminent change in the restoration strategies that the fertilizer company has proposed for the environmental regeneration of zones 2 and 3 of the phosphogypsum stack. It is also a priority to include zone 4 in the new restoration plans since preliminary actions seem to have been futile. Concerning zone 1, also previously-restored, its potential to generate acid leachates during the contact with weathering agents is lower. Nevertheless, it contributes to the pollution of the estuarine environment and should be also included in the new plans of regeneration.

6. CONCLUSIONS

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4 This paper focuses on a phosphogypsum stack as potential contamination source to the Ría of Huelva
5 estuary (SW Spain). The phosphate fertilizer factory ceased dumping in 2010, thus an imminent restoration of
6 the area is planned. In particular, the study evaluates the future restoration works planned for some disposal
7 zones by comparing with other zones that have been already restored following the same action guidelines. It is
8 the general belief that the edge leakages or outflows draining inside the stack and discharging into the estuary
9 have its origin in the infiltration of industrial process water ponded on the surface of the unrestored zones
10 through the porous medium. Thus, planned restoration measures involve removal of ponded process water and
11 cover with topsoil. However, some geochemical tracers such as REE patterns and Cl/Br ratios have allowed us to
12 rule out the ponded process water as main vector of contaminants and suggest that these restoration actions
13 would not involve the cessation of the leaching. The acid leachates have geochemical signatures typically found
14 in seawater due to a possible connection between the stack and the estuary by saline intrusion. In this sense,
15 already-restored zones act as a pollution source on the estuary through edge outflows just as unrestored zones,
16 which strengthens this argument and reveals the inefficiency of adopted measures. According to this study, it is
17 of critical importance to define again the basic guidelines for the development of restoration actions for the
18 whole phosphogypsum stack in order to limit the exposure of estuarine ecosystems to acidity and toxic
19 contaminants.
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ACKNOWLEDGEMENTS

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44 This work was supported by the Government of Andalusia through the research project ‘Phosphogypsum:
45 from the environmental assessment as a waste to its revaluation as a resource (P12-RNM-2260)’. R. Pérez-López
46 also thanks the Spanish Ministry of Science and Innovation and the ‘Ramón y Cajal Subprogramme’ (MICINN-
47 RYC 2011). C.R Cánovas was funded by the European Union’s Seventh Framework Program, Marie
48 Skłodowska-Curie actions and the Ministry of Economy, Innovation, Science and Employment of the Junta de
49 Andalucía by the program TalentHub (COFUND - Grant Agreement 291780). The analytical assistance of María
50 Jesús Vílchez from the CIDERTA of the University of Huelva is gratefully acknowledged.
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FIGURE CAPTIONS

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4 FIGURE 1. Location map of the phosphogypsum disposal piles on the salt-marshes of the Tinto River and
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6 sampling points of edge outflows. Some field pictures are also shown (see explanation in the text).

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8 FIGURE 2. Values of pH, EC and concentration of major elements in edge outflows of the four zones of the
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10 phosphogypsum stack. Both average and standard deviation are shown graphically for each zone.

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12 FIGURE 3. Concentration of trace elements in edge outflows of the four zones of the phosphogypsum stack.
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14 Both average and standard deviation are shown graphically for each zone.

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16 FIGURE 4. NASC-normalized REE patterns for edge outflows of (a) zone 2, (b) zone 3 and (c) zone 4 of the
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18 phosphogypsum stack; shadowed area = variability range and dash line = average value. Red dashed-dot
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20 lines refer to the normalized patterns for the three samples of perimeter channels.

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22 FIGURE 5. Plots of $(\text{HREE}/\text{MREE})_{\text{NASC}}$ vs. $(\text{MREE}/\text{LREE})_{\text{NASC}}$ ratios (left side) and Cl vs. Br concentrations
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24 (right side) for the samples collected in (a,b) zone 2, (c,d) zone 3 and (e,f) zones 1 and 4 of the
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26 phosphogypsum stack. REE pattern and Cl/Br ratio for the estuarine/sea-water end-member were taken
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28 from Elbaz-Poulichet and Dupuy (1999) and Sánchez-Martos et al. (2002), respectively; whereas both data
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30 for the process water end-member were taken from Pérez-López et al. (2015). In the NASC-normalized
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32 ratio plot, a scheme has been inserted in (e) for illustrating the general shape of the REE profile in the
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34 different fields of the graph (see more explanation in Stolpe et al., 2013). Note that legends of (a), (c) and
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36 (e) are the same as in (b), (d) and (f), respectively.

ELECTRONIC SUPPLEMENT

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46 FILE KML. This file contains the Google map of the zones described in this article.

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52 TABLE S1. Compilation of pH, electrical conductivity, Eh, Cl/Br ratio and elemental contaminant analysis in
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54 the samples of edge outflows (EO) and water in perimeter channels (PC).

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Figure 1
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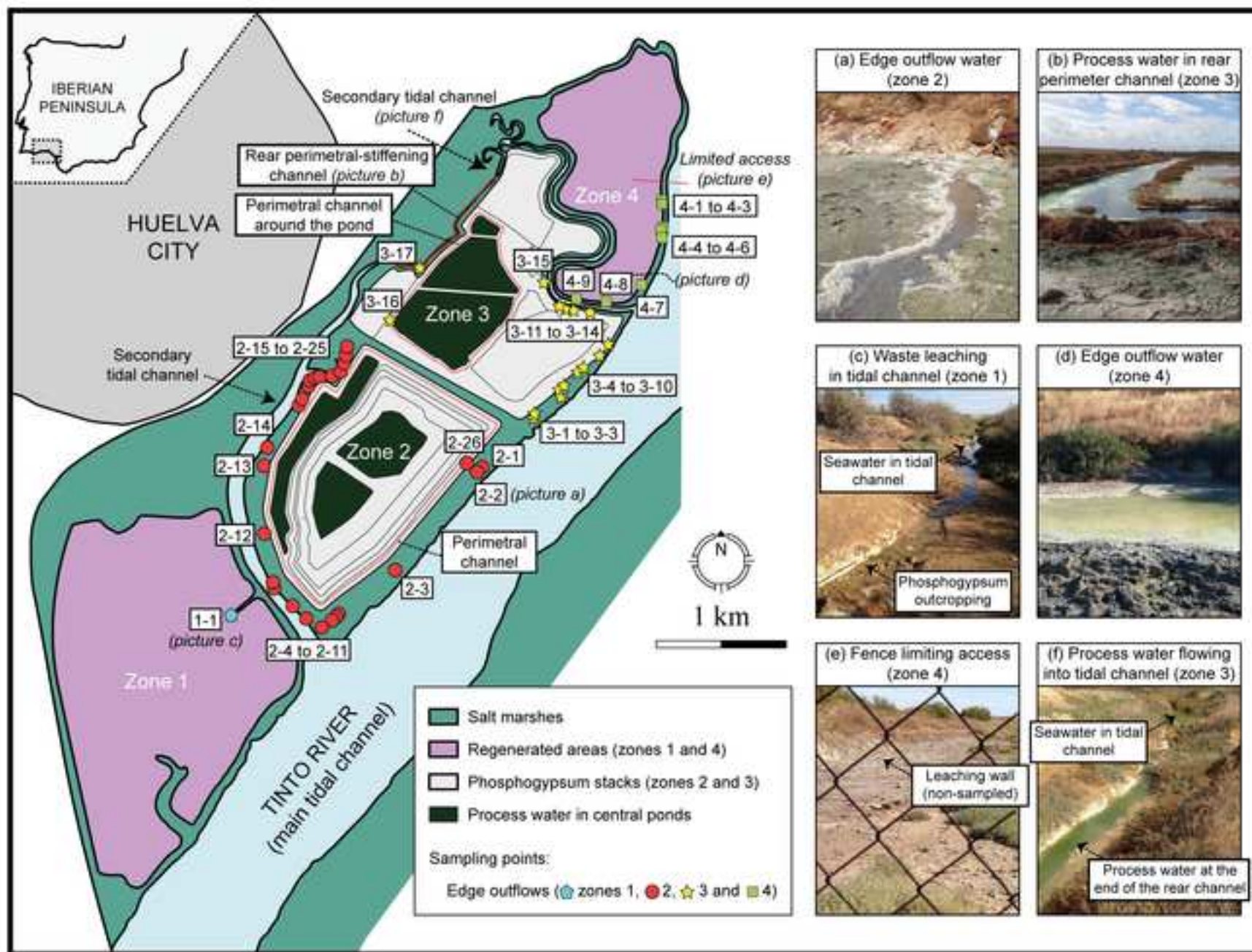


Figure 1

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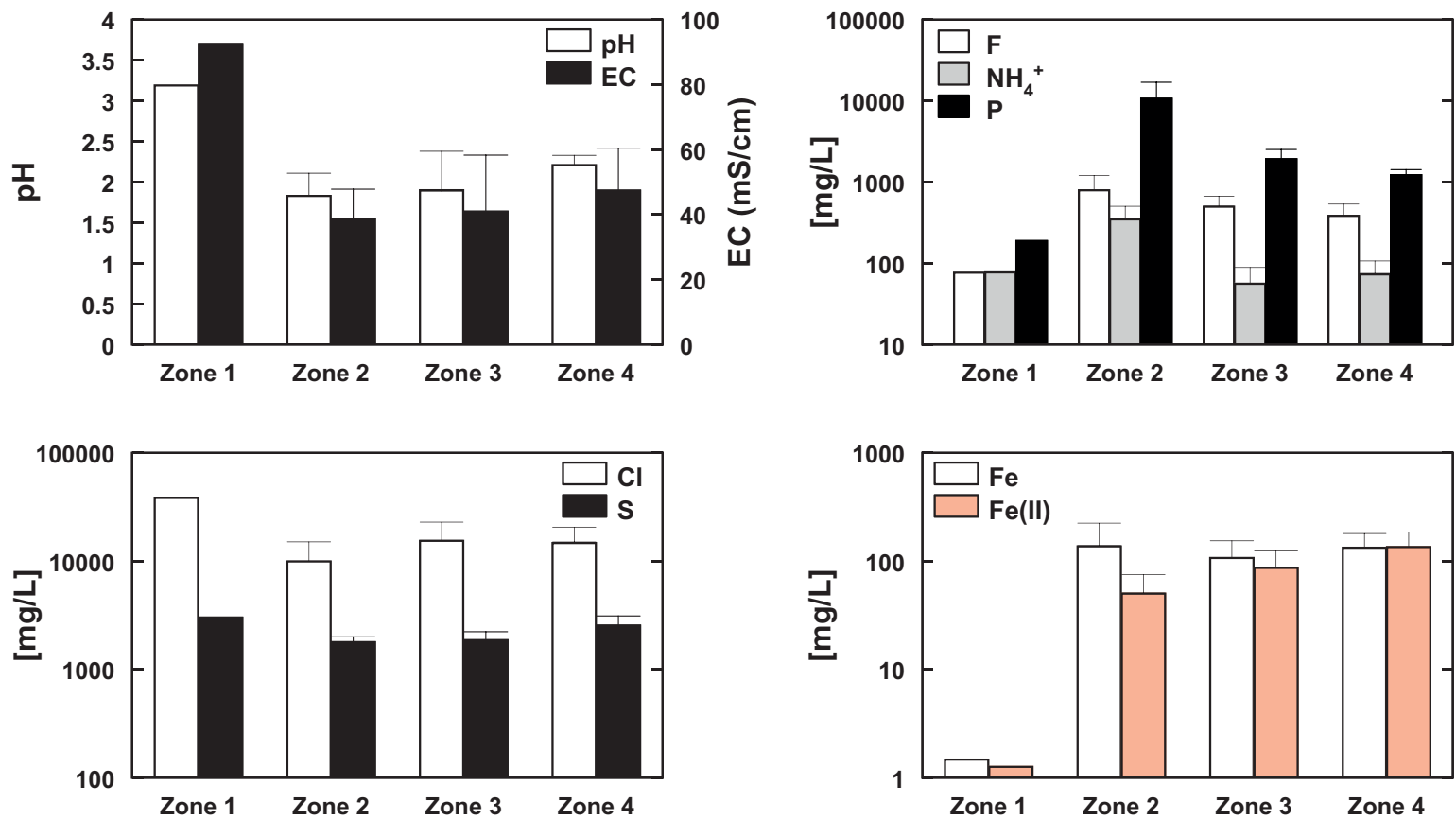


Figure 2

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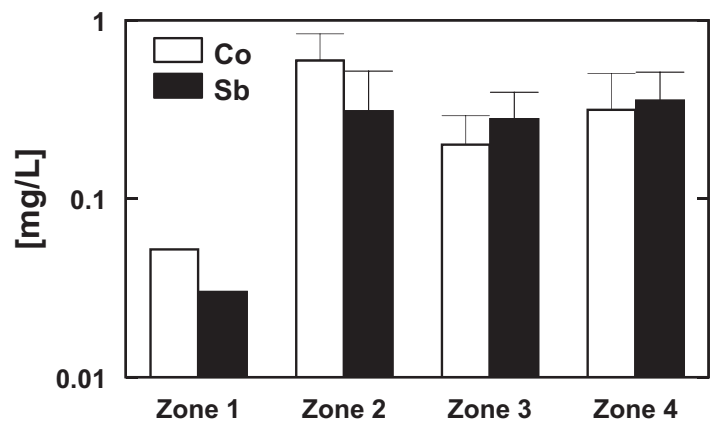
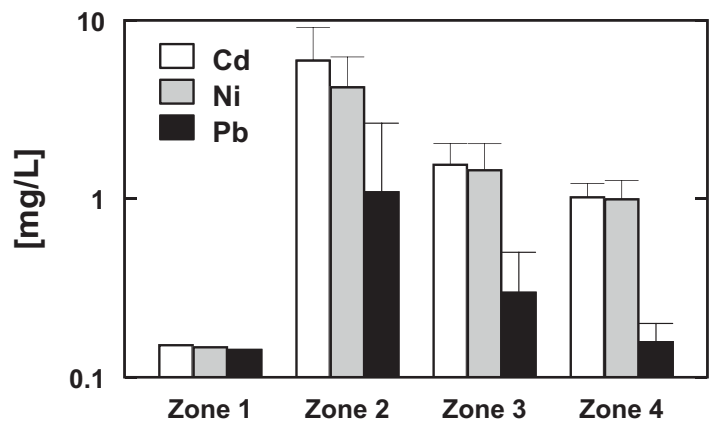
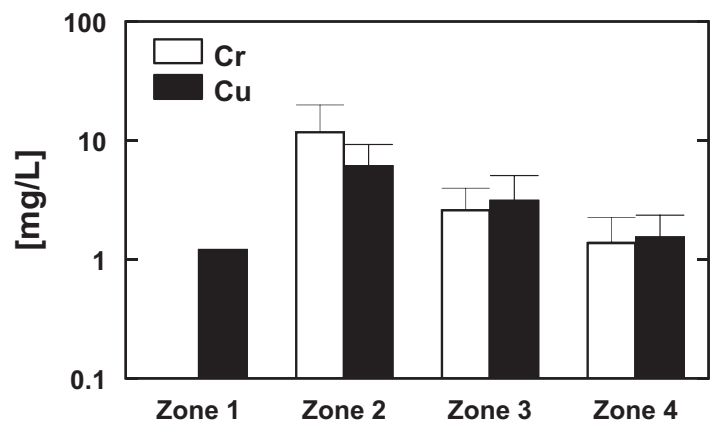
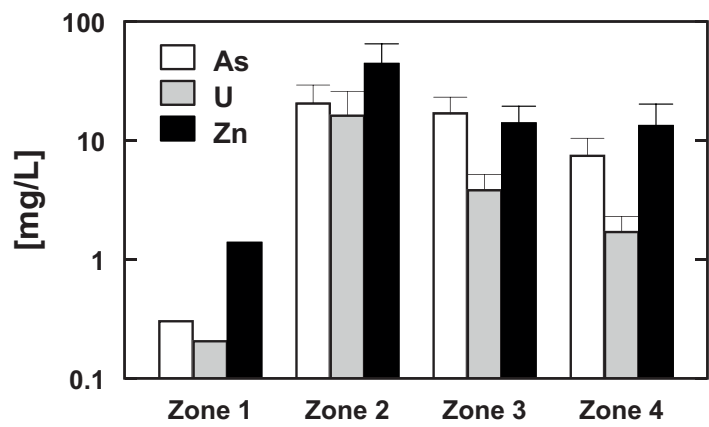


Figure 3

Figure 4

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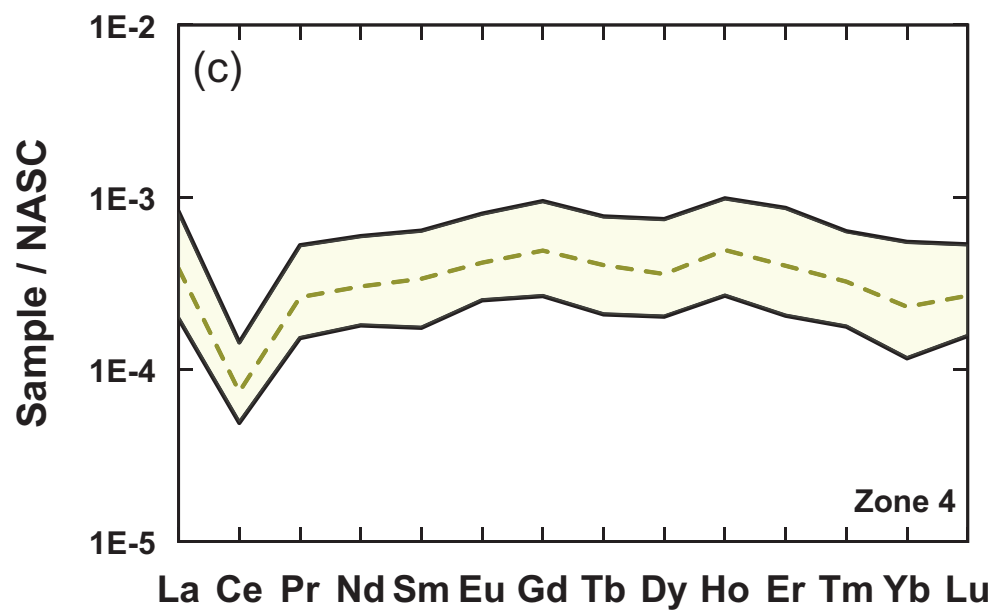
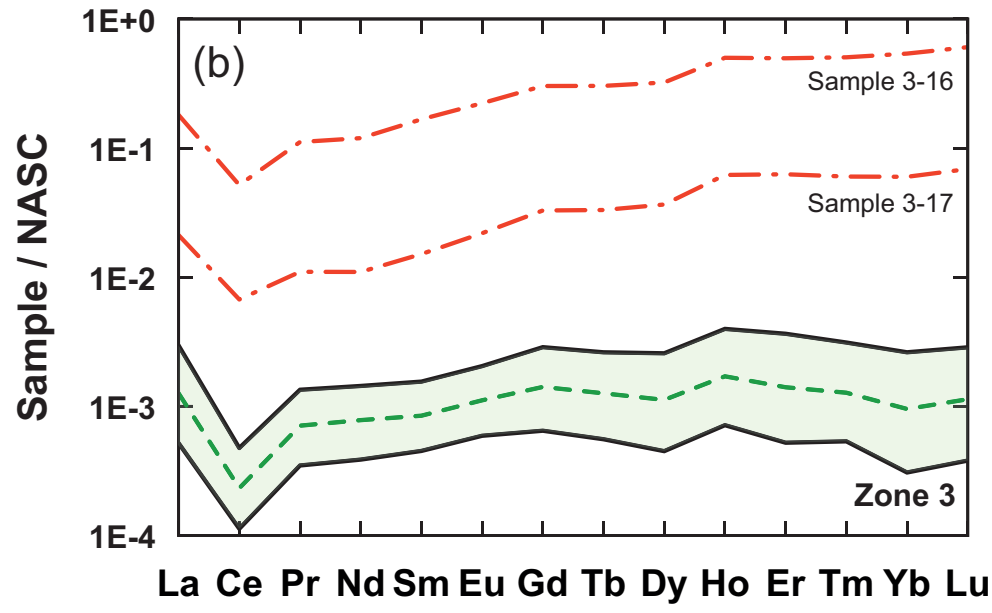
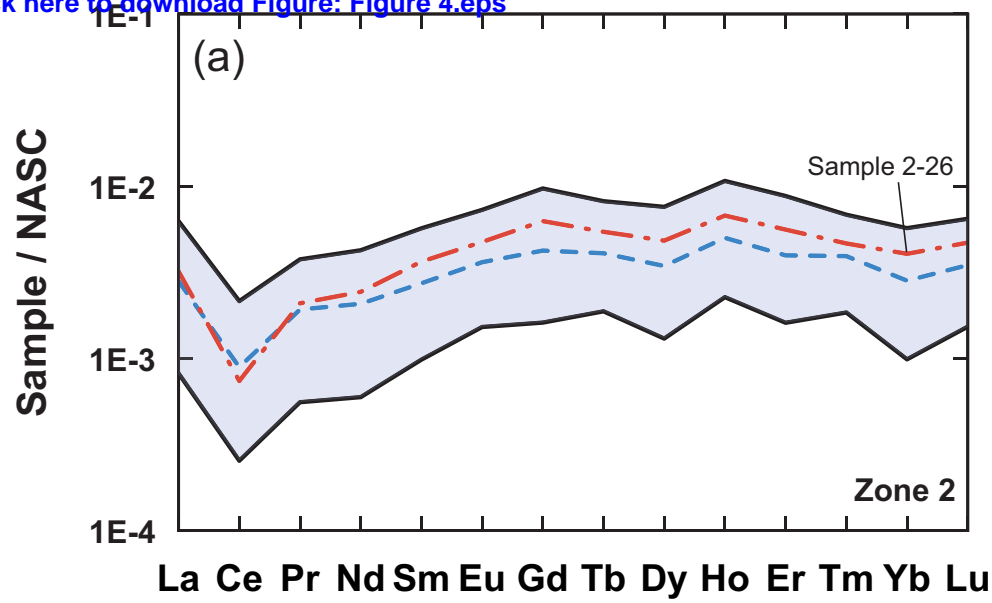


Figure 4

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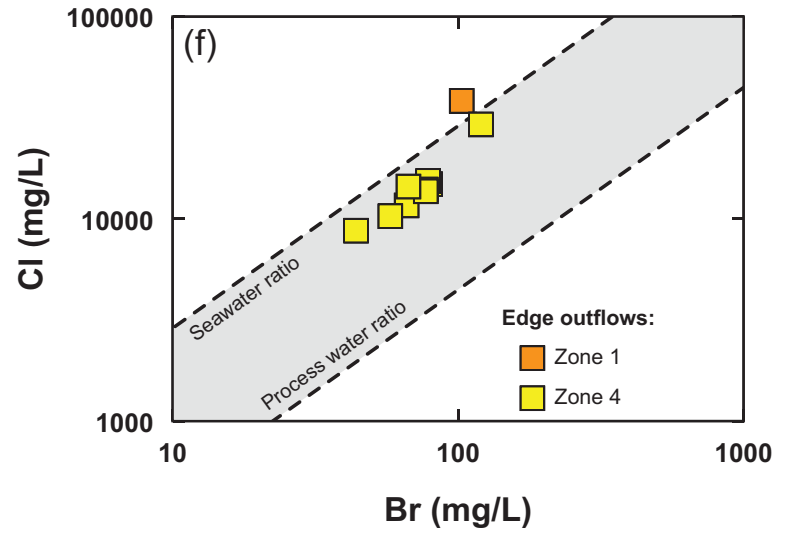
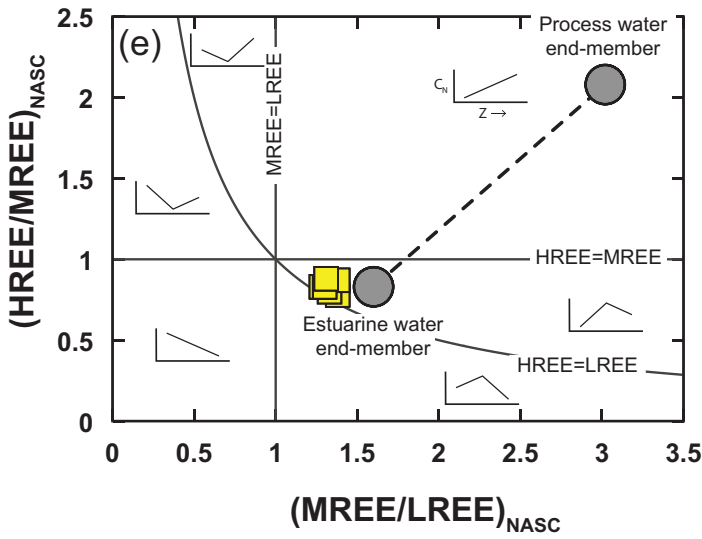
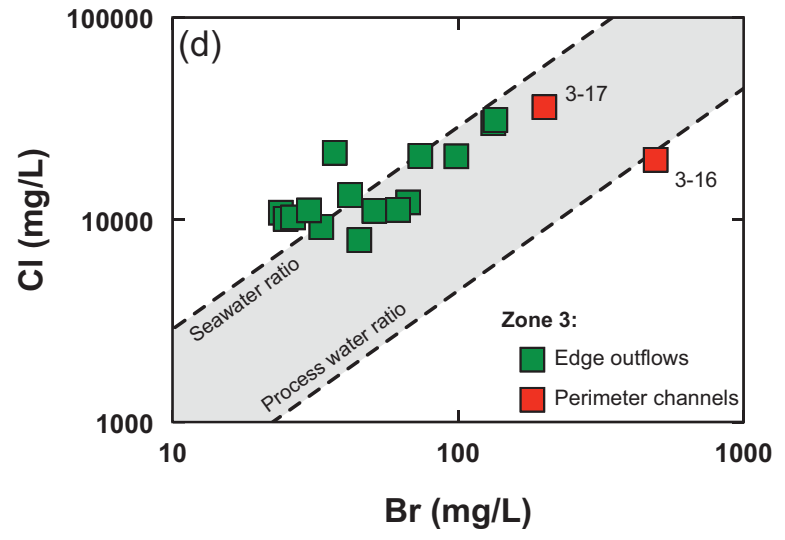
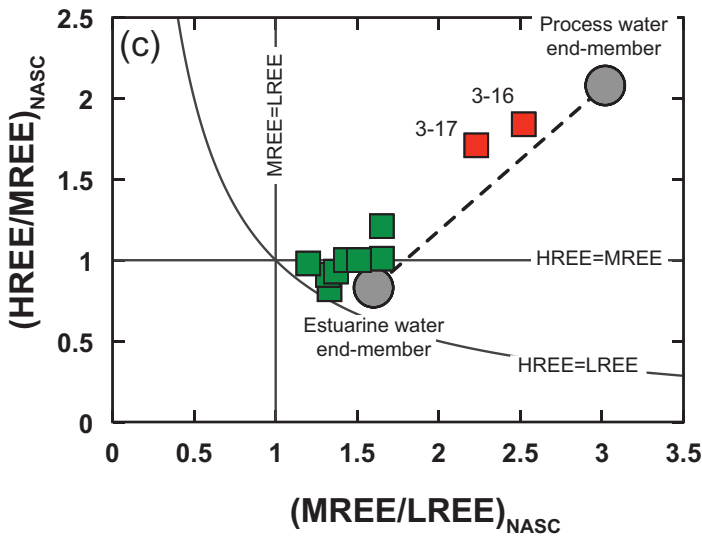
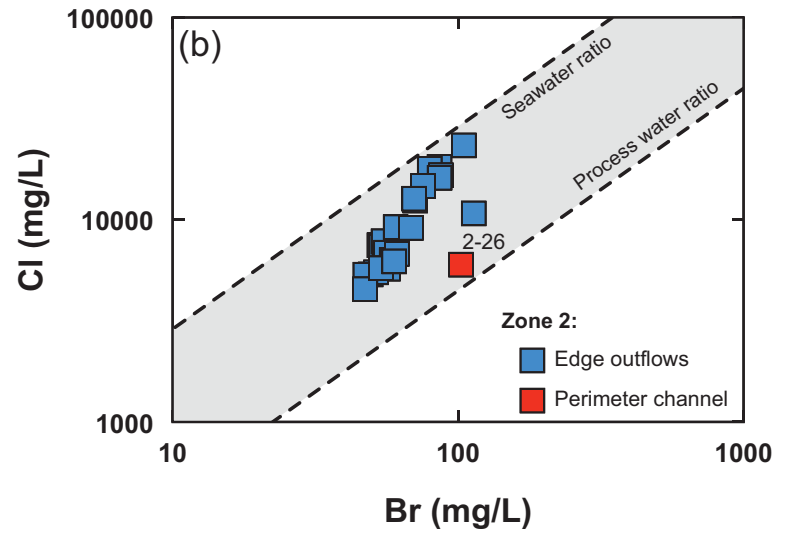
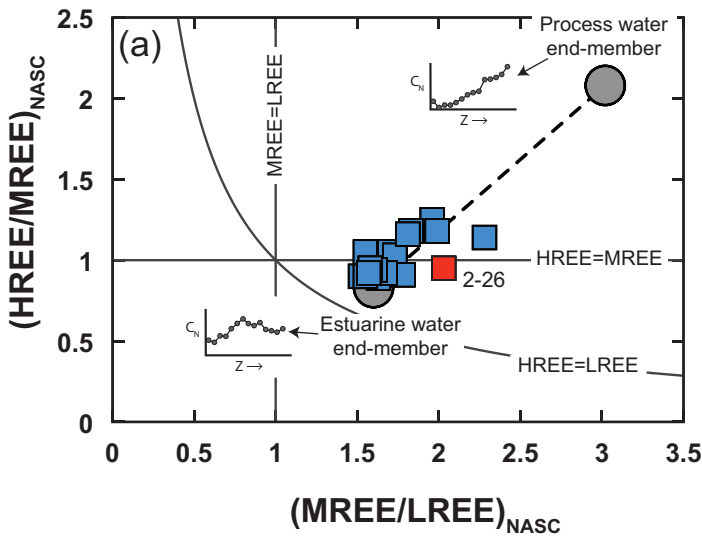


Figure 5