

Research papers

Phosphogypsum weathering and implications for pollutant discharge into an estuary

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ABSTRACT

Approximately 100 million tons of phosphogypsum were stockpiled onto marsh soils of the Tinto River estuary (Huelva, SW Spain). This study focuses on the hydraulic response of the phosphogypsum stack to the different weathering agents, as well as on the hydrochemical behavior of highly acidic and polluted effluents from its leaching during different hydrological conditions. To address these issues, a CTD-Diver was installed in a borehole within a phosphogypsum stack profile, which recorded the variations in the water-table of the stack, and edge outflows samples were collected around the perimeter of the stack during four sampling periods in different seasons. During dry periods, the water-table of the stack remains almost static and is controlled only by the tide oscillations. However, during rainy events this water-level rapidly increases up to 20 cm and subsequently decreases, defining peaks that coincide with the rainfalls. Having a hydraulic connection to the sea and groundwater flow in conduits, the phosphogypsum stack behaves as an anthropogenic karstic-coastal aquifer. Regarding the hydrochemical behavior of the edge outflows, the concentrations of most pollutants (e.g., PO₄, Al, As, Cd or U) showed a slight decrease from the dry-warm to the rainy period. These leachates releases high concentrations of contaminants to the estuary, e.g., PO₄, As and U (average values of 5000, 6.9 and 3.0 t/yr, respectively). The results obtained in this study could contribute to the development of effective treatment systems for leachates from phosphogypsum stack of Huelva and to minimize their impact on the surrounding estuarine environment.

1. Introduction

The growing industrial activity during the last five decades, to satisfy the needs of an increasingly developed and globalized world population, has resulted in a significant growth of industrialized zones around the world. In this sense, the increasing industrialization of estuaries around major shipping routes promotes environmental concerns due to these areas are particularly sensitive to metal pollution. The Ría de Huelva estuary, formed by the confluence of the Odiel and Tinto Rivers (SW Spain), is a clear example of extensive development and industrialization. In this case, part of the industrial activity has been focused on the manufacture of phosphoric acid (H₃PO₄) for the production of phosphate fertilizers. As a result, an unwanted by-product, commonly known as phosphogypsum (mainly gypsum, CaSO₄·2H₂O), is generated by the chemical digestion of phosphate rock (i.e., fluorapatite, Ca₅(PO₄)₃F) with sulfuric acid (H₂SO₄).

Phosphogypsum frequently contains impurities such as metal/oids

(e.g., As and Cd) and radionuclides from the decay series of ²³⁸U (i.e., U, Ra and Rn) (Macías et al., 2017; Rutherford et al., 1994). Consequently, these toxic impurities limit the commercial usage of phosphogypsum. In fact, only around 15% of the phosphogypsum produced worldwide is recycled, mainly for the production of buildings materials (Cánovas et al., 2018). With respect to the remaining 85%, it is transported as an aqueous slurry along with a residual fraction of the reagents (i.e., sulfuric acid) and products (i.e., phosphoric and hydrofluoric acids) from the manufacturing process and then stored in stacks, without any type of previous treatment, on large flat areas close to the phosphate fertilizer industries (Tayibi et al., 2009). Most phosphogypsum wastes are stockpiled in coastal areas or directly dumped into the sea (e.g., El Samad et al., 2014; El Zrelli et al., 2016; Pérez-López et al., 2016; Sanders et al., 2013) and, hence, these wastes are usually exposed to strong weathering processes such as leaching by rainwater and/or seawater (Macías et al., 2017; Zielinski et al., 2011).

The phosphate fertilizer industry located in the Ría de Huelva

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estuary has been generating and dumping phosphogypsum for almost 40 years over a huge stack (approx. 100 million tons of wastes stockpiled on around 12 km² of surface) near the city of Huelva. The waste was deposited directly onto the marsh soils of the Tinto River estuary with no barrier or liner to avoid infiltration. The presence of acidic solutions trapped in the pores of the phosphogypsum makes the stack to behave similarly to an unconfined aquifer with highly-polluting groundwater (Pérez-López et al., 2011). When groundwater reaches the below-waste filled marsh level, these solutions flow laterally until emerging at the edges of the pile and forming superficial leakages known as edge outflows (Pérez-López et al., 2015, 2016). As a result, the phosphogypsum stack is a continuous source of pollution into the estuary due to the release of large volumes of acid effluents, i.e., around 335,000 m³/yr, with high concentrations of dissolved pollutants, such as PO₄, F, Fe, Al, Zn, Cr, Cu, As, Sb and U, among others (Pérez-López et al., 2016).

Previous studies reported that the edge outflows have a geochemical fingerprint that indicates a predominantly estuarine origin (Papaslioti et al., 2018; Pérez-López et al., 2016). The findings proposed that the intertidal estuarine water accesses to the phosphogypsum stack, possibly through the secondary tidal channels that are currently covered by the pile, washing the waste in depth and returning to the estuary in the form of edge outflows. We cannot rule out that a part of this water may be recirculated and previously exposed to the stockpiles. Nevertheless, this multiple leaching process must be negligible due to the continuous renewal of water in the estuary because of tidal cycles. Although geochemical connection between the estuary and the phosphogypsum stack has been previously shown, the hydraulic response of the stack to estuarine fluctuations, as well as the influence of other possible weathering agents such as rainwater, remains unclear. To bridge this gap in knowledge, the main objectives of this work are to assess (1) the temporal hydrological response of the water-table at the waste pile against possible weathering agents, as well as (2) the possible seasonal influence on the hydrochemistry of the edge outflows and therefore on the discharge of pollutants to the estuary. To our knowledge, the studies carried out so far to characterize the pollution from edge outflows are based on single sampling campaigns (Papaslioti et al., 2018; Pérez-López et al., 2016), while the present study has analyzed the hydrochemistry of the leachates that emerge from the phosphogypsum stack during several sampling campaigns under different hydrological conditions. The information obtained in this study could be useful for the optimization of future remediation systems for acid and contaminated discharges from phosphogypsum stacks, mainly in coastal areas worldwide.

2. Materials and methods

2.1. Study site

The Huelva phosphogypsum stack is located in the tidal prism of the Ría de Huelva estuary, which ranges between 37 and 82 million m³ along a tidal half-cycle (6 h) (Grande et al., 2000). Since 1968 -when the industrial activity began- until its cessation in 2010, approximately 3 million tons of phosphogypsum were produced each year. From 1968 to 1997, the phosphogypsum was transported and deposited on four disposal areas using seawater, which was later discharged after waste decantation to the estuary without any type of treatment. However, in 1997 a legislative change forced the fertilizer company to present a new waste management project to avoid any direct discharge into the estuary (OSPAR, 2002, 2007). According to the new management policy, from 1997 to 2010, the waste was stored in a large pyramidal pile on a single zone already used previously. In addition, the transport and decantation of the phosphogypsum was carried out through a closed-loop system of freshwater, known as process water, instead of the old open-circuit system of seawater used until then. The process water was stored in shallow ponds on the stack in order to promote evaporation as a measure to reduce its volume.

At present, the phosphogypsum stack is comprised of four different

disposal modules; while zones 1 and 4 are already considered as restored, zones 2 and 3 are currently pending restoration in the near future. The previous restoration consisted in covering the bare phosphogypsum with a soil cover. Zone 1 (4.5 km² of area and 2–3 m of average thickness) is covered by a 25 cm thick layer of natural soil with vegetation; while zone 4 (3.0 km² and 8 m) has a more complex cover that consists of several layers: 1 m of construction debris, 2 m of inert industrial wastes and 30–50 cm of vegetable soil (in ascending order). On the other hand, in the unrestored zones 2 (2.7 km² and up to 30 m in height) and 3 (1.8 km² and 8–12 m), the phosphogypsum is directly exposed to weathering conditions. Both zones still contain surface ponds with process water characterized by extreme acidity and contaminant load, due to its continuous use in the closed-circuit system and to the evaporation to which it is subjected. Despite restoration measures, the four disposal modules currently show numerous edge outflows along their perimeters that continuously discharge pollutants to the Ría de Huelva estuary (Pérez-López et al., 2016). In addition, it is also strongly affected by the historical mining in the Iberian pyrite belt (IPB). As a consequence, estuarine waters show high dissolved metals concentrations, e.g., Zn, Al, As, Cu and Pb (average values of 90 µg/L, 60 µg/L, 48 µg/L, 30 µg/L and 1.5 µg/L, respectively) (Hierro et al., 2014). Other evidence of that contamination is the high concentrations of some metals observed in the estuary sediments (i.e., 1000 mg/kg of Zn, 824 mg/kg of Cu and 789 mg/kg of Pb, among others; Borrego et al., 2013), which are between 9 and 25 times higher than values analyzed in sediments from non-affected estuaries, e.g., the Piedras River one (Borrego et al., 2013).

2.2. Sampling

The perimeter of the four zones of the phosphogypsum stack was inspected in order to collect edge outflow waters during four sampling campaigns in different seasons (Fig. 1a): May-June 2014 and 2015 (warm-dry periods), November 2014 (rainy period) and June 2016 (beginning of warm-dry period after rainy events). The accumulated rainfall for 2016 (i.e., 628 mm) was higher than the annual average in the study site (i.e., around 500 mm), while 2014 and 2015 years the rainfall values were close to or below the annual mean value (i.e., 534 and 359 mm, respectively). In this same sense, the rainfall accumulated between May and June 2017 was around 116 mm, this value was one and two orders of magnitude higher than those recorded for those same months in 2014 and 2015 (i.e., 19 and 1 mm, respectively). During the different sampling campaigns, a total of 215 edge leachate samples were collected from 95 different discharge points. Some of the phosphogypsum leachate discharge points could not be collected during some of the sampling campaigns due to the existence of a diffuse groundwater flow that sometimes masks the punctual discharges and hinders the exact location of the edge outflows. In this sense, no samples were taken just after rainy events due to an increase in the diffuse flow, leaving a gap of at least 10 days for safety issues. The pH, redox potential (ORP) and electrical conductivity (EC) were measured in the field using a portable Multiparametric Crison MM 40 + equipment. Measured ORP was referenced to the standard hydrogen electrode (Eh), as proposed by Nordstrom and Wilde (1998). Rainfall and temperature data from a meteorological station (at 1 km from phosphogypsum stack) were provided by the Regional Environmental Authorities and the Spanish Meteorological Service.

For the continuous control of the water-table variations in the stack, a CTD-Diver was installed in a bore-hole of 4.5 m of depth within a phosphogypsum profile in the zone 3 (around 8 m of waste thickness), and a BaroDiver was used to compensate measurements with atmospheric pressure. The installed sensors were manufactured by Schlumberger (accuracy for pressure: ±0.1%). In the moment of installation, the water-table was found at 2.67 m beneath the surface and the CTD-Diver was submerged about 18 cm. So, results will be also corrected with respect to the immersion depth. The measurement period

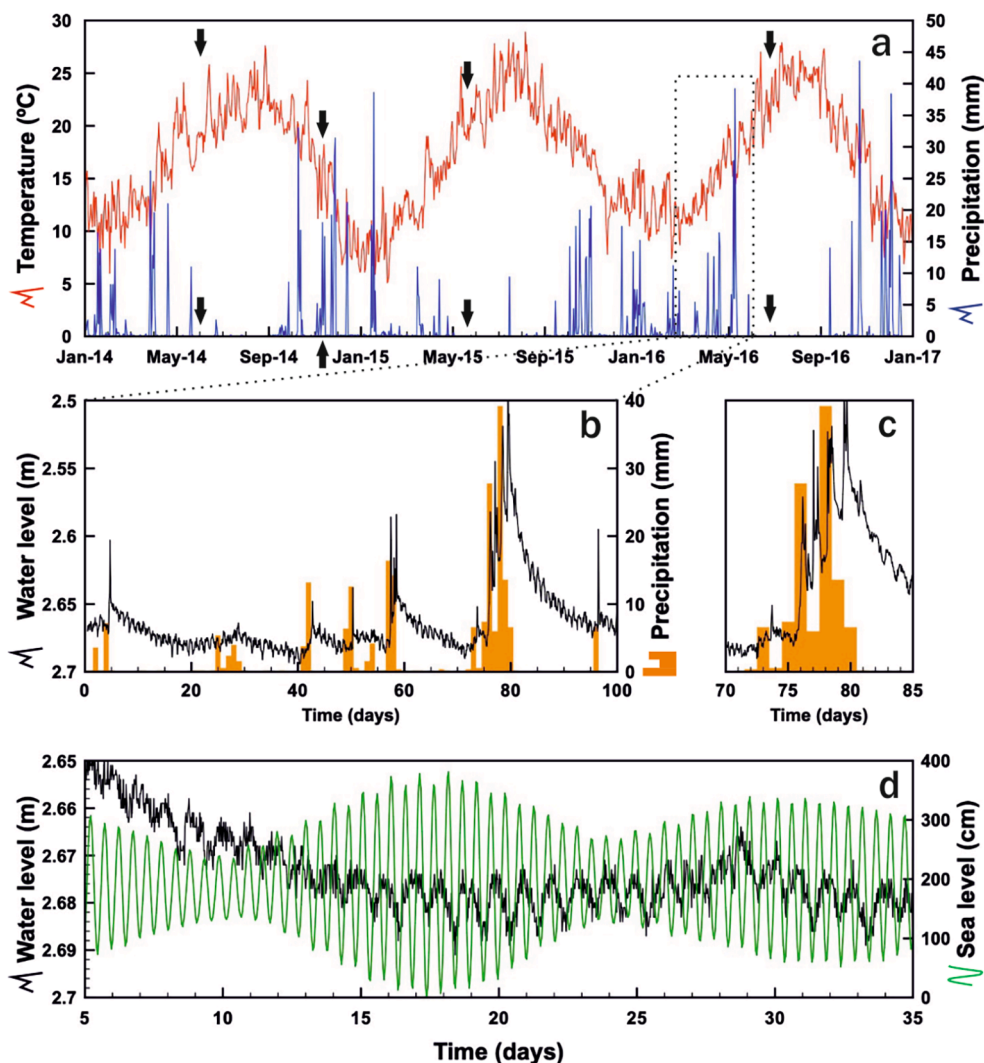


Fig. 1. A) Daily evolution of rainfall and temperature during the study period. the arrows indicate the date on which the different sampling campaigns were carried out, b) response of the water-table of the phosphogypsum stack during rainy events, c) zoom of the relationship between certain rainy episodes and the water-level in the stack and d) relationship between the water-table level of the pile and the tidal fluctuations.

comprised from February 22nd to June 28th 2016, with a sampling frequency of 10 min. Sea level variation measurements during the same period were also obtained from a buoy (at 500 m from phosphogypsum stack) belonging to the Spanish Wave Coastal Network. 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.

2.3. Chemical analyses

Edge outflow samples were filtered through 0.45 μm membrane filters and divided into two aliquots; one unacidified for anion and ammonia determination and another acidified with HNO_3 to pH less than 1 for major and trace element analysis. All liquid samples were stored in high-density polyethylene bottles previously washed with HCl (10%) for 24 h, and subsequently rinsed with Milli-Q water (18.2 M Ω , Millipore), and stored in sterile plastic bags to prevent contamination. As long as possible, the float method was used to estimate the flow rate at the sampling points of edge outflows.

Concentrations of anions (Br, Cl and F) and ammonia in all the unacidified samples were determined by high performance liquid chromatography (HPLC) using a Metrohm 883 basic ion chromatograph (IC) 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 and Zn). 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 $\mu\text{g/L}$ for trace elements. All analyzes were performed in the laboratories of the University of Huelva. Three laboratory standards (i.e., QCSTD 27, ICP-MS-QC1-1 and ICP-MS-QC2-1), prepared with concentrations within the range of the samples, were analyzed with every 10 samples to check for accuracy. These laboratory control materials were prepared from the certified reference material NIST-1640 (NIST, USA). 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 included in each sequence of analyzes (standard curve). The average measurement error was less than 5%. A statistical analysis was performed using the statistical package. A Principal Component Analysis (PCA) of the results was performed to analyze the relationships among the different variables and seasonal patterns of edge outflows chemical composition. The PCA is based on a reduction in the number of variables in a multivariate dataset, conserving as much variance as possible in the dataset. The Spearman's correlation matrix was used because some

variables did not show a normal distribution (Davis, 2002).

3. Results and discussion

3.1. Hydrological response to weathering

The daily evolution of rainfall and temperature in the study area from 2014 to 2016 (Fig. 1a) shows a cyclic pattern characteristic of semi-arid Mediterranean climate, with a rainy season in winter and a dry-warm season in summer. The annual average rainfall during this time series was 510 mm, and most rain events were short but intense downpours between October and April. During the hydraulic monitoring period, the accumulated rainfall was 220 mm and the events had a direct response in the water-table of the phosphogypsum stack (Fig. 1b). The water-table was quite stable during the study period but increased up to 20 cm during the rainy events. Fig. 1c shows in detail the relation between some rainy episodes and water-table level in the stacks, indicating that the response of the system is immediate; i.e., without delay between the rainfall and water-table increases. Just after rain episodes, around half the height increased by the water-table is immediately recovered, defining peaks that coincide with the rainfalls. The water-table recovers more slowly its original state during a period of 5–15 days depending on the intensity of the rains.

In periods with absence of rains, the water-table shows low variability during most of the time (± 2 cm). However, when zooming in, small cyclical oscillations can be observed within these stability periods. These piezometric oscillations seem to be influenced by the tidal fluctuations, as observed from the data recorded by the buoy belonging to the Spanish Wave Coastal Network (Fig. 1d). The data of the buoy provided clear information on the semidiurnal character of the tidal oscillations, i.e., two high tides and two low tides are recorded alternately each day, which is consistent with the tidal regime of the study area (Borrego et al., 1995). The piezometric oscillations show maximum and minimum amplitudes that match the tidal cycles with a certain delay. Nevertheless, the second daily low tide often appears to be masked in the water-table variation, which could be due to its lower amplitude in relation to the first one. Moreover, the monitoring was carried out in a rainy period where there may be a higher contribution of fluvial flood events that also masks the piezometric tidal oscillations.

3.2. Hydrochemical characterization

During the four sampling campaigns (i.e., May-June 2014, November 2014, May-June 2015 and June 2016), a total of ninety-five edge outflow points were identified around the whole perimeter of the phosphogypsum stack (Fig. S1). Zone 2 was by far the phosphogypsum disposal area where more discharging points were found, i.e., 51 edge leachates (samples 2-1 to 2-51), followed by zone 3 with 28 (samples 3-1 to 3-28) and zone 4 with 15 (samples 4-1 to 4-15). However, a large part of the perimeter of zone 4 could not be sampled since a fence restricts the access. Therefore, the total number of edge outflows emerging from the supposedly restored zone 4 could be even higher than that described in this manuscript. Finally, only one acid leachate was identified in zone 1. However, this acidic water sample is the result of the interaction of outcropping phosphogypsum and seawater during rising tide in a tidal channel and is therefore not strictly considered an edge outflow (Pérez-López et al., 2016). The number of edge outflows found in each zone of the phosphogypsum stack could be directly related to the thickness of waste piled up and/or the extent of marsh soils covered by the zone. On the one hand, the higher the height of the waste pile, the greater the thickness of the saturated zone and, therefore, the greater the potential for storing acidic and contaminated interstitial water. In this sense, the absence of edge outflows in zone 1 is likely due to the low thickness of phosphogypsum, which determines that the whole profile of weathering corresponds to unsaturated zone; i.e., there is not a large stock of water in the deep pores that can subsequently emerge at the

edges of the stack (Pérez-López et al., 2016). On the other hand, the larger the disposal area, the greater the number of secondary tidal channels covered by the stockpiled waste (Fig. 2), and therefore, the greater the hydraulic connection between the estuary and the zone, which could explain a greater number of edge outflows. The average flow found during the warm-dry periods was 0.2 L/s, with rates commonly comprised between 0.1 and 1.5 L/s. These values were only slightly higher during the rainy period (0.1–2.0 L/s, average of 0.4 L/s). These slight differences in the flow measured between the different periods studied could be because sampling was not carried out strictly during the rainy events, leaving a time lapse of at least 10 days for security reasons as stated before. Therefore, taking into account the hydraulic response of the stack, the flows found during the rainy period were probably measured during a period of the water-table recession after rainfall events, where the water-table state of the stack was close to the pre-rainfalls conditions.

Phosphogypsum edge outflows are characterized by high acidity and EC values, as well as by containing high concentrations of potentially toxic metal/loids (Tables S1-S4). With respect to zone 1, the sample resulting of the interaction of phosphogypsum and seawater displayed a lower acidity and pollutant concentration than the edge outflows released from the other disposal areas of the stack, with values oscillating between samplings depending clearly on the degree of tidal influence (Table S1). The edge outflows of zone 2 showed the highest acidity and pollutant concentrations, irrespective of the sampling period. Thus, these acid leachates displayed high concentrations of pollutants, such as PO_4 , F, Al, Zn and As (average values of the four sampling ranging between 16,444 and 32,633 mg/L, 696–943 mg/L, 75–120 mg/L, 33–44 mg/L and 16–20 mg/L, respectively) and to a lesser extent of Cu, Cd, Cr, Ni, Sb and U (Figs. 3 and 4). On the other hand, the edge outflows emerging from zone 3 showed both slightly lower pH values and higher pollutant concentrations than those found in the zone 4, reaching values up to 2 to 3 times higher for PO_4 and metal/loids such as Al, Cu, Cr, Ni, Cd, As and U (Tables S3 and S4). On the contrary, the leachates of zone 4 showed average concentrations of SO_4 and Fe higher than the rest of the edge leachates (Fig. 3). The dissolved concentrations of the main contaminants (i.e., Fe, Al, Zn, As, Cu, Cd, Cr and Ni) in the edge outflows emerging from the phosphogypsum stacks were between 1 and 3 orders of magnitude higher than those measured in solutions resulting from leaching experiments, where phosphogypsum waste samples were reacted with distilled water and organic solvents (average values of 3.01 and 1.40 mg/L for Al, 0.65–0.34 mg/L for Zn, 0.37–0.19 mg/L for As, 0.25–0.01 mg/L for Fe, 0.10–0.01 for Cu, Ni, Cd and Cu; Macías et al., 2017). This important difference in the contaminant concentrations is probably due to the short period of interaction time of the phosphogypsum wastes with the extracting solutions (i.e., 18 and 24 h for the leaching experiment with the organic solvent and with distilled water, respectively) and the solid: liquid ratio, which is noticeably higher (1:20 and 1:10) in the case of the leaching tests.

3.3. Restoration measures influence on the edge outflows hydrochemistry

The dissimilarities observed in the concentration of pollutants of the edge leachates between the different zones of the stack could be due to a combination of several factors such as the dumping history of phosphogypsum in each of the disposal areas, the morphodynamic domain of the estuary in which each zone is located and the preliminary restoration actions to which some zones have been subjected (Papaslioti et al., 2018; Pérez-López et al., 2016, 2018). Thus, the higher concentrations of pollutants observed in leachates from zone 2 than those from zones 3 and 4 would be closely related to the dumping history in this zone, since zone 2 is the only disposal area in which phosphogypsum was transported from the industry using the recirculated and evaporated process water with the closed-loop system installed after 1997 (see Section 2.1). On the other hand, the vegetation cover spread in zone 4 as a restoration

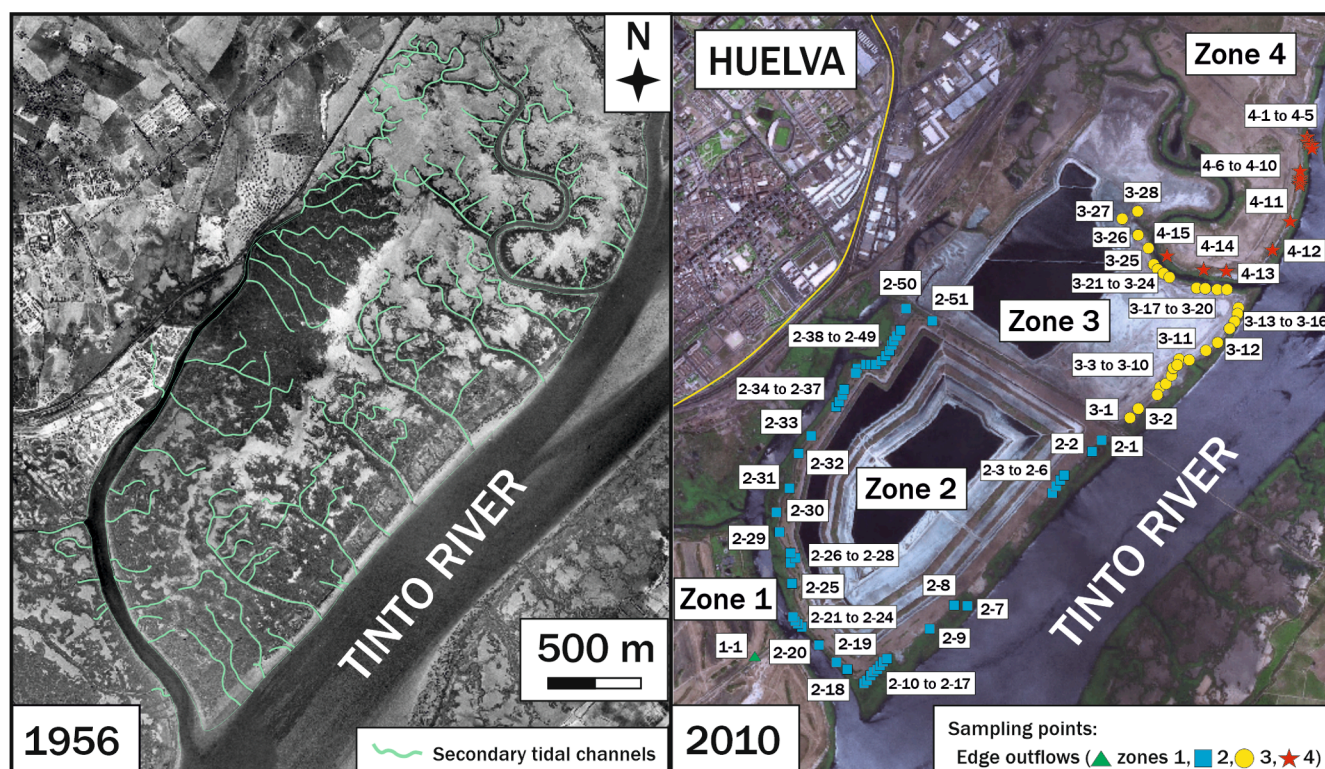


Fig. 2. Overlay of aerial images of the marshes occupied by the phosphogypsum stack. Before starting the waste deposition (1956) and after finishing the deposition of phosphogypsum (2010).

measure could explain the lower concentrations of most pollutants in this zone than in the non-restored zones (Table 1). This is because the topsoil layer could be favoring sulfate-reduction processes and therefore the precipitation of metal sulfides, which would cause the removal of part of the pollution contained in the pore-solutions (Castillo et al., 2012; Pérez-López et al., 2018). This hypothesis becomes more relevant when comparing zones 3 and 4, since the phosphogypsum was deposited in a similar way in both zones using an open circuit system with seawater but zone 4 has undergone further restoration. Moreover, the zone 3 is currently naked and exposed to weathering with a large surface pond storing process water. The contribution of the process water infiltration to the composition of the edge leachates that emerge in this zone of the stack, although minimal (around 9% calculated using stable isotopes; Papaslioti et al., 2018), could also explain the slightly higher concentrations observed in the leachates collected in zone 3 with respect to zone 4 (Table 1). On the other hand, a higher fluvial influence in the edge leachates of zone 4 could explain the highest average concentrations of SO_4 and Fe measured compared to those found in the other zones. According to Papaslioti et al. (2018), zone 4 of the phosphogypsum stack is closer to the fluvial domain and hence the composition of the leachates that emerge in this zone is more influenced by the Tinto River (around 80–87% determined by stable isotope analysis), which is highly affected by acid mine drainage (AMD), i.e., acidic and sulfate- and iron-rich waters from the leaching of abandoned mining wastes mainly from the Riotinto mines (Cánovas et al., 2021; Nieto et al., 2013).

The influence of the different end-members on the hydrochemistry of edge outflows can be seen in Fig. 5a, where the results of the PCA for variables and samples are shown. Both factors (i.e., F1 and F2) explain 68% of variance and seem to be related to the different origin of pollutants in the outflows. As can be seen, three different groups of elements can be identified; i) those related to seawater, including Na, Cl, Mg, K, Br or SO_4 , ii) those related to the acidic waters of the Tinto River, such as Fe, Sb, Pb, Cu, Zn or As, and iii) those related to phosphogypsum wastewaters such as F, Cr, U, PO_4 , NH_4 and other trace metals. However,

It is not surprising that some elements (e.g., As or Zn) are common between the different groups, taking into account that the edge outflows originate from the leaching of the phosphogypsum stack with water of estuarine origin. Thus, the closeness of each sample to the different end-members (i.e., seawater, process water and Tinto River water) would define the level of influence of each end-member in these samples (Fig. 5b).

3.4. Seasonal variability of the edge outflows hydrochemistry

As mentioned above, the Huelva phosphogypsum stack behaves as an anthropic aquifer with numerous springs releasing large amounts of pollutants to the Ría de Huelva estuary. These edge outflows showed low hydrochemical variability under the different hydrological conditions studied, i.e., warm-dry period, rainy period and beginning of warm-dry period after rainy events (Figs. 3 and 4). However, small fluctuations can be observed during the different scenarios. Thus, the lowest pH values measured in the leachates from zones 2 and 3 occurred in the warm-dry periods (i.e., May–June 2014 and 2015) (average of 1.83–1.98 and 1.90–2.12, respectively), while the highest values were measured in the rainy period (average pH values of 2.17 and 2.31, respectively) and beginning of warm-dry period after rainy events (average pH values of 2.04 and 2.18, respectively). On the other hand, the pH values of the leachates from zone 4 remained almost constant during the different seasons, with average values between 2.21 and 2.27. The restoration measures implemented in this area likely minimize the infiltration of rainwater.

Regarding the seasonal variability in the concentrations of pollutants, these can be broadly classified into two groups according to their behavior during the different hydrological conditions. On the one hand, a group that includes most contaminants (e.g., PO_4 , F, Al, Zn, Cr, Ni, As, Cd, Sb or U) whose dissolved concentrations decrease during the rainy period (i.e., November 2014) as a result of a dilution effect due to the recharge of rainwater (Figs. 3 and 4). On the other hand, a group that

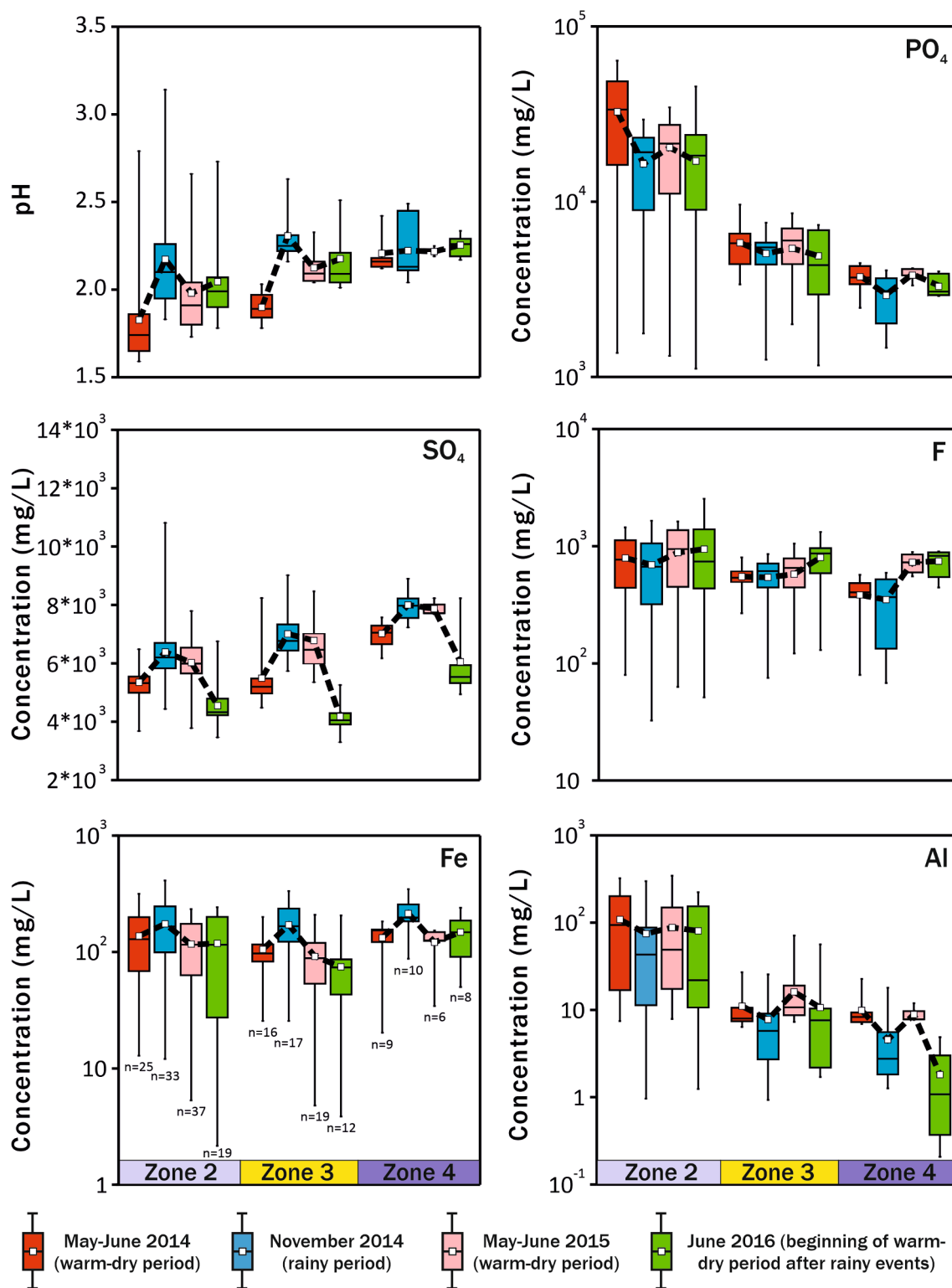


Fig. 3. Box and whisker plots of pH and anions and major cations concentrations in the different sampling campaigns (May-June 2014 and 2015 (warm-dry periods), November 2014 (rainy period) and June 2016 (beginning of warm-dry period after rainy events)). Boxes represent 25th and 75th percentile range, while the horizontal lines at the whiskers ends depict the maximum and minimum values. The median and mean are represented by a horizontal line and a square, respectively, inside the boxes.

comprises pollutants such as SO₄ and Fe, which suffered an increase in the concentrations measured during the rainy period compared to the values analyzed in the leachates collected during the previous warm-dry period (i.e., May-June 2014) (Fig. 3). This increase in concentration of SO₄ and Fe observed during the rainy season is due to the increasing

concentration of these dissolved pollutants in the Tinto River as a consequence of the washout of sulfate evaporitic salts, which are formed along the riverbanks and mine sites, mainly during the summer months and between rainfall events during warm-dry springs (Cánovas et al., 2021; Olías et al., 2006). The dissolution of these minerals together with

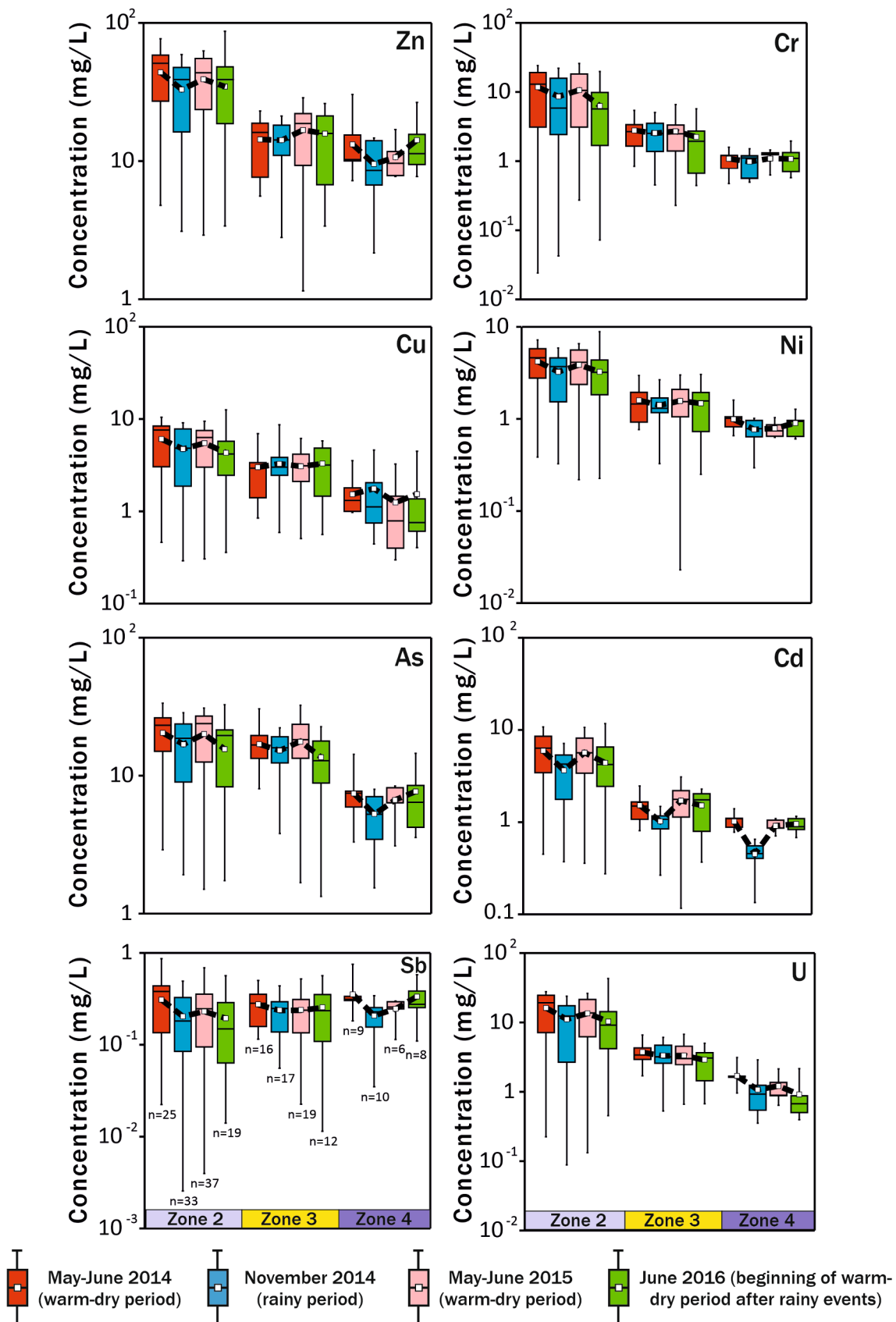


Fig. 4. Box and whisker plots of minor cations concentrations in the different sampling campaigns (May-June 2014 and 2015 (warm-dry periods), November 2014 (rainy period) and June 2016 (beginning of warm-dry period after rainy events)). Boxes represent 25th and 75th percentile range, while the horizontal lines at the whiskers ends depict the maximum and minimum values. The median and mean are represented by a horizontal line and a square, respectively, inside the boxes.

Table 1
Compilation of the physicochemical parameters and concentration of contaminants of the edge outflows collected in the unrestored zones 2 and 3 and restored zone 4 during the different sampling campaigns.

	pH	EC (mS/cm)	Eh (mV)	PO ₄ (mg/L)	SO ₄ (mg/L)	F (mg/L)	Cl (mg/L)	Fe (mg/L)	Al (mg/L)	Zn (mg/L)	As (mg/L)	Cu (µg/L)	Cr (µg/L)	Cd (µg/L)	Ni (µg/L)	Sb (µg/L)	U (µg/L)
Unrestored zones																	
Zone 2																	
Minimum	1.59	19.2	178	833	3466	32.6	4308	2.32	0.97	2.91	1.50	290	24.1	276	218	2.55	88.2
Maximum	3.14	73.7	377	63,741	10,814	2541	27,081	411	344	86.9	33.6	12,604	25,970	11,762	8857	865	43,109
Mean	2.01	38.3	294	21,367	5736	820	11,282	140	93.8	37.6	18.5	5168	9561	4939	3661	234	12,847
Median	1.95	36.1	295	20,800	5822	783	9150	134	53.3	42.2	21.4	5552	8494	4794	3878	244	1239
Percentile 25	1.83	31.9	281	10,255	4995	421	6597	64.2	15.0	20.4	12.1	2648	2594	2429	1945	82.8	4946
Percentile 75	2.11	46.2	306	27,462	6347	1246	15,882	198	151	51.7	25.4	7763	16.9	6869	5363	362	2126
SD	0.30	12.0	22.0	13,790	1078	505	5588	89.8	102	19.5	10.3	2953	7646	2943	1927	169	9114
Zone 3																	
Minimum	1.78	18.6	245	1037	3304	75.3	7934	3.85	0.93	1.15	1.33	506	229	116	22.9	11.4	297
Maximum	2.63	85.9	345	9617	9021	1324	25,441	333	70.9	28.8	32.4	8684	6577	3085	3051	564	6755
Mean	2.13	37.6	282	5339	6093	590	14,781	113	11.6	15.1	16.1	3156	2531	1448	1466	252	3315
Median	2.09	33.5	280	5794	5959	613	12,296	97.0	8.60	16.1	16.7	3106	2483	1460	1424	248	3188
Percentile 25	2.01	28.3	274	4206	4967	453	10,843	74.3	6.62	8.20	12.6	1592	1387	1047	1040	152	2371
Percentile 75	2.24	41.7	286	6575	6964	773	18,223	154	13.4	20.0	19.6	4187	3403	1846	1905	345	4405
SD	0.20	15.1	15.5	1968	1536	275	5928	67.7	11.3	6.47	6.19	1716	1500	603	640	132	1559
Restored zone																	
Zone 4																	
Minimum	2.04	30.4	230	1465	4938	67.9	8143	20.2	0.20	2.16	1.53	298	475	134	295	34.9	354
Maximum	2.49	78.2	298	4465	8897	900	16,575	347	22.7	30.3	14.3	4611	1859	1400	1599	752	4192
Mean	2.23	45.6	265	3325	7571	499	14,616	159	6.27	11.9	7.67	1551	1433	813	866	286	1327
Median	2.22	44.5	265	3385	7557	513	13,711	154	6.42	10.3	7.88	1119	1207	863	869	271	1217
Percentile 25	2.13	36.0	260	2907	6822	368	11,154	123	2.24	8.19	5.75	751	863	562	683	237	724
Percentile 75	2.31	48.4	272	3847	8080	665	15,596	196	8.30	14.9	9.36	1803	1411	1092	1011	334	1657
SD	0.12	12.7	12.5	739	1734	245	5523	66.5	5.01	5.53	3.24	1178	907	290	236	134	843

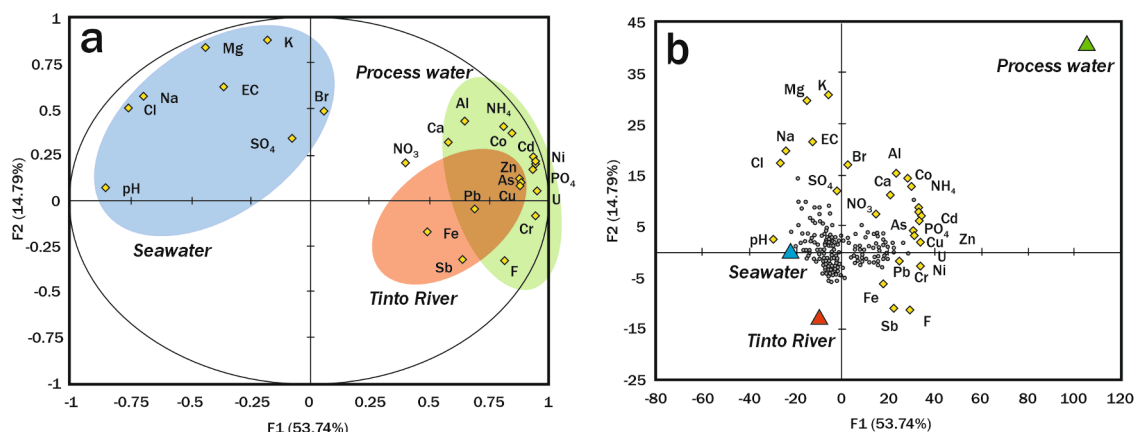


Fig. 5. Principal component analysis (PCA) variables (a) and samples (b), including the main end-members (i.e., Tinto river, process water, and seawater) responsible of hydrochemical variability of edge outflows.

the sweeping of sulfide oxidation products from mine sites lead to increasing metal concentrations in river waters entering the estuary. As mentioned above, there is a hydraulic connection between the estuary and the stack, and therefore it seems reasonable to think that certain variations in the hydrochemistry of the estuarine water could be reflected in the chemical composition of the discharges from the phosphogypsum stack.

In order to study the significance of seasonal hydrochemical variations of edge outflows, a statistical test was performed on samples collected during the rainy and dry seasons. As variables did not exhibit a normal distribution, the non-parametric test of Wilcoxon was selected, applying both the signed test and the Wilcoxon signed-rank test. The signed test compares the number of exceeding cases between populations without considering the magnitude of these differences, while the Wilcoxon signed-rank test considers this magnitude (Table S5). As a result, a spatial pattern was observed considering the seasonal differences noticed between the dry and rainy periods; the closer to the river the higher statistical differences in variables were recorded. For instance, the zone 4, the closer to the Tinto River, exhibited significant statistical differences for As, Ni, Co, U, Sb, Cd, Fe, SO₄, Zn, Al, Ca, and PO₄, between both periods. Only some metals such as Cr, Pb and Cu, together with F, Cl and pH showed similar distributions in both periods. In the case of zone 3, located downstream to the ocean, statistically significant differences were only observed for pH, Fe, SO₄, Sb, Al and Ca, while PO₄ showed only significant differences in the signed test. The zone 2, the farther area from the river (excluding zone 1, with only one sample), exhibited the lower number of variables displaying statistically significant differences for pH, Al, Ca, SO₄ and Fe, although in the latter two variables these differences were only observed in the signed test. These results supports previous findings about the control exerted on the hydrochemical spatial variations of edge outflows by the closeness to the Tinto River and its variability along the year. In addition, the phosphogypsum stack contaminates the surrounding system, causing disturbances in the estuary and the aquatic biota. For this reason, a continuous monitoring is highly recommended to evaluate if these disturbances are temporary or permanent.

4. Environmental implications

According to the hydrological response of the phosphogypsum stack, it can be considered as an anthropogenic aquifer with a similar hydrogeological behavior than coastal karstic aquifers. In fact, karstic features are widely recognized in phosphogypsum stacks worldwide (Lottermoser, 2010). Arfib and Charlier (2016) proposed a hydrological conceptual model for coastal karst aquifers divided into three reservoirs (deep, slow and fast), which could be adjusted to the results observed in

the current study (see Fig. 1). The deep reservoir would be characterized by brackish water, with low variations of discharge. This reservoir would represent the storage function of the aquifer, with a long residence time, strongly affected by saline intrusion. Under these circumstances, the water-level shows a low variability most of the time only controlled by tidal oscillations. In these prevailing conditions, waters may move by diffuse slow flow through the primary porous matrix which could supply the spring during low-flow period. On the other hand, both the slow and the fast reservoirs would be characterized by freshwater input. The slow reservoir would represent the storage and the recession after rainfall events, whereas the fast reservoir would be characterized by a rapid infiltration and transfer through the aquifer during rainy events. Under these circumstances, the water quickly enters and emerges from the stack likely through large karst channels caused by gypsum dissolution.

Regarding the hydrochemical behavior of leachates from the phosphogypsum stack, it is worth highlighting the low variability (although statistically significant in some cases) showed by these highly acidic and polluted waters under different hydrological conditions. However, it is of critical importance to sample in safe conditions the stack immediately after intense rainfall events, when a rapid discharge is observed and sharper hydrochemical differences would be expected. Thus, the results reported in this study have positive implications in the design of potential effective remediation treatments, since notable fluctuations in flow rates and pollutant load can cause operational problems in the treatment systems.

The findings obtained allow calculating the pollutant load that finally reaches the Ría de Huelva estuary with some reliability given the observed chemically homogeneous response throughout the system. Thus, an overall approach has been performed to calculate the metal loads released by the stack in each sampling period. To obtain the values in each sampling, the average concentrations of all the sampling points and the bulk discharge have been used. Considering all the edge outflows located around the perimeter of the phosphogypsum stack, a bulk discharge of acid leachates of around 500,000 m³/yr has been estimated. However, these results may be underestimated due to the existence of diffuse edge outflows that are difficult to measure. These leachates release enormous amounts of pollutants to the estuary, e.g., PO₄, F, Fe, Zn, As, U, Cu, Cd and Ni (average values of 5000 t/yr, 300 t/yr, 76 t/yr, 11 t/yr, 6.9 t/yr, 3.0 t/yr, 1.7 t/yr, 1.1 t/yr and 1.0 t/yr, respectively) (Table 2). Nevertheless, this estuarine environment is also affected by the Odiel and Tinto Rivers and their acidic and metal-rich waters due to AMD discharges from abandoned mining districts in the Iberian Pyrite Belt (IPB) (Nieto et al., 2013). In this sense, Table 2 also shows the average pollutant loads contributed by both rivers in the periods 1995–2003 (Oliás et al., 2006) and 2004–2006 (Nieto et al.,

Table 2

Comparison of the average pollutant loads released by the phosphogypsum stack into the Ría de Huelva estuary with the discharges from the mining activity in the IPB during the period 1995–2003 (Oliás et al., 2006)^a and during the period 2004–2006 (Nieto et al., 2013)^b, plus the effluents poured by the factories of the 21 Huelva industrial complex between 2003 and 2006 (Pérez-López et al., 2011)^c. In addition, this table shows the contribution (%) of the pollutant load from the stack that reaches the estuary with respect to the total.

	Phosphogypsum stack (t/yr)	AMD ^a (t/yr)	AMD ^b (t/yr)	Industrial estate ^c (t/yr)	Phosphogypsum stack contribution (%)
PO ₄	5000	–	–	–	–
F	300	–	–	–	–
Fe	76.3	7922	1719	10.7	0.95–4.21
Zn	10.5	3475	649	3.39	0.32–1.66
As	6.86	35.5	1	0.23	16.2–84.9
U	2.96	–	–	–	–
Cr	2.27	–	–	0.04	–
Cu	1.67	1721	412	–	–
Cd	1.13	11.0	3	0.03	9.07–26.6
Ni	1.00	36.2	5	0.20	2.67–16.1

2013). The results reported by these authors indicate a high variability in the average pollutant load transported by the Odiel and Tinto Rivers, associated to hydrological variations between periods. Comparing both sources of contamination, i.e., phosphogypsum leachates and AMD-affected Tinto and Odiel rivers, the phosphogypsum stack would be responsible for an average contribution of 16–85% of As, 9–27% of Cd, 3–16% of Ni, 1–4% of Fe and 0.3–2% of Zn of the total discharge reaching the estuary. In addition, as mentioned above, an important industrial complex is located in the Ría de Huelva estuary. Different industrial activities developed in this complex can also discharge metal-rich effluents directly into the estuary (Pérez-López et al., 2011). In this sense, these authors calculated the average pollutant load from the Huelva industrial complex between 2003 and 2006 (no current data available). This value was much lower than that contributed by the Tinto and Odiel rivers, exhibiting values of one to two orders of magnitude lower for most of the pollutants (Table 2). However, Pérez-López et al. (2011) did not contemplate in the study the contribution of pollutants to the estuary from the phosphogypsum stack as a pollution source also of industrial origin. The capacity of contamination of the phosphogypsum pile is more significant taking into account that its extension is three orders of magnitude lower than the area of the fluvial basins (i.e., around 3979 km²). In addition, some of the pollutants (e.g., PO₄, F and U) discharged into the estuary from the phosphogypsum stack are negligible in the mine waters. For these reasons, the treatment of effluents from the phosphogypsum stack is essential to minimize the pollution that reaches the Ría de Huelva estuary. In this sense, the application of passive Dispersed Alkaline Substrate (DAS) technology for highly acidic and contaminated phosphogypsum leachates has shown to be highly effective in reducing the pollutant load and acidity (Millán-Becerro et al., 2020, 2022).

5. Conclusions

The results obtained in this study clearly indicate that the Huelva phosphogypsum stack behaves as an anthropic aquifer with karstic features. This aquifer shows two feeding ways; a continuous recharge of estuarine water in the deep zone of the stack, where phosphogypsum and marsh soil are directly in contact, and a punctual recharge by rainwater that infiltrates through the surface of the phosphogypsum stack and circulates through dissolution conduits. Thus, the water-table of this aquifer is controlled mainly by tidal fluctuations, showing low variability most of the time (± 2 cm). However, the water-table of the stack rapidly increased up to 20 cm during the rainy events studied. Just after rainfall events, around half of the height increased by the water-table is instantly recovered, while pre-rainfalls conditions are reached

within a period between 5 and 15 days depending on rainfall intensity.

Edge outflows sampled around the whole perimeter of the phosphogypsum pile show generally low hydrochemical variability under different hydrological conditions. However, small variations in pollutant concentrations have been observed during the different periods. The mechanisms responsible for such variations are; on the one hand a dilution by rainwater recharge during the rainy period, which cause a slight decrease in concentration of most dissolved contaminants (e.g., PO₄, F, Al, Zn, Cr, Ni, As, Cd, Sb or U) observed in the edge outflows; and on the other hand, the dissolution of the sulfate evaporitic salts precipitated during the summer along the banks of the Tinto River and mine sites, which cause an increase in the dissolved concentration of SO₄ and Fe in the river water and subsequently in the leachates released from the phosphogypsum stack during the rainy season.

The stack releases high concentrations of pollutants such as PO₄, F and U (average values of 5000 t/yr, 300 t/yr and 3.0 t/yr, respectively), which are only found in phosphogypsum leachates. In addition, between 16 and 85% and 9–27% of the total content of As and Cd, respectively, that reach the Ría de Huelva estuary come from the phosphogypsum stack.

CRedit authorship contribution statement

Ricardo Millán-Becerro: Investigation, Data curation, Writing – original draft, Visualization. **Rafael Pérez-López:** Funding acquisition, Methodology, Writing – review & editing. **Carlos R. Cánovas:** Funding acquisition, Project administration, Writing – review & editing. **Francisco Macías:** Funding acquisition, Conceptualization, Writing – review & editing. **Rafael León:** Investigation, Data curation.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.jhydrol.2022.128943>. These data include Google maps of the most important areas described in this article.

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