



Tracing acid mine drainage from an accidental spill on the Estuary of Huelva (SW Spain)[☆]

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ABSTRACT

The Estuary of Huelva in southwestern Spain is severely impacted by acid mine drainage (AMD), primarily due to extensive mining activities in the Iberian Pyrite Belt (IPB), and to a lesser extent by industrial sources. The AMD has led to significant contamination of the Odiel and Tinto rivers, which carry high loads of metals into the estuary. In May 2017, an accidental spill occurred at La Zarza mine, releasing approximately 270,000 m³ of acidic water contained in a pit lake. This event increased the contamination levels in the Odiel River and subsequently in the Estuary of Huelva and the Atlantic Ocean. The current focus of our investigation is to understand the geochemical behavior of contaminants during estuarine mixing and evaluate the environmental impact of the spill, from the river to the littoral. Key findings include the chronic exposure of the estuary to mining pollutants, with specific contaminants escaping retention processes and altering the metal background levels in the Gulf of Cádiz. This study highlights the need for effective control measures in historical abandoned mining districts worldwide to prevent similar environmental disasters in the future.

1. Introduction

Acid mine drainage (AMD), a process primarily associated with massive sulfide as well as coal mining, is one of the main causes of water pollution worldwide (Nordstrom, 2011). Sulfides are stable under reducing conditions; however, sulfide oxidation under atmospheric conditions releases acidity, sulfates, iron, and other metal(loid)s into solution, affecting the quality of surrounding water bodies. The Odiel and Tinto rivers (SW Spain) are located in the Iberian Pyrite Belt (IPB), which contains some of the largest massive sulfide deposits in the world (Sáez et al., 1999). Mining activities in the IPB, especially since the second part of the 19th century, have left a legacy of over a hundred abandoned mining districts, including open pits, underground workings, and enormous volumes of AMD-producing wastes. Consequently, the Odiel and Tinto river basins are severely affected by AMD; i.e., around 427 km of the Odiel fluvial network (37 % of the water courses) and the entire main course of the Tinto River (Cánovas et al., 2007; Sarmiento et al., 2009). As a result, the Odiel and Tinto rivers maintain low pH

values (median value of 3.5 and 2.7, respectively; Cánovas et al., 2007) throughout the year and carry high loads of metals to a common estuary known as Ría de Huelva (Olías et al., 2006; Nieto et al., 2013). Since the late 20th century, it has been well established that the low pH and high concentrations of pollutants in river waters are characteristic of AMD, directly linked to the oxidation of sulfide minerals in the IPB (Elbaz-Poulichet and Leblanc, 1996). Subsequent studies have further reinforced this connection by using various geochemical tracers such as rare earth elements (Pérez-López et al., 2010), specific ion ratios (Cánovas et al., 2018) and stable isotopic analyses (Packman et al., 2023). In the Estuary of Huelva, a series of geochemical reactions derived from neutralization by seawater retain some contaminants such as Fe, Pb and Al, but others escape the retention processes reaching the Atlantic Ocean (Papastlioti et al., 2024). Thus, the estuary suffers from chronic exposure to pollution from abandoned mines, leading to an enrichment of dissolved metals in the seawater of the Gulf of Cadiz shelf, with metal speciation in the water column and comparisons to non-impacted sources further confirming that the Tinto and Odiel rivers

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are the primary contributors to these pollutant anomalies (Van Geen et al., 1997; Elbaz-Poulichet et al., 2001). In addition, the estuary is affected by a secondary pollution source from huge phosphogypsum stacks produced by the phosphate fertilizer industry in adjacent areas, which were disposed directly on the estuarine marshes of Tinto River. Indeed, highly acidic and contaminated leachates are discharged, contributing significantly to the contamination of the estuarine environment (Millán-Becerro et al., 2023).

In this context of perennial pollution of the environment, approx. 270,000 m³ of acidic waters contained in La Zarza pit lake were accidentally released in May 2017, after the rupture of a concrete plug in an old gallery connected to such pit. Thus, enormous amounts of pollutants quickly reached the Odiel River and subsequently the Estuary of Huelva and then, presumably, the Atlantic Ocean. More information regarding the accidental spill from La Zarza, with especial focus on its influence on the river concentrations, can be found elsewhere (Olías et al., 2019). In this sense, large accidental spills can occur due to the lack of control measures in mining facilities, especially in abandoned districts, causing a severe impact on the environment as well as human health (e.g., Hudson-Edwards, 2016). Some cases of mine tailing dam failures and collapse of galleries in abandoned mines have been reported worldwide leading to the release of large amounts of water and pollutants into the environment (e.g., Grimalt et al., 1999; Younger, 2002; Macklin et al., 2003; Kossoff et al., 2014; Bureau of Reclamation, 2015; Hudson-Edwards, 2016). The failure of the tailing dam at the Aznalcóllar mine (SW Spain) in 1998 released around 6 million m³ of pyrite sludge and acidic waters and caused a huge environmental disaster in the Agrio and Guadiamar rivers, which empty into the wetlands of the Doñana National Park, an area of enormous ecological value (Olías et al., 2021). The accident of Baia Mare (Romania) in 2000 released 0.1 million m³ of toxic wastes, containing tons of Cu, as well as other metals, and cyanide, which reached the Szamos and Tisza rivers, important tributaries of the Danube River (Soldán et al., 2001). More recently, in 2014, a partial embankment breach of the Mount Polley tailings dam in British Columbia (Canada) led to the release of around 25 million m³ of mine tailings and water into the Quesnel river watershed. However, the concentration of pollutants was much lower than those released during the Aznalcóllar collapse. Some of the accidental spills can even reach the sea. For instance, in 2015 the Fundão Dam break released millions of tons of metal-rich tailings into the Doce river basin, causing catastrophic damage and potential ecological effects that reached the Atlantic Ocean (e.g., Neves et al., 2016; Segura et al., 2016; Wanderley et al., 2016). This episode caused likely the biggest environmental disaster of this kind in the world. However, geochemical reactions involved during mixing between mine spills and seawaters have not been addressed still in detail.

The accidental spill from La Zarza affected a river already contaminated by abandoned mining, resulting in a significant increase of pollutants transported and discharged into the estuary (Olías et al., 2019). Studying geochemical tracers, such as Rare Earth Elements (REE) fractionation, can serve as a reliable proxy for assessing acid drainage pollution in environmental systems (Delgado et al., 2012; Wu et al., 2024). Nevertheless, the application of geochemical tracers may be less effective for identifying an accidental AMD spill in systems that are already chronically and strongly impacted by AMD. Moreover, real-time monitoring of the mixing of the accidental spill with the sea could fill a knowledge gap in the current literature. Thus, the main objectives of this study are: (1) to elucidate the behavior of contaminants from the accidental spill from La Zarza during its mixing with seawater in the Estuary of Huelva, (2) to verify the effect of the accidental spill on the background levels of contaminants related to the chronic inputs received by the estuary from legacy mining, and (3) to study the effect of the spill on the concentration of contaminants reaching the Atlantic coastal waters.

2. Study area

The La Zarza mine, located in the Spanish part of the IPB (37°42'35"N, 6°51'10"W), was the third largest mine in this sector with a total production of 40–45 million tons of ore (Pauwels et al., 2002). Its localization can be consulted at KML file - Google Earth™ of the Supplementary Information (SI). This mine was exploited, like other mines in the IPB, since pre-Roman and Roman times (Olías and Nieto, 2015), which is evidenced by the existence of Roman shafts and galleries (Pinedo Vara, 1963). The most important of these galleries were La Algaida (1800 m long) and Los Cepos (800 m long) (Olías et al., 2019). Modern exploitation began in 1853 through the chamber and pillar method until it became open-pit mining in 1888. By 1920, the open-pit had reached a depth of about 130 m, and open-pit exploitation ceased, although underground mining continued using the cut and fill method, reaching depths close to 300 m. In the 1980s, a severe crisis due to a sharp drop in demand for mineral led to the gradual closure of mines in the IPB. Mineral extraction in La Zarza mine ended in 1991, although acid water pumping operations continued until 1995 to prevent from water table rising. In the 1990s, some remediation actions were undertaken along the Odiel river basin with little success (Sainz et al., 2003), including the concrete plugging of the Los Cepos gallery. The water level in the pit lake over time rose by more than 52 m from 2002 to 2016, with an average value of 3.8 m/yr. Since 2011, the water level was higher than the Los Cepos adit, thus, the pressure exerted by the stored water caused the breakage of the concrete plug of Los Cepos gallery on May 17th, 2017, resulting in the release of around 270,000 m³ of extremely polluted waters, equal to one-seventh of the water volume stored in the pit lake. The discharge flowed approximately 4 km through the Mojafre Stream before reaching the Olivargas River, which flows into the main course of the Odiel River approximately 300 m downstream. The composition of the water released during the spill revealed rather high concentrations of toxic metal(loid)s: up to 2883 mg/L of Fe, 624 mg/L of Al, 208 mg/L of Mn, 139 mg/L of Zn, 125 mg/L of Cu, 6.75 mg/L of As, 5.83 mg/L of Co and 4.53 mg/L of Ni (Olías et al., 2019). These concentrations are similar to the water composition stored in La Zarza pit lake (Sánchez España et al., 2008). The total load of pollutants released during the spill has been calculated from the estimated volume of water spilled and the dissolved concentrations, reaching around 780 ton of Fe, 170 ton of Al, and 1.8 ton of As, as well as other significant concentrations of potentially toxic elements such as Cd, Cu, Pb and so on (Olías et al., 2019).

3. Methodology

3.1. Sampling

The pollution plume from La Zarza reached the Estuary of Huelva two weeks after the accident. Before entering the estuary, the maximum concentration for most elements was found on May 31st, with registered effects until June 20th (Olías et al., 2019). Accordingly, a sampling campaign was carried out along the Odiel river sub-estuary on May 30th by boat, from the fluvial zone (samples O14 to O1) to the marine zone (samples C8 to C1). Sampling locations can be consulted at Fig. 1 and KML file - Google Earth™ of the SI. Some samples were also taken on May 31st on the nearest coastline within the Gulf of Cádiz (samples F, G, H and S; Fig. 1). In addition, 11 sampling points were also sampled on June 15th. For comparison purposes, another sampling campaign was conducted just one year after the spill, in 2018, following the same procedure. Streamflow data were obtained from a gauging station located at the middle course of the Odiel River. Daily data of rainfall were taken from a weather station located 10 km to the East of La Zarza mine.

Samples were taken at a depth of 10 m using a Van Dorn bottle to minimize contamination from the ship. Values of pH, electrical conductivity (EC), oxidation-reduction potential (ORP), and temperature

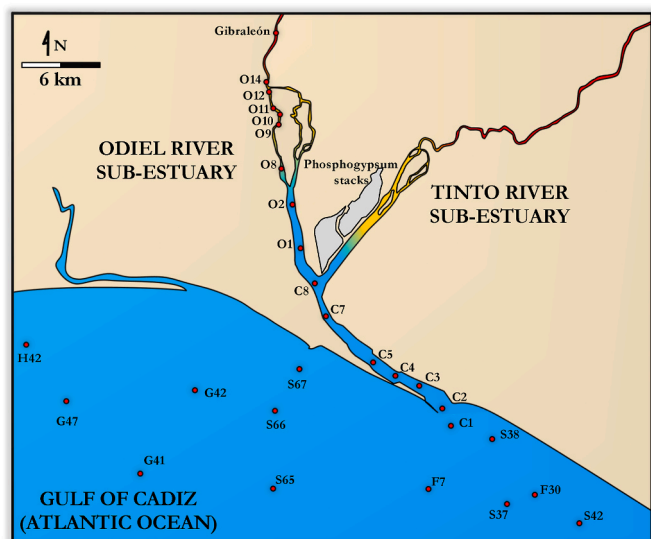


Fig. 1. Sketch map of the Estuary of Huelva, showing sampling points along the Odiel river sub-estuary and the nearest coastline within the Gulf of Cádiz for all the sampling campaigns. The pH gradient is represented by colors, from red (approx. 2.5) to blue (approx. 8.0). (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

were measured on-site using a Crison MM40+ portable multiparameter device. Calibration of field instruments was conducted with standard solutions. Each sample was divided into two acidified aliquots: one filtered through 0.45 μm filters for cation analysis in the dissolved fraction, and another unfiltered for analyzing cation concentrations in the total fraction (dissolved + particulate). A third aliquot was filtered but not acidified for anion analysis. Full details about the methodology can be found in [Papaslioti et al. \(2024\)](#).

3.2. Chemical analyses

Major cations were analyzed via Inductively Coupled Plasma-Atomic Emission Spectroscopy (ICP-AES; Jobin Yvon Ultima 2) at the University of Huelva. Trace elements were measured using Inductively Coupled Plasma-Mass Spectrometry (ICP-MS; Thermo Scientific iCAP TQ ICP-MS, using He as collision gas and Ar as dilution gas) at the University of Montpellier (AETE ISO Platform). An internal standard solution (Be, Sc, Ge, Rh, Ir) was used to address signal drift. Accuracy was validated against certified reference materials (SLEW-3 and CASS-6) with results within 10 % of certified values for element concentrations \gg 3 times the detection limits (except for Zn and Cd with results within 20 % of certified values). The detection limits varied from 0.02 to 0.2 mg/L for major elements, while for trace elements, limits ranged between 0.23 $\mu\text{g/L}$ (Zn) and 3.44 pg/L (La). Anions were determined using ion chromatography (Dionex DX-120) at the University of Huelva.

3.3. Modelling

Saturation indices were determined by the PHREEQC code v.3.4 ([Parkhurst and Appelo, 2013](#)) using the WATEQ4F database ([Ball and Nordstrom, 1991](#)) enlarged with thermodynamic data from [Yu et al. \(1999\)](#) for the solubility of schwertmannite. This database relies on extended Debye-Huckel equations and provides accurate activity calculations in chloride dominated solutions with ionic strengths below 1 mol/L. The ORP measurements were corrected to the standard hydrogen electrode to determine Eh values ([Nordstrom and Wilde, 1998](#)). From the end-members (fluvial and marine) in the sampling of the accidental spill of La Zarza, a mixing model was also developed in the estuary using the MIX code ([Carrera et al., 2004](#)). The MIX code is based on a linear

mixing equation, which assumes that the concentration of an element in a mixture is a weighted combination of the concentrations of the end-members involved. The model uses a mixing matrix and solves a system of linear equations to determine the relative fractions of each end-member in the mixture. These fractions are calculated using the measured concentrations in the samples and the known concentrations of the end-members, with the goal of estimating the mixing proportions between freshwater and marine waters at sampling points. This approach is useful in estuarine systems where waters of different origins mix, and it allows for the examination of mixing dynamics based on certain elements with a clearly conservative behavior (Cl, Na, Sr and Li). This information will be used to discern the conservative or non-conservative behavior of the contaminants during the estuarine mixing by comparing the theoretical concentrations of each element with the measured concentrations.

4. Results and discussion

4.1. Input and evolution of contaminants in the estuary

Estuarine mixing processes are mainly controlled by the tidal regime and the river water contribution, which in turn is controlled by rainfalls, especially in drainage basins composed of impermeable materials. The cumulative precipitation during the week prior to sampling was 0.2 mm for the 2017 campaign and 6.6 mm for the 2018 campaign, while the precipitation during the month prior to sampling was 61.2 mm in 2017 and 51.4 mm in 2018. Additionally, the tidal coefficient on the sampling day was 57 in 2017 and 79 in 2018. Mixing dynamics are primarily determined by the tidal coefficient, as it dictates the range of pH variation during mixing. While comparing sampling campaigns with different tidal coefficients presents challenges, the sampling campaigns selected for this study exhibit sufficiently similar tidal coefficients, allowing for reliable comparisons of contaminant behavior. Despite these similarities, the average river flow during the week prior to sampling was three times lower in May 2017 (0.645 m^3/s) than in May 2018 (1.989 m^3/s) probably due to the different precipitation accumulated three months prior to sampling (213.6 vs. 599.4 mm in 2017 and 2018, respectively).

The effect of the La Zarza spill passing through Gibralfaro, just before entering the estuary ([Fig. 1](#)), is evident when comparing pH values (2.56 in 2017 vs. 3.21 in 2018), as well as the concentration of some metals, much higher in 2017, e.g., 177 mg/L of Fe, 113 mg/L of Al, 14 mg/L of Cu, 721 $\mu\text{g/L}$ of Co or 71 $\mu\text{g/L}$ of As ([Table S1](#)). Particularly significant are the concentrations of Fe, As, and Pb, with values 15, 10, and 5 times higher, respectively, during the accidental spill at this point. Other metals such as Ni, Cu, Mn, and Co showed concentrations that were approximately double in 2017. However, elements like Al, Cd, and Zn showed similar values in both sampling periods ([Table S1](#)), indicating that the accidental contribution of these metals is less significant compared to the usual fluvial concentration. The water chemistry of the Odiel River in Gibralfaro is well-documented through weekly sampling covering a wide range of fluvial conditions over several hydrological years; such information has been published in previous studies (e.g., average pH data of 3.76, range of 2.95–5.05; [Nieto et al., 2007](#)). While the values observed one year after the spill in Gibralfaro are in line with historical values, the concentrations during the spill far exceed the maximum values observed in these previous studies, especially for Fe and As. The total concentrations (dissolved plus particulate) of metals in both samplings (May 2017 and 2018) just at the estuary entrance coincide with dissolved concentrations due to the low pH values observed ([Table S1](#)). Consequently, the amount of metals transported to the estuary in particulate form can be considered negligible.

In the Odiel river sub-estuary ([Fig. 1](#)), fluvial water affected by AMD undergoes progressive pH neutralization from acidic river values to alkaline values typical of seawater. The increase in pH is concomitant to a progressive decrease in the dissolved concentration of most

contaminants, mainly due to dilution by mixing with seawater, although precipitation and sorption processes cannot be ruled out for some contaminants. These sharp variations of pH and the behavior of contaminants are chronically observed in both Odiel and Tinto river subestuaries as a consequence of the long-lasting AMD-associated pollution, but were enhanced during the transit of the accidental spill due to higher metal(loid) concentrations. In this context, the Odiel river subestuary can be zoned based on pH and chlorinity values (Fig. 2 and S1): (1) a fluvial influence domain up to 6 km away from Gibraleón, with low pH values (between 2.5 and 4.2) and chloride concentrations (between a few ppm and 12 g/L), (2) a fluvial-marine mixing domain (from 6 to 11 km away from Gibraleón) with intermediate values of pH (from 4.2 to 7.5) and chloride concentrations (from 12 to 18 g/L), and (3) a marine influence domain (> than 11 km away from Gibraleón) with high values of pH (from 7.5 to 8.0) and chloride concentrations (from 18 to 22 g/L). A sharp decrease in metal concentrations is observed during the sampling of May 2017 from the fluvial to the marine domains: from 14,970 to 4.48 µg/L of Fe, from 37,933 to 30.0 µg/L of Al, from 9822 to 9.17 µg/L of Mn, from 6855 to 30.1 µg/L of Zn, from 5149 to 8.73 µg/L of Cu, or from 259 to 0.42 µg/L of Co (Table S1). However, this decrease was not the same for all elements; for instance, it can be observed a decrease of 1780 times for Fe, 1260 for Al, 527 for Cu, 227 for Zn or 80 for Cd, which suggests the existence of geochemical processes leading to these differences. In the next section, we will discuss the hydrogeochemical processes triggered by neutralization during the accidental spill (Figs. 2 and 3) and one year after the spill (Figs. S1 and S2).

4.2. Behavior of contaminants in the estuary

The behavior of contaminants during estuarine mixing can be classified into conservative (i.e., contaminants remain in solution with no participation in chemical reactions) or non-conservative (i.e., contaminants are transferred to particulate material by precipitation/sorption) by comparison between their total concentrations (dissolved plus

particulate) and their dissolved concentrations throughout the estuary. This simple comparison allows us to predict element behavior, avoiding the masking effect of the decrease in concentration due to dilution within the estuary. We could assume non-conservative behavior for an element when the dissolved concentrations decrease both absolutely and relatively (expressed as a percentage) in relation to the total concentration (dissolved plus particulate). The main metal of mining origin and the most contributed to the estuary, namely iron, exhibits a non-conservative behavior (Fig. 2 and S1). Most of the dissolved Fe precipitates during the pH increase in the range of 3.5–5.5, right at the beginning of the fluvio-tidal mixing domain in both samplings. The concentration of Fe in solution probably decreases due to precipitation since Fe passes from being 100 % in the dissolved fraction at the beginning of the fluvial domain to nearly 100 % in the particulate fraction in the marine domain. On the other hand, As exhibits a peculiar behavior. In both samplings, dissolved As concentrations tend initially to decrease by precipitation concomitantly with the decrease in Fe concentration, shifting from being 100 % in the dissolved fraction to reaching a minimum of 50 % by transfer to the particulate fraction. However, at pH values above 6, As concentrations increase again in solution while Fe continues to decrease (Fig. 2 and S1). This increase is particularly significant in the May 2018 sampling, where As concentrations reach 100 % in the dissolved fraction at pH values above 7.5 (Fig. S1). Other elements exhibiting non-conservative behavior include Al, the second most contributed mining-metal to the estuary, along with Pb and to a lesser extent Cu (Figs. 2 and 3, S1 and S2).

Saturation indices provided by the PHREEQC code (Fig. S3) indicate oversaturation across a wide range of pH in estuarine waters with respect to Fe oxy-hydroxysulfates such as schwertmannite. Only samples highly influenced by the river showed oversaturation with respect to jarosite. Concerning Al hydroxysulfates such as basaluminite and alunite only samples with pH between 4.0 and 7.0 showed oversaturation. On the other hand, waters with pH higher than 5.0–6.0 also exhibited slight oversaturation with respect Fe(OH)₃ and gibbsite. Despite the apparent

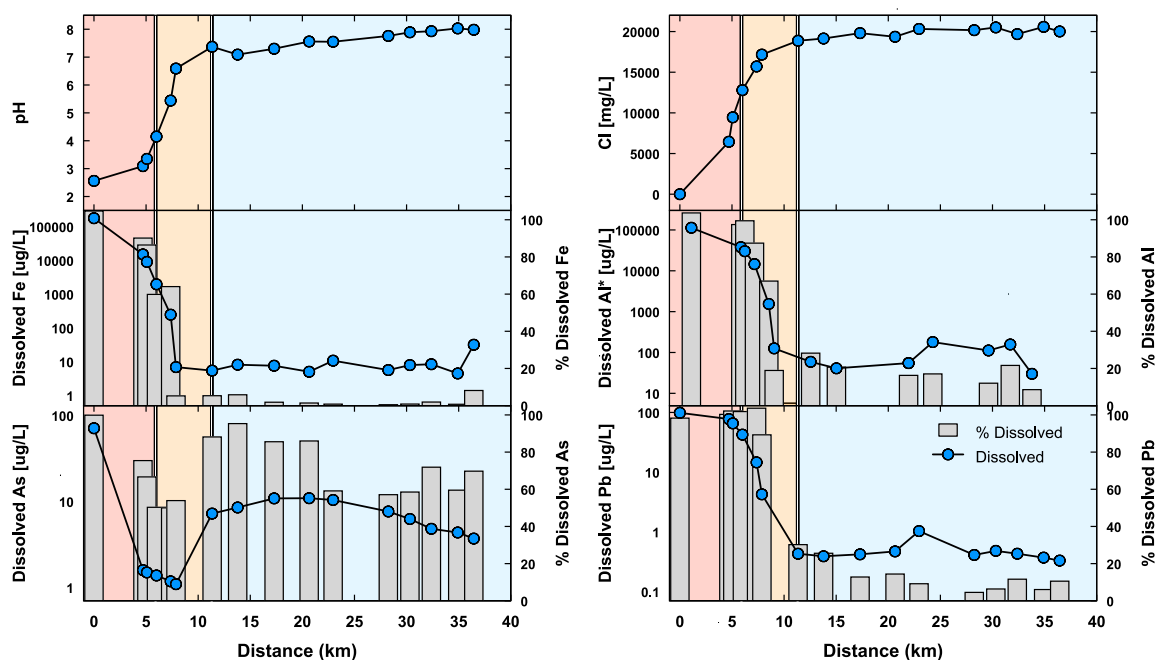


Fig. 2. Evolution of pH and dissolved concentrations (line with blue circles) of Cl, Fe, Al, As, and Pb, as well as dissolved percentages with respect to total (grey bars) of Fe, Al, As and Pb, along the Odiel river sub-estuary during the accidental spill that occurred in May 2017. *Al concentrations were determined by ICP-OES (instead of ICP-MS) with some values below the detection limit. Colour fields refer to fluvial (reddish), fluvio-tidal (orangish) and marine (bluish) domains. Distance varies from km 0 (Gibraleón) to km 36.5 (C1). See KML file in the supporting information. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

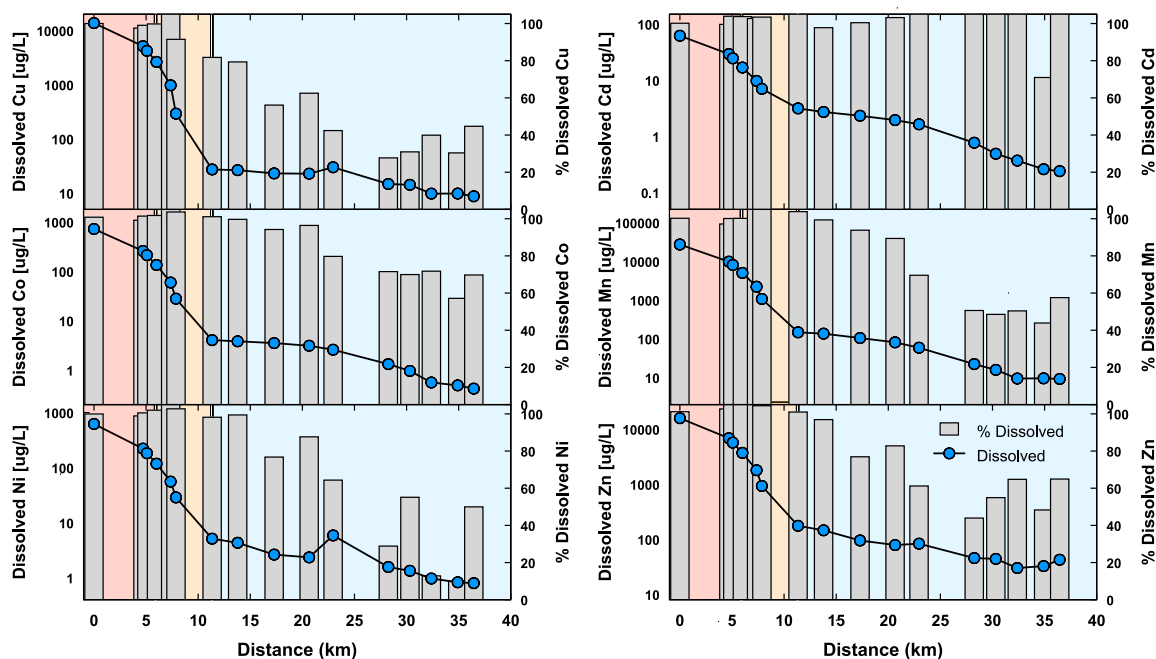


Fig. 3. Evolution of dissolved concentrations (line with blue circles) and dissolved percentages with respect to total (grey bars) of Cu, Cd, Co, Mn, Ni and Zn along the Odiel river sub-estuary during the accidental spill that occurred in May 2017. Colour fields refer to fluvial (reddish), fluvio-tidal (orangish) and marine (bluish) domains. Distance varies from km 0 (Gibraleón) to km 36.5 (C1). See KML file in the supporting information. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

oversaturation of estuarine waters with respect to these phases, schwertmannite and basaluminite appear to be the main Fe and Al minerals formed within the estuary due to the neutralization of acidic river waters with seawater, as supported by mineralogical evidence presented by Cánovas et al. (2022) and Pérez-López et al. (2023). Schwertmannite precipitates at pH 2.0–4.0, while basaluminite forms at pH 4.5–6.0, as a result of two progressive pH buffering stages occurring during the alkaline neutralization of Fe(III)-Al-SO₄-rich AMD solutions through mixing with circumneutral waters, such as clean river water and seawater (Pérez-López et al., 2023; Papaslioti et al., 2024). Both poorly crystalline oxyhydroxysulfates remove Fe and Al from the solution during the neutralization and play an important role in the behavior of other non-conservative elements such as As, Cu, and Pb (Carrero et al., 2017). In fact, the high affinity of schwertmannite for As at acidic pH values is widely known, both in the Estuary of Huelva and in similar acidic environments worldwide (e.g., Carlson et al., 2002; Fukushi et al., 2004; Asta et al., 2010; Parviainen et al., 2015). The retention-release behavior of As must be related to the pH-dependent adsorption capacity of schwertmannite. Under acidic conditions, the surface of schwertmannite becomes protonated and therefore positively charged; whereas the main aqueous species of As correspond to negatively charged oxy-anions across a wide pH range, from acidic to alkaline values. Both aspects explain the high affinity of As for schwertmannite through adsorption. However, the surface of schwertmannite dehydroxylates and becomes negatively charged under alkaline conditions, leading to the desorption of As, which remains negatively charged. The pH value that represents the inflection point between positive and negative adsorption sites for a mineral is known as the point of zero charge (PZC), which is $pH_{PZC} = 7.2$ for schwertmannite (Jönsson et al., 2005). The change in the surface properties of schwertmannite due to increasing pH likely explains the rise in As concentrations in solution during neutralization with seawater. Therefore, despite being apparently non-conservative, significant loads of As may transit across the estuary and reach the marine system.

On the other hand, other elements seem to exhibit a conservative

behavior, that is, the dissolved concentrations match the total concentrations (dissolved plus particulate); and the element remains in solution with no transfer to the particulate fraction by precipitation. Elements with a conservative behavior are Cd, Co, Mn, Ni, and Zn, with around 100 % in the dissolved phase during the fluvial and fluvio-tidal mixing domains (Fig. 3 and S2). The conservative trend of these metals is explained by the formation of aqueous complexes in the studied pH range, which does not favor their partitioning in the precipitated solid phases (Papaslioti et al., 2018). In addition, the potential for adsorption of metals onto Fe minerals is strongly pH-dependent. At pH values below neutrality, the surface charge of precipitated particles and the protonation of their adsorption sites produce repulsion of positively charged free ions such as Cd, Co, Mn, Ni, and Zn (Achterberg et al., 2003; Braungardt et al., 2003). Whereas at slightly alkaline pH, the sorption of these elements to Fe minerals may be inhibited by competition for the adsorption sites of the main cations present in seawater, such as Ca and Mg, which also have a positive charge (Millward and Moore, 1982; Achterberg et al., 2003).

However, a fraction of some of these conservative elements (Co, Mn, Ni, and Zn) seems to partition into the particulate phase in the strictly marine domain (more than 11 km away from Gibraleón), especially in 2017 during the transit of the accidental spill of La Zarza (Fig. 3 and S2). This could be explained by the high concentrations of dissolved Fe that enter the estuary during the accidental spill compared to the usual Fe concentrations in this system (up to 15 times higher, as stated before). In both cases, almost 100 % of Fe is transferred to the particulate phase by schwertmannite precipitation (Pérez-López et al., 2023; Papaslioti et al., 2024); however, the amount of Fe precipitates must have been much more significant during the La Zarza spill. Although the adsorption capacity of positive cations by schwertmannite at alkaline pH is limited by the high competition with other positive cations such as Ca and Mg, as indicated above, given the existence of enormous amounts of flocculated material during the spill, there is a greater possibility of adsorption and retention of metals such as Co, Mn, Ni, and Zn than under normal conditions, explaining why a portion of these metals was found in the

particulate fraction in the marine domain.

However, the previous approach based on the distribution of elements between dissolved and particulate phase in the water column does not consider that particulate matter may settle and/or be resuspended, altering this relationship. For this reason, a mixing model was also developed to confirm the findings previously described. The mixing model for the La Zarza spill was created for the Odiel river sub-estuary section using two end-members: the most fluvial sample (O14) and a seawater sample (S65). Several samples could have been selected as the representative seawater end-member in the mixing model (see Table S1). However, the selected sample was the one that met the following criteria: highest pH and chloride concentration, as these are typical characteristics of seawater, but lowest concentration of metals associated with the fluvial influence of AMD, to minimize the impact of this component on the seawater end-member. This model was used for elucidating and quantifying retention and/or release processes, completely ruling out the decrease in element concentrations due to dilution during mixing with seawater. Conservative behavior would be indicated by values estimated from the theoretical mix between end-members (Y-axis) identical to the measured values (X-axis), plotting the points on a straight line with a unit slope between both end-members (Fig. 4). Measured values below the theoretical values, i.e., above the theoretical mixing line, would indicate non-conservative behavior due to precipitation and/or sorption; while measured values above the theoretical values, i.e., below the mixing line, would indicate non-conservative behavior due to dissolution and/or desorption and/or a third end-member not considered in the mixing process. Calculating

how far each point deviates from the mixing theoretical line allows quantifying the percentage of retention or release of that element.

Data confirm the non-conservative behavior of Fe and Al with precipitation percentages up to around 100 % for both elements between samples O10 and O1, where values of 76.7 % and 98.9 % seawater contribution were observed, respectively (Fig. 4). Consequently, all the Fe and Al entering the estuary in dissolved form precipitate, becoming part of the particulate material within the Odiel river sub-estuary. Confirming previous observations, other non-conservative elements in the same interval are Cu and Pb, with a maximum removal of approximately 70 %, which is concomitant with the precipitation of Fe and Al (Fig. 4). Arsenic exhibits an off-on behavior of initial removal between O12 and O9 (17.2 % and 88.6 % of seawater) of up to 40 % of the amount entering the estuary and subsequent release between O8 and O1 (more than 98.5 % seawater) with values above 100 % (Fig. 4). The precipitation-release inflection point is at pH between 6.59 and 7.37, which corroborates a behavior associated with the surface charge of schwertmannite formed by Fe precipitation to $pH_{PZC} = 7.2$ (Jönsson et al., 2005).

Elements like Co, Mn, and Ni show a conservative behavior according to the mixing model with very similar theoretical and measured concentrations (Fig. 4), which matches the comparison between dissolved and total (dissolved plus particulate) concentrations for samples from that section of the estuary (Fig. 3). However, the concentrations of Cd and Zn follow a release pattern between samples O9 and O1 (Fig. 4), with percentages above 100 % in the case of Cd, despite their conservative behavior according to the comparison between dissolved and

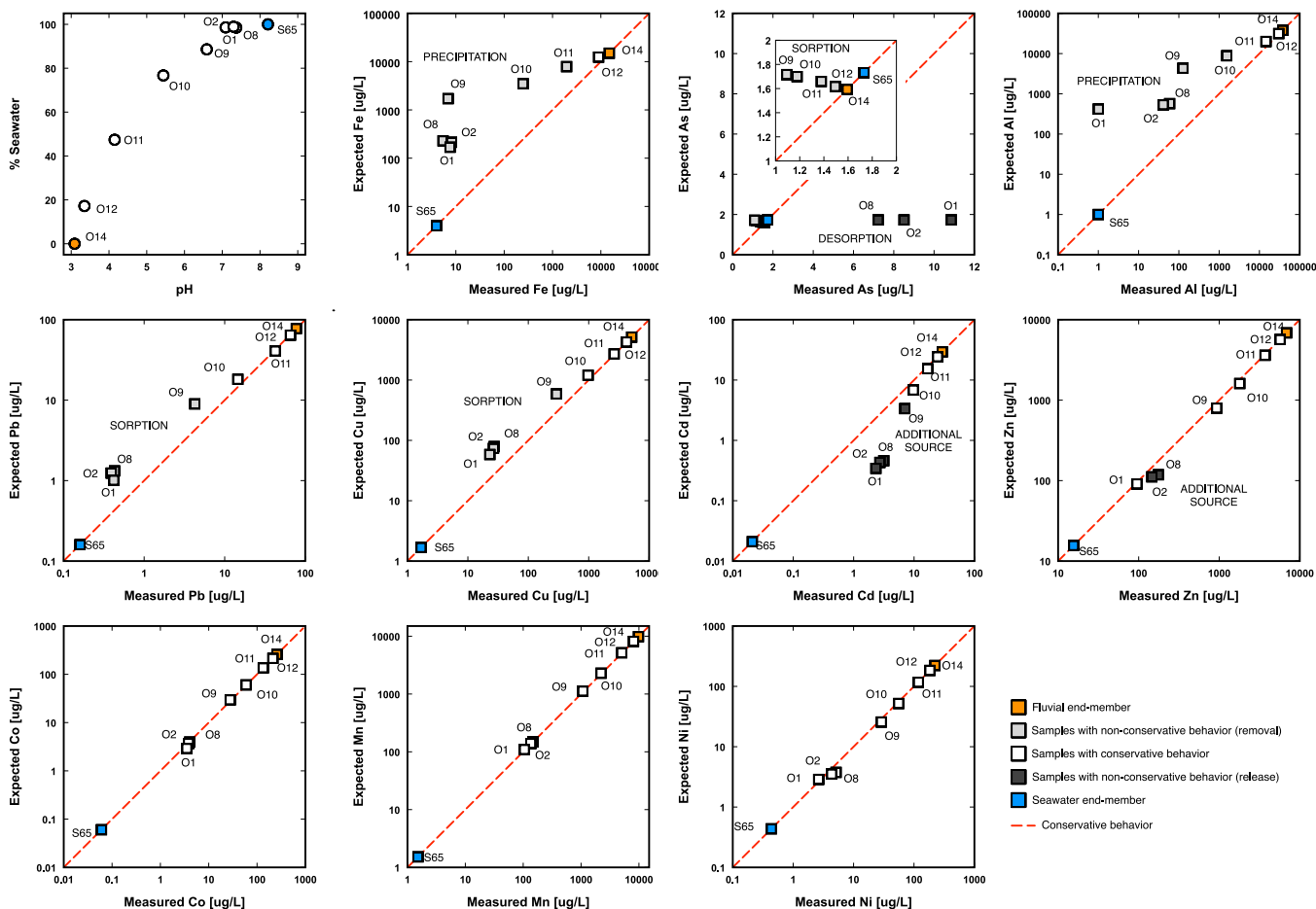


Fig. 4. Evolution of percentage of seawater contribution as a function of pH and correlation between the measured concentrations and the concentrations expected from theoretical mixing model of end-members using the MIX code for the May 2017 sampling.

total (dissolved plus particulate) concentrations (Fig. 3). The fact that the mixing model indicates release of Cd and Zn despite their conservative behavior could indicate the possible existence of a third end-member not considered in the theoretical mix. In this sense, this anomaly could be related to the influence of the leachates from the phosphogypsum stack located on the right bank of the salt marshes of the Tinto river sub-estuary, which is very close to the confluence with the Odiel river sub-estuary. Phosphogypsum stacks can be seen on the KML file and Fig. 1. Precisely As, Cd and Zn are discharged into the estuary from these stacks with a very significant contribution percentage compared to the discharge from the Tinto and Odiel rivers (Millán-Becerro et al., 2023). Therefore, As would have two sources in the final part of the Odiel river sub-estuary: the phosphogypsum stack and the desorption processes from schwertmannite.

4.3. Comparison with the situation a year after the spill

The concentrations of toxic elements throughout the estuary depend on the river inputs of pollutants and their mixing with alkaline seawater, which are influenced by fluvial flows and tidal conditions. To avoid this effect and properly compare the concentrations from the spill with subsequent conditions, the dissolved AMD elements are plotted against chloride concentration. Logically, the concentrations of mining-derived metals during the La Zarza accident are higher than in subsequent conditions (Fig. 5 and S4). These differences are consistent with those observed in the fluvial reach before entering the estuary (Gibraleón sampling point), being especially significant for elements such as Fe and Pb, and to a lesser extent for other elements such as Co, Cu, and Ni. These data again reflect that accidental spill contributed more significantly for some elements such as Fe or Pb in relation to others. However, the differences observed between the accidental spill and the situation one year later are pronounced in the fluvial domain but progressively decrease towards the marine domain (Fig. 5). Both situations converge

right at the confluence between the sub-estuaries of the Odiel and Tinto rivers (point C8; Fig. 1). At this point, two circumstances coincide: (1) there is a high influence of seawater with percentages over 98.9 % in the mix (data corresponding to O1 according to the mixing model), and (2) the Tinto river sub-estuary is more affected by AMD than the Odiel river sub-estuary (Nieto et al., 2007). Both circumstances could mask the accidental spill in the marine domain; however, slightly higher concentrations of some elements such as Fe, Pb, and Zn are still observed (almost double on average). The situation of As, on the other hand, is somewhat particular due to its precipitation and subsequent release behavior; concentrations decrease drastically right at the estuary entrance in both samplings in the fluvial and intermediate domains and then increase in the marine domain, also reaching higher concentrations during the La Zarza accidental spill (Fig. 5).

To study the effect of the La Zarza spill on the nearby coastal waters of the Gulf of Cadiz, total concentrations (dissolved plus particulate) were used instead of dissolved concentrations for two reasons. On the one hand, total concentrations allow studying the effect of the greater amount of flocculated Fe particulate material during the accidental spill compared to the situation one year later, both on the mobility of non-conservative elements (As, Cu, and Pb) and other elements that are conservative under normal conditions but seem to slightly sorb to Fe precipitates during the accidental spill (Co, Mn, Ni, and Zn). On the other hand, the dilution of contamination by seawater is so high that it is preferable to use total concentrations instead of dissolved ones, since the latter would be closer to the detection limits of the analytical techniques. In this sense, for almost all these mentioned elements, the total concentrations on the nearby coast of the Gulf of Cadiz are higher during the La Zarza accidental spill compared to the situation one year later. Total concentrations are especially higher for Co, Fe, Ni, Pb, and Zn, varying from almost three times higher (Co) to even thirty times higher (Zn) (inner squares in Fig. 5). Therefore, we can assume that despite a lower volume of water discharged into the estuary during the accidental spill

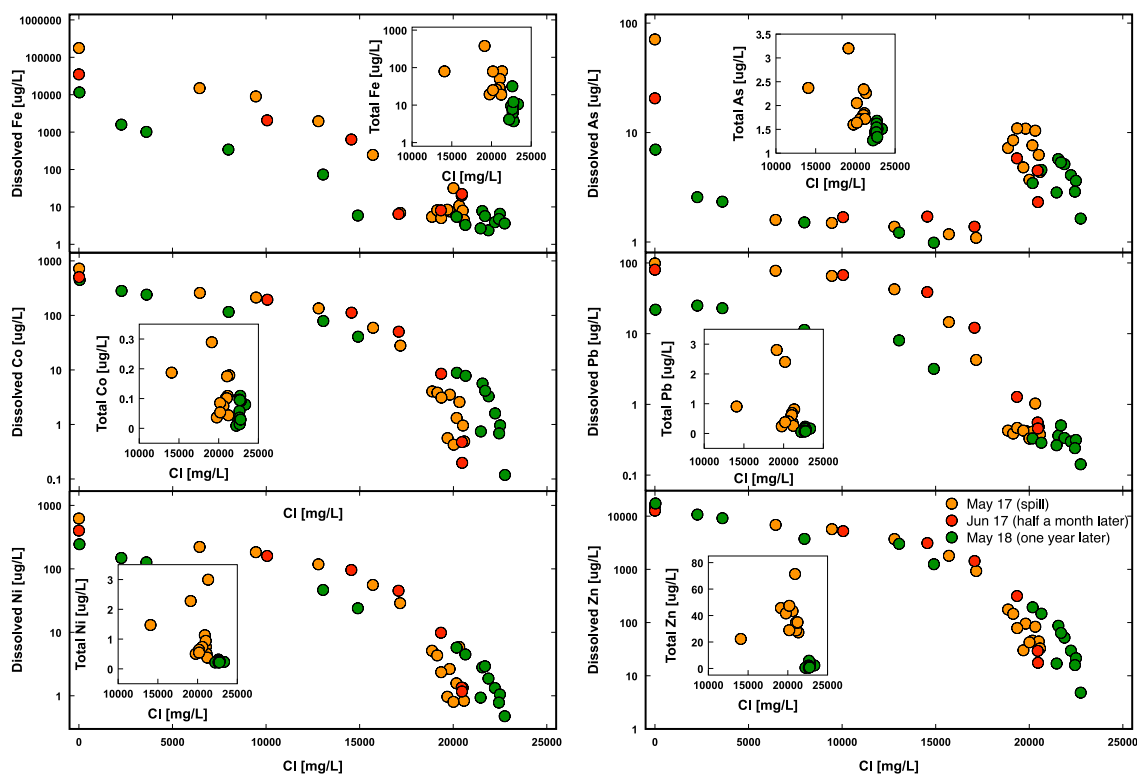


Fig. 5. Dissolved concentrations of Fe, As, Co, Pb, Ni and Zn in the Odiel river sub-estuary against chlorinity. The small inner graphs represent the total concentrations of the same elements in the nearest littoral samples.

compared to the sampling one year later (three times less flow, as mentioned earlier), the effect of the spill on the input of pollutants to the Atlantic Ocean seems significant, although the main impact occurs especially in the upper reaches of the estuary.

4.4. Environmental implications

Accidental spills can lead to the release of large quantities of contaminants, degrading water quality and threatening aquatic life in nearby water bodies. As stated in the Introduction, notable incidents such as the catastrophic failures of tailing dams at Aznalcóllar (Spain, 1998), Baia Mare (Romania, 2000), and Mount Polley (Canada, 2014) have caused severe environmental harm, with variations in the types and concentrations of pollutants released. Depending on the intensity of these pollution events, these problems can be transferred downstream of these water courses, reaching even the oceans. Only of few cases of this nature have been reported worldwide in literature. For example, the collapse of the Fundão Dam in Minas Gerais (Brazil) released more than 50 million m³ of tailings, of which approximately 39.2 million reached the Doce river watershed, affecting aquatic and terrestrial living organisms in the river course (Segura et al., 2016). The tailing muds traveled downstream a distance of around 663 km reaching the Brazilian coast (Almeida and Takahashi, 2022), altering the concentrations of dissolved oxygen, pH, salinity, and suspended particulate matter in the Doce river estuary (Viana et al., 2020), increasing the metal levels in coastal sediments (Sartori et al., 2023) and causing a severe effect on living organisms (Fernandes et al., 2020).

This spanning impact from mine site to coastal systems is also reported in this study, where enhanced levels of metal pollution were observed in the Estuary of Huelva after this spill. The metal exposure to living organisms in this environmental system has been previously studied. For instance, it has been reported high levels of Zn, Cu, Mn, Cd, and As in tissues of barnacles (*B. Amphitrite*) in the estuary associated to the existing high dissolved concentrations (Morillo and Usero, 2008). Vicente-Martorell et al. (2009) came to the same conclusions from metal analyses in fish tissues of gilt-head bream (*S. aurata*), a pelagic fish commonly found in estuaries. This metal exposure is not only limited to the exposure of dissolved concentrations, as recently reported by Cánovas et al. (2020) which suggest the importance of metal-rich colloids passing through biological membranes. Then, an increase of metal-rich particulates in the water column, like that reported in this study, may also pose a severe risk to aquatic organisms, especially those filter-feeding. On the other hand, Sammut et al. (1996) attributed to metal-rich colloids in an estuary affected by acid sulfate soils severe damaging effects on fish, fish larvae, oysters and other organisms by clogging their gills. Therefore, the occurrence of these events may increase the exposure of metals to aquatic organisms and its bioaccumulation across the whole food chain.

To avoid these harmful effects constraining preventive measurements should be put into practice to guarantee the safety of mining installations, especially those abandoned in mining districts exploited in the past, where a lack of control measurements is frequent. If occurred, a fast response should be provided by both companies (in active mines) and administration, which imply an efficient coordination between implied actors and the application of the required resources. An example of such quick response is that provided after the failure of the tailing dam at the Aznalcóllar mine (SW Spain) in 1998. Among the immediate corrective measures, the sealing of the breach in the dam and the reinforcement and raising of the wall that separates the Guadiamar River from the Doñana National Park, were adopted to avoid the arrival of these contaminants to Doñana (Olías et al., 2021). Afterwards, the metal-rich sludge was removed from the soils and safely landfilled, while the acidic waters were treated, avoiding an irreversible damage to this natural area. Another remarkable example of fast response was reported by Byrne et al. (2018) in Mount Polley tailings dam, where the environmental clean-up operations were quite rapid; less than one year

after the event a significant volume of the spilled tailings were removed, and extensive river restoration procedures were applied.

5. Conclusions

This study examines the environmental impact of the La Zarza spill in May 2017 on the Estuary of Huelva, focusing on the contamination of river, estuarine, and littoral environments. The spill led to a significant increase in contaminant concentrations in the river, particularly for Fe, As, and Pb, just before entering the estuary. Other metals like Co, Cu, Mn, and Ni were also elevated compared to post-spill concentrations, while Al, Cd, and Zn showed no significant difference. In the estuary, the mixing of acidic river water with seawater led to pH neutralization and a reduction in dissolved contaminants. A mixing model revealed that contaminants displayed both conservative (e.g., Cd, Co, Mn, Ni, Zn) and non-conservative (e.g., Al, Fe, Cu, Pb) behaviors. The behavior of As was notable, as it precipitated with Fe at acid pH but later desorbed at circumneutral pH. The spill also impacted the littoral zones, with elevated concentrations of Co, Fe, Ni, Pb, and Zn observed, indicating its influence on the Atlantic Ocean. Overall, the La Zarza spill had substantial and lasting environmental effects, emphasizing the need for ongoing monitoring and management of such incidents. The study highlights the complex dynamics of contaminant behavior in estuarine systems and stresses the importance of distinguishing between conservative and non-conservative processes to accurately assess environmental impacts. Future efforts should focus on strengthening monitoring practices to minimize the ecological damage from similar events.

CRediT authorship contribution statement

Rafael Pérez-López: Writing – review & editing, Writing – original draft, Visualization, Supervision, Funding acquisition, Conceptualization. **Carlos R. Cánovas:** Writing – review & editing, Writing – original draft, Visualization, Supervision, Funding acquisition, Conceptualization. **Francisco Macías:** Writing – review & editing, Investigation. **M. Dolores Basallote:** Writing – review & editing, Investigation, Conceptualization. **Rémi Freydier:** Writing – review & editing, Resources, Methodology. **Manuel Olías:** Writing – review & editing. **José Miguel Nieto:** Writing – review & editing.

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.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <https://doi.org/10.1016/j.envpol.2025.126033>.

Data availability

No data was used for the research described in the article.

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