CAUSES AND IMPACTS OF A MINE WATER SPILL FROM AN ACIDIC PIT LAKE (IBERIAN PYRITE BELT)

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Capsule: “An accidental discharge (270,000 m^3 of acidic and metal-rich waters) from an abandoned pit lake to the Odiel River and its estuary caused a significant additional increase in the contaminant levels”

ABSTRACT

In May 2017, a spill from La Zarza pit lake (SW Spain) resulted in the release of approximately 270,000 m^3 of extremely acidic waters to the Odiel River. Around 780 × 10^3 kg of Fe, 170 × 10^3 kg of Al, 2.15 × 10^3 kg of As and high amounts of other trace metals and metalloids were spilled. The purpose of this study is to explain the causes, consequences and impacts of the mine spill on the receiving water bodies. To this end, an extensive sampling along the mine site, river and estuary as well as a hydrological model of the pit lake was performed. Around 53 km of the Odiel River’s main course, which was already contaminated by acid mine drainage (AMD), were affected. The mine spill resulted in an incremental impact on the Odiel River water quality. Thus, dissolved concentrations of some elements increased in the river up to 450 times; e.g. 435 mg/L of Fe and 0.41 mg/L of As. Due to low pH values (around 2.5), most metals (e.g. Cu, Zn, Mn, Cd) were transported in the dissolved phase to the estuary, exhibiting a conservative behavior and decreasing their concentration only due to dilution. However, dissolved concentrations of Fe, Cr, Pb, Se, Sb, Ti, V and especially As decreased significantly along the river due to Fe precipitation and sorption/coprecipitation processes. At the upper zone of the estuary, a noticeable increment of metal concentrations (up to 77 times) was also recorded. The water balance illustrates the existence of groundwater inputs (at least 16% of total) to the pit lake, due probably to local infiltration of rainwater at the mining zone. The probable existence of an ancient adit connected to the pit lake indicates that potential releases could occur again if adequate prevention measures are not adopted.

Keywords: La Zarza; acid mine drainage; water pollution; Iberian Pyrite Belt.

1. INTRODUCTION

Acid mine drainage (AMD), a process mainly related to sulfide and coal mining, is one of the main causes of water pollution worldwide. Sulfides are stable under reducing conditions, however when minerals are exposed to atmospheric conditions oxidation takes place, leading to the release of acidity, sulfates, iron and other metals and metalloids, which affects the quality of surrounding water bodies. A detailed description of origin, transport and fate of major and trace elements during AMD processes can be found in Nordstrom (2011). The Odiel River basin (SW Spain) is located in the Iberian Pyrite Belt (IPB), which contains some of the largest sulfide deposits in the world. Mining activities developed in the Odiel basin, above all since the second part of the 19th century, have left a severe environmental legacy; around 427 km of the Odiel fluvial network (37% of the water courses) is affected by AMD (Sarmiento et al., 2009). As a result, the Odiel River maintain low pH values (median value of 3.5; Cánovas et al., 2007) along the year and carries high loads of metals (Olías et al., 2006).

On the other hand, the lack of control measures in mining facilities, especially in abandoned districts, can lead to large accidental spills that inevitably cause a profound impact on the environment as well as human health (e.g., Hudson-Edwards, 2016). As such, the effects of mine tailing dam failures have been considerable due to the release of large amounts of water and tailing-bearing pollutants into the environment (e.g., Grimalt, 1999; Hudson-Edwards, 2016; Kossoff et al., 2014; Macklin et al., 2003).

Accidental discharges from galleries in abandoned mines are also common (e.g., Bureau of Reclamation, 2015; Mayes and Jarvis, 2016; Walton-Day and Mills, 2015; Younger, 2002). In underground mines, the construction of concrete plugs has represented a widely-used technique for controlling water's access to operational zones since the early twentieth century, and since around the 1970s, the same technology has also been used to prevent outflows from mine adits (Bureau of Reclamation, 2015). The origin of accidental spills from mine adits may be associated with: 1) the breakage of some of these plugs, and 2) the accumulation of water as a consequence of mine gallery collapse, and subsequently the sudden drag of the plug by the water (Bureau of Reclamation, 2015; Younger, 2002).

In the Spanish part of the IPB exist 22 pit lakes in derelict mines, most of which are acidic (Sánchez España et al., 2008). On May 17, 2017, a volume of approximately 270,000 m^3 of AMD waters was spilled after the concrete plug of an old adit connected to La Zarza pit lake collapsed. The acidic waters rapidly reached the Odiel River and later the Ría de Huelva estuary (Fig. 1).

With the exception of some recent incidents (EPA, 2016), accidental discharges from old mining galleries are rarely detailed in the literature. Therefore, the objective of this work is to explain the causes, characteristics, consequences and implications of the spillage of the La Zarza mine to the Odiel River. The results obtained in this study may be useful for the analysis and prevention of potential spills in other mining areas around the world.

2. STUDY AREA

The Odiel River is one of the main rivers draining the IPB, with a surface area of 2.333 km^2 and a length of 140 km. The basin is mainly underlain by materials of low permeability; thus, the river discharge is very irregular depending on rainfalls. Normally, daily discharges are lower than 3 m^3/s, but daily values higher than 2000 m^3/s can be reached in rainy years (Olías et al., 2006).

The IPB forms part of the South Portuguese Zone of the Hercynian Iberian Massif. A detailed description of the lithostratigraphic units can be found in Tornos et al. (2009). The main characteristic of the IPB is the existence of numerous deposits of massive sulphides, primarily constituted by pyrite (FeS_2) and with minor amounts of chalcopyrite ($CuFeS_2$), sphalerite (ZnS) and galena (PbS), which have been intensively exploited since the mid-nineteenth century. La Zarza mining district is located in the central part of the IPB (Fig. 1). The altitude varies between 200 m south of the mining area and a maximum of 326 m close to the open pit. The region has a Mediterranean climate, with an average rainfall of approximately 750 mm and an average temperature of about 16.5 °C. Summers are dry and warm, while winters are wet and relatively cold.

The exploited area has an elongated shape with an E-W direction about 2,900 m in length, an average width of 100 m, and depths of up to 300 m (Strauss et al., 1981). In this deposit, massive pyrite was mined for sulfuric acid manufacturing and, secondarily, for copper extraction. The sulphide reserves that exist today are estimated at 110 million tonnes, with average grades of 0.7% Cu, and continue to represent one of the largest deposits of the IPB (Pauwles et al., 2002). The Perrunal mine, which exploited the same deposit, is located just to the west of La Zarza mine (Fig. 1).

La Zarza mine, as well as other mines in the IPB, have been exploited since pre-Roman and Roman times (Olías and Nieto, 2015), evidenced by the existence of about 800 Roman mine shafts (Checkland, 1967; Gonzalo y Tarín, 1888; Pinedo Vara, 1963) and several Roman galleries (Fig. 1) around the area. The most important of these were La Algaida, 1,800 meters long, and Los Cepos, 800 meters long (Fig. S1A; Supporting Information).

Modern exploitation began in 1853. One of the first mining tasks was to widen and rehabilitate the Los Cepos gallery to drain the mine and facilitate ore transportation (Gonzalo y Tarín, 1888). Exploitation was conducted by means of the room-and-pillar method until the onset of open pit mining in 1888, which enabled a large increase in production. By 1920, the open pit had reached a depth of about 130 m and opencast exploitation ceased, although underground mining continued using the cut-and-fill method, reaching depths close to 300 m. In the 1980s, a strong crisis led to the progressive closure of the mines at the IPB. Ore extractions in La Zarza mine finished in 1991, although pumping operations continued until 1995. La Zarza was the third largest mine in the Spanish part of the IPB, with a total production of 40-45 million tonnes of ore (Pauwels et al., 2002). 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 Los Cepos gallery.

3. METHODOLOGY

3.1. Hydrogeochemistry data

Following the May 17 spill, a periodic sampling began on May 19 in the Odiel River at Sotiel (17 km downstream from the mine, Fig. 1) and Gibraleón (just before the estuary). Approximately two to three samples were collected per week, with a higher frequency immediately after the accident. In total, 26 samples in Sotiel and 20 samples in Gibraleón were collected until July 17. In addition, some samples were taken in the mine zone.

Samples were filtered (0.45 µm pore size), acidified to $pH < 2$ with nitric acid 65% Merck Suprapur®, stored in HDPE bottles and refrigerated until analysis. Raw samples (not filtered but acidified) were also collected to study the metal particulate transport caused by the spill, thus the difference between concentrations in the filtered and unfiltered samples can be associated with particulate matter. The temperature, pH, electrical conductivity (EC), and oxidation-reduction potential (ORP) were measured in situ using a Crison MM40+ multimeter. A three-point calibration was performed for both EC (147 µS/cm, 1,413 µS/cm, and 12.88 mS/cm) and pH (4.01, 7.00, and 9.21), while ORP was controlled using two points (240 and 470 mV). ORP measurements were corrected to the standard hydrogen electrode to calculate pE (Nordstrom and Wilde, 1998).

The samples were analyzed for the determination of Al, Ca, Cu, Fe, K, Mg, Mn, Na, S, Si and Zn by Inductively Coupled Plasma-Atomic Emission Spectroscopy (ICP-AES) and by Inductively Coupled Plasma-Mass Spectroscopy (ICP-MS) for minor and trace elements (As, Be, Cd, Co, Cr, Li, Ni, Pb, Sb, Sc, Se, Sr, Th, Ti, U and V) at the R+D laboratories of the University of Huelva. Detection limits were 200 µg/L for Al, Ca, Fe, K, Mg, Mn, Na, S, Si and Zn (ICP-AES); and between 1 and 2 µg/L for minor and trace elements (ICP-MS). Multi-elemental standard solutions elaborated with certified standards supplied by SCP SCIENCE were used for calibration. They were run at the beginning and end of each analytical series. Certified Reference Material SRM- 1640 NIST freshwater type was also analyzed.

Analytical data from previous studies (Sánchez España et al., 2005, 2008; Sarmiento, 2007; Sarmiento et al., 2009) were used to establish the baseline conditions of the area before the spill. Available analysis of the Odiel River in Sotiel (April 4 and May 17) and Gibraleón (May 5) from the Regional Water Authority were also used, although for these samples only some elements were analyzed.

On the other hand, a sampling was performed on May 30 along the Odiel River estuary. Samples were collected from a ship using a Van Dorn bottle at 2 m below the surface to avoid contamination. In total, 9 samples were transferred into ultraclean HPDE bottles after filtration. The samples were then acidified with ultrapure HNO_3 and analyzed by iCAP TQ ICP-MS at the HydroSciences laboratory of the University of Montpellier. Estuarine water reference material for trace metals (SLEW-3) were also analyzed to check the analytical accuracy. In addition, samples were taken to analyze chloride by ion chromatography (Dionex DX-120) at the R+D laboratories of the University of Huelva.

3.2. Streamflow data and meteorological information

Streamflow data were obtained from the Sotiel gauging station, located at the middle course of the Odiel River (sampling point of Sotiel, Fig. 1). The daily data of rainfall, temperature, solar radiation and wind speed were taken from a weather station located 10 km to the east of La Zarza mine. Daily evaporation was calculated using the equation of Penman (1948):

$$EV = \frac{\Delta Rad_n + \gamma E_a}{\Delta + \gamma} \tag{1}$$

where EV is evaporation from a free surface (mm/day), Δ is the slope of the saturation vapor pressure curve (kPa/°C), γ is the psychrometric constant (kPa/°C), Rad_n is the net daily radiation at the water surface (mm/day), and E_a (mm/day) is the aerodynamic component depending on the average daily wind speed and vapor pressure deficit. The detailed estimation procedure is described in Allen et al. (1998).

3.3. Water level and water balance in the open pit

In order to obtain the evolution of the water level in the open pit lake, the Digital Terrain Model (DTM) and orthophotos of the following dates were used: Jul 1998, Oct 2002, Aug 2004, Oct 2005, May 2007, May 2009, Aug 2011, May 2013 and July 2016. The area of the flooded surface was calculated from each orthophoto. Open pit level contour lines were ascertained from the DTM, thus obtaining the relationship between elevation and surface in the open pit. In this way, the water level in the pit lake can be estimated from the flooded surface observed in each orthophoto, as well as the volume of stored water (Moreno González et al., 2018).

Due to the high slope of the open pit walls (~100%; see Fig. S1C of the Supporting Information), the water inputs to the pit lake were calculated assuming that rainfalls collected in the drainage catchment of the open pit (coinciding approximately with the open pit limits; Fig. 1) become surface runoff, i.e., that there are no infiltration or evapotranspiration losses from soil. This assumption considers the maximum possible amount of water inputs. Evaporative outputs were also estimated by calculating the average water surface between two consecutive orthophotos and multiplying by the cumulative evaporation (from the daily values obtained from equation 1) between both orthophoto dates.

4. RESULTS AND DISCUSSION

4.1. **Flooding evolution of the open pit**

Mining in La Zarza led to the existence of a large open pit (830 m long, 240 m wide and 130 m deep). Following the conclusion of pumping in 1995, the water table started to recover, initially flooding the deepest part of the extensive underground gallery system below the bottom of the open pit. In 1998 the open pit remained dry, but in 2002 the beginning of the flooding could be observed in the lower part of the pit, located to the east (Fig. S2; Supporting Information). In 2004, two independent lakes (east and west) were formed, separated by a relatively higher area in the middle of the open pit. This situation remained at least up to 2009. Since 2011, both parts were connected to form a single lake, which persists to this day (Fig. S2). In 2016 the pit lake was 690 m long, with an average width of about 110 m (Fig. S2). Figure S1.C shows the pit lake in May 2017 after the plug break, where a yellowish band in the pit walls (~3.5 m high) due to the sharp lowering of the water level can be identified.

The water level in the pit lake over time has been obtained from the DTM and the available orthophotos. These data reveal that the water level rose by more than 52 m from 2002 to 2016 (Table S1 and Fig. 2), with an average value of 3.8 m/yr. Since 2011, the water level was higher than the Los Cepos adit (Fig. 2) and the progressive overpressure exerted by the stored water caused the adit to collapse in May 2017. The water rise was higher during the early years of flooding and slowed over time, although some fluctuations can be observed depending on rainfall between the dates corresponding to each orthophotograph (Fig. 2). However, since 2013, the water table seems to be approximately stable, with a rise of just 0.5 m observed from 2013 to 2016. The volume of water stored in the pit lake in 2016 was 1.93 hm^3.

The average precipitation recorded between October 2002 and July 2016 was approximately 782 mm, while the evaporation for the same period was 1,694 mm (Table S1). Based on rainfall and evaporation data for each period among consecutive orthophotographs, the surface inputs and losses by evaporation from the flooded surface of the pit lake can be estimated (Table S1). It can be noted that inputs due to rainfall are higher than losses by evaporation, although the latter increased progressively due to the increase in flooded surface in the pit lake (Table S1 and Fig. S3).

Groundwater inputs during mining exploitation were small owing to the low permeability of materials, hence the water pumped primarily corresponded with the infiltration of rainwater, with an average value of 0.13 hm^3/yr (Junta de Andalucía, 1986). Water inputs estimated from rainfall are around 0.19 hm^3/yr, higher than the volume of water pumped during the period of mining activity assuming that the entire rainfall collected in the drainage catchment feeds the open pit. In spite of this fact, the increase of water stored in the pit lake is higher than the difference between surface inputs and evaporation outputs (Table S1, Fig. S3), implying the existence of other inputs of water to the pit lake. These groundwater inputs can be calculated as the volume increase plus the losses by evaporation minus the inputs from rainfall, providing a total input of 0.51 hm^3 from October 2002 to July 2016 (0.035 hm^3/yr, that is 16% of the total inputs). The source of these inputs could be: 1) groundwater from a regional flow coming from the northern area, at a higher altitude, or 2) recharge of the pit lake through water infiltration at the mining zone, favored by the increase of rock fracturing in the surrounding of the pit due to mining operations. As can be observed in table S1 and figure S3, groundwater contributions (inputs minus outputs) are closely dependent on rainfalls (the Pearson correlation coefficient between them is 0.87), varying between 0.02 hm^3/year in dry years to almost 0.2 in wet ones. This indicates a local flow rather than a regional one, which should be more regular and not so affected by the rains of each year. Also, the low value of the hydraulic conductivity of the IPB materials (around 10^{-9} m/s; Moreno et al., 2018) does not support a significant regional flow to the open pit. Thus, groundwater inputs to the pit lake must come from rainwater infiltration near the mining zone. In this sense, some possible sources are: a) rainfall and runoff intercepted by some borrow pits located to the east of the pit (Fig. 3), used as a source of materials for filling the mining voids (fill-and-cut mining method); and b) waters coming from the Perrunal mine (Figs. 1 and 3), located to the west of La Zarza, which exploits the same deposit (Cánovas et al., 2016). Although both mines were not connected by galleries, underground discharges from Perrunal were detected in the last phase of La Zarza's exploitation.

On the other hand, the slowdown of water level rise observed in recent years (Fig. 2) must be connected to the increment of losses by evaporation (concomitant to the increase in the flooded surface) together with scarce rainfall collected between 2013 and 2016 (631 mm compared to the average of 782 mm; Table S1). Nevertheless, under a normal rainfall regime, the water level will rise up to that losses by evaporation equalize inputs. Given that water inputs due to rainfall are 0.19 hm^3/yr and groundwater inputs are 0.035 hm^3/yr, a total input of 0.23 hm^3/yr can be considered. In order to balance this annual volume by evaporation, it would be necessary for the total surface in the pit lake exposed to evaporation to be 14 ha, equivalent to a height of 245 m, i.e., 31 m above the water level observed in the pit lake in 2016 (Fig. 2).

Nevertheless, the pit lake could not reach hydrological equilibrium with evaporation in the future due to the existence of unknown adits located below the expected equilibrium level, which would act as drainage. These old galleries may be blocked by collapses, acting as a plug until the pressure exerted by the accumulation of water causes a drastic release, similar to that in the Wheal Jane mine in southwest England in 1992 (Younger, 2002). In this sense, as commented in the Study Area section, there is abundant information of another Roman gallery (Algaida adit; Fig. 1) in historical documents (e.g. Checkland, 1967; Gonzalo y Tarín, 1888), although its location is not known today. In order to avoid another possible spill, control measures based on a detailed hydrogeological study of the system must be adopted.

4.2. Baseline conditions previous to the spill

Intensive mining activity at La Zarza caused the accumulation of huge volumes of spoil heaps and other mining wastes at this mine site, covering a surface of approximately 1 km^2 (Fig. 1). Several watercourses draining the mining area, affected by acid mine drainage (AMD), circulate to the south and are collected by a creek (Fig. 1), with pH values below 3 even during high-flow conditions, as well as significant dissolved concentrations of Fe (37-300 mg/L), Al (29-142 mg/L), and As (up to 0.59 mg/L) according to previous studies (Sarmiento, 2007). Although it was sealed with a concrete plug in the 1990s, the mine gallery causing the spill generated a permanent outflow of around 0.5-3.0 L/s of acidic water (Fig. S1A), with moderate pollutant content (around 30 mg/L of Fe, 55 mg/L of Al, 45 mg/L of Mn and <5 mg/L of Cu and Zn) (Sánchez España et al., 2005 and own data from a sampling in 2015; Table S2). According to Sarmiento (2007), La Zarza mine released an average load of 620 kg/day of Fe, 190 kg/day of Al and 3 kg/day of As to the Odiel River, of which the Algaida stream (Fig. 1) is the main contributor.

Furthermore, most of the Odiel fluvial network is deeply affected by AMD due to the different mining discharges received along its basin (Nieto et al., 2013; Sánchez España et al., 2005; Sarmiento et al., 2009). Thus, the Odiel River exhibits pH values close to 3.5 in its middle and lower reaches, with concentrations of around 50 mg/L of Al and between 5 and 20 mg/L of Fe, Cu, Mn and Zn (Cánovas et al., 2007; Sarmiento et al., 2009).

4.3 The spill of May 2017

The pressure exerted by the stored water caused the breakage of the concrete plug of Los Cepos gallery on May 17, 2017, resulting in the release of around 270,000 m^3 of highly polluted waters, equal to one-seventh of the water volume stored in the pit lake. The composition of the water released during the spill revealed rather high concentrations of toxic metal/oids (up to 2883 mg/L of Fe, 624 mg/L of Al and 6.75 mg/L of As; Table S2), similar to the water composition stored in La Zarza pit lakes (Sánchez España et al., 2008). On the other hand, the composition is totally different from the water previously leaked from the sealed gallery (Table S2). This fact, along with the water level in the pit lake, indicates that the leakages observed in the sealed gallery before the spill did not come from the pit lake but most likely from subsurface flows of water infiltrated in the waste dumps, which had lower concentrations of toxic elements. Total concentrations (dissolved plus particulate) of the spilled water were similar to dissolved counterparts due to the low pH values observed (consequently, only dissolved concentrations are shown in Table S2).

The total load of pollutants released during the spill has been calculated from the estimated volume of water spilled (270,000 m^3) and the dissolved concentrations, reaching around 780×10^3 kg of Fe, 170×10^3 kg of Al, 1.8×10^3 kg of As, etc. (Table S2). Urgent remediation measures were initiated after the spill was detected. On the one hand, such actions were focused on preventing the release of acidic waters from the pit lake by injecting waterproofing materials into the adit (Fig. S1B). In this way, most of the acidic water was released during the first two days after the plug broke. On the other hand, around 50,000 m^3 of acidic waters released from the pit lake were retained in an old mining dam downstream of the gallery (Fig. S1D) and in other dams built specifically to avoid its discharge into the Odiel River. Given that the dams were not totally watertight, a pumping system was installed to collect and pump the leakages upstream. The acidic waters stored in the dams were treated by a combination of passive and active treatments: 1) circulation through limestone drains, with grain diameters between 0.1 and 3 cm, and 2) addition of caustic soda.

In comparison with the pollutant load carried annually by the Odiel River (Galván et al., 2016; Olías et al., 2006), the contribution of the spill was relatively small (≤ 3%), with the exceptions of Fe and As (22 and 6% of the annual load, respectively; Table S2). Nevertheless, compared with other cases of mine spills worldwide, the pollutant load released during La Zarza mine spill was very high. Thus, in the Gold King mine spill (Colorado, USA), which affected around 550 km of the Animas and San Juan rivers, 113,000 m^3 of acidic waters were released (EPA, 2016). This spill was caused by the drastic release of acidic waters stored in underground galleries as a consequence of the breaking of an unconsolidated wall (Rodriguez-Freire et al., 2016). Although these waters did not exhibit extreme concentrations, the weathering of mine materials led to a noticeable increase of particulate matter and suspended colloids, such that most (>95%) of the total metal/loid transport (e.g., 433×10^3 kg of Fe, 41×10^3 kg of Al, and 0.36×10^3 kg of As) took place by the particulate/colloidal phase (EPA, 2016). This phase is less dangerous for living organisms, hence fish mortality episodes and other impacts for aquatic ecosystems were not observed following the spill (EPA, 2016). The amounts of pollutants released in this spill were much lower than in the case of La Zarza.

A similar incident occurred in 1992 in the Wheal Jean mine (SW England), in which around 50,000 m^3 of acidic waters were accidentally released due to the breakage of an adit plug following the conclusion of pumping operations (Younger, 2002). As far as we know, no information exists regarding the total load of toxic elements released during the spill, although the figures may have been significant considering the high concentrations recorded along the Carnon River, where values of up to 450 mg/L of Zn and 600 µg/L of Cd were measured (NRA, 1994). The presence of high contents of Fe oxyhydroxides caused an extremely large visual impact, stimulating public concerns and the adoption of a long-term solution to the incident (Younger, 2002).

4.4 Impacts on the Odiel River

The spill affected a total length of 53 km of the Odiel River (Fig. 1). As previously mentioned, these watercourses were previously affected by AMD and the aquatic ecosystems are characterized by the absence of mollusks (Pérez-Quintero, 2011) and other higher organisms. The presence of life in these waters is limited to acidophilic microorganisms (e.g., López-Archilla and Amils, 1999), thus in spite of the high loads of pollutants released to the surrounding water bodies, the impact of the mine spill on aquatic ecosystems was rather small.

The mine spill occurred following intense rainfalls (50 mm between May 10 and 12), which led to a sharp river flow increase (Fig. 4), masking the effect of the mine spill on the river flow. The flow on May 17 was 3.9 m^3/s, but decreased rapidly and after five days was lower than 1 m^3/s and from June 4 onwards lower than 0.2 m^3/s (Fig. 4).

The spill effect was clearly indicated by a slight decrease in pH and a notable increment of EC values at Sotiel and Gibraleón (Fig. 4). In addition, the visual impact on the river was evident at Sotiel on May 17, when the water color turned to bright red, different from the conditions normally observed in this river reach (Fig. S1E-F). The effect was also evidenced by the high concentrations of Cd, Ni and Pb observed in samples collected by the Water Regional Authority on May 17 (only these elements were measured; Fig. 5). The dissolved concentrations peaked on May 19, when concentrations of 437 mg/L of Fe, 117 mg/L of Al, and 0.41 mg/L of As were found (Fig. 5). These values are much higher than those typically recorded at this sampling point (around 75 mg/L of Al, and between 10 and 20 mg/L of Fe, Cu, Mn and Zn; Galván et al., 2016 and Sarmiento et al., 2009). The increased concentrations observed after the mine spill were more significant for those elements exhibiting a higher difference between the spilled water and the Odiel River before the incident, such as Fe and As (Fig. 5).

From May 19, metal/loid concentrations at Sotiel quickly decreased until May 31 when the impact of the mine spill apparently disappeared. From this date, an increase in concentrations was observed (Fig. 5), due to: 1) the decrease in runoff generated during the rainfall of May 10-12, as reported by Cánovas et al. (2012) who studied hydrochemical changes during a flood event at this location; and 2) the trend of increasing concentrations typically observed in the rivers of this area due to the increase in evaporation processes during the dry season (Cánovas et al., 2007). Iron does not follow this general trend, decreasing continuously in concentration (Fig. 5), suggesting the occurrence of intense in-stream precipitation processes.

The dissolved element load carried by the river at Sotiel between May 17 and May 31 has been estimated from flow and analytical data. Given that some hydrochemical information gaps exist, this estimate is reliant on certain assumptions: 1) concentrations on May 18 (not available) were considered similar to those on May 19; and 2) based on the ratio in values of Cd and Ni concentration between samples collected on May 17 and 19, the concentration of the other metals on May 17 (no available) was estimated. Nevertheless, according to the trend observed from May 19 onwards, concentrations in May 18 were probably higher than in May 19, thus the obtained values could underestimate the element load at Sotiel. Some examples of the obtained values can be seen in Figure S4. The estimated loads obtained for Al, Be, Cd, Co, Cu, Mn, Ni, Sc, Th, U and Zn were between 90 and 116% of the amounts released by the spill at La Zarza (Table S2). Taking into account the uncertainties of this estimation, it can be assumed that these elements follow a conservative behavior between the spill point and Sotiel. On the other hand, values obtained for Cr (82% of the total released), Fe (71%), Se (69%), Pb (61%), Ti (46%) and especially As (26%) indicate a non-conservative behavior. This implies that approximately 30% of the Fe and 75% of the As released by the mine spill were retained in the La Zarza-Sotiel reach by precipitation/sorption processes. These processes constitute a permanent sink for some trace elements along the drainage network of the Odiel River, especially during the dry season (e.g. Sánchez-España et al., 2006; Olías et al., 2006). On the other hand, Sb and V were found below the detection limit at Sotiel, indicating that these elements were also intensely removed from the river water.

The low streamflow made the contaminant plume to move slowly through the river. At Gibraléon, before the confluence with the estuary (Fig. 1), the maximum concentration for most elements was reached on May 31, two weeks after the mine spill occurrence, while its effect was evident until June 20 (Fig. 5). For most elements, the maximum concentrations observed at Gibraleón were around 20-30% lower than those recorded at Sotiel, and the plume pass was more gradual owing to dispersion processes (Gandolfi et al., 2001). However, the maximum Fe concentration was almost 60% lower than at Sotiel (Fig. 5), highlighting the importance of Fe precipitation processes. The decline in peak concentration observed between both sampling points for Ti (62% lower at Gibraleón), Se (48% lower), and especially As (83% lower) was also striking. Antimony and V concentrations remained below the detection limit.

On the other hand, the maximum concentrations of U and Pb at Gibraleón were slightly higher than at Sotiel, while Al was slightly lower (Fig. 5). Other AMD sources located between both sampling points could have affected these figures, especially the confluence of the Oraque River, an AMD-affected watercourse that generally accounts for between 18 and 32% of the total pollutant load at Gibraleón (Galván et al., 2016). Moreover, the occurrence of re-dissolution and/or desorption processes from sediments as a consequence of the decrease in pH values owing to the spill could affect the dissolved concentrations of some elements.

No available flow data exist at Gibraleón. However, the flow at this location can be estimated from the difference in concentrations observed between this sampling point and Sotiel. It can thus be concluded that only about 3% of the total As released during the mine spill to the Odiel River reached the Ría de Huelva estuary, being retained in the sediments by coprecipitation/sorption processes. In the case of Ti, Fe and Se, only around 23, 35 and 49%, respectively, of the spilled load would have arrived at the estuary.

4.5 Impacts on the estuary

Concerning the impact on the Ría de Huelva estuary, mortality episodes or other impacts to aquatic ecosystems were not observed after the spill. Samples collected on May 30 in the upper part of the estuary (O14 to O10; Fig. S5) exhibited pH values between 3 and 5.5, with dissolved concentrations of Fe, Zn and Cu of up to 15, 6.8 and 5.1 mg/L, respectively. Circumneutral pH values (6.5 at point O9; Fig. S5) were recorded 7 km downstream of the tidal influence limit due to the mixing of river and estuarine waters, and so mining metal concentrations notably decreased (Fig. 6).

As in the case of the Odiel River, the estuary has undergone chronic pollution by AMD (Borrego et al., 2002; Braungardt et al., 2003; Elbaz-Poulichet et al., 2001; Hierro et al., 2014). Concentrations of toxic elements along the estuary are contingent on pollutant inputs from the river and mixing with neutral seawater, which are in turn influenced by the interplay of river discharges and tides. In order to avoid this effect and adequately compare the concentrations after the spill with previous conditions, elements from AMD are represented against chloride concentration (Fig. 6). Only samplings carried out during the same season (spring and beginning of summer) were considered (Braungardt, 2000; Elbaz-Poulichet et al.; 2001; Hierro et al., 2014). It can be noted that the Cu and Fe concentrations were higher (between 5 and 77 times) than usual values in the upper part of the Odiel estuary. On the other hand, Cd, Zn and other AMD-related elements showed similar values to previous data (Fig. 6). The reduction in metal concentrations was primarily due to dilution with large proportions of seawater, as well as the precipitation of some elements (mainly Fe and Al) owing to the pH increase (Hierro et al., 2014).

In spite of the high load of metal/loids released, the impact of the spill seems to have been limited to the upper reaches of the estuary. A similar case was observed during the Wheal Jane mine spill, which was considered the most significant case of mining pollution in the United Kingdom (Banks et al., 1997), generating a pollutant plume along the Fal estuary, although the environmental impacts were (surprisingly) not severe (Somerfield et al., 1994). Younger et al. (2002) attributed this to water stratification due to density differences between the mine and estuarine waters, limiting the exposure of benthos to pollutants, and dilution and dispersion processes of pollutants exerted by the large volume of estuarine waters.

5. CONCLUSIONS

The lack of control measures in mine sites, especially in derelict mines, can lead to large accidental spills. The mine spill from La Zarza pit lake (SW Spain) in May 2017 caused the release of around 270,000 m^3 of acidic and extremely metal-rich waters to the Odiel River: approximately 780×10^3 kg of Fe, 170×10^3 kg of Al, 2.15×10^3 kg of As and important amounts of other metals and metalloids.

The spill affected a total river length of 53 km and constituted an incremental impact on the river and estuary water quality, already deteriorated by mining activities. River concentrations were increased up to 450 times; reaching maximum concentrations of 437 mg/L of Fe, 0.96 mg/L of Ni, 0.41 mg/L of As 17 km downstream of the mine. Elements such as Al, Be, Cd, Co, Cu, Mn, Ni, Sc, Th, U and Zn were conservatively transported to the estuary due to low pH values (below 2.8), while Cr, Fe, Se, Pb, Ti, V, Sb and especially As were intensively transferred to the river sediments by Fe precipitation and coprecipitation/sorption processes. Thus, it is estimated that only 3% of the As released by the spill reached the estuary.

As a consequence of previous rainfalls, the river flow during the spill was 3.9 m^3/s, but decreased rapidly. Thus, the contaminant plume travelled progressively along the river and the pollutant peak arrived to the estuary 14 days after the spill. The spill effect caused increasing metal concentrations (from 5 to 77 times) in the upper section of the estuary, while similar conditions to previous studies were observed in the lower section where the marine influence is greater. Nevertheless, the environmental impacts on the estuarine biota should be monitored in future studies.

The analysis of the pit lake flooding evolution indicated that the lake has not still achieved the hydrological equilibrium, with a rise of around 52 m from 2002 to 2016, slowing down in recent years. The water balance shows the existence of groundwater inputs (at least 0.51 hm^3 from 2002 to 2016) to the pit lake, which are probably due to the infiltration of rainwater in the mining zone adjacent to the open pit. Considering the estimated average inputs to the pit lake and the annual evaporation values in the area, a water level rise of approximately 31 m (above the current level) would be required to reach the equilibrium. On the other hand, potential outflows could be generated through an ancient adit whose location is currently unknown. In order to avoid future problems, a detailed investigation of the distribution of old mining works should be carried out.

The existence of 22 pit lakes in the IPB, most of which originated recently after the cease of mining activities at the end of the twentieth century, pose a significant environmental concern. Due to the huge volume of acidic waters stored, a case-by-case study of these systems is urgently needed in order to assess the risks of mining spills and accordingly to adopt necessary prevention measures.

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FIGURES

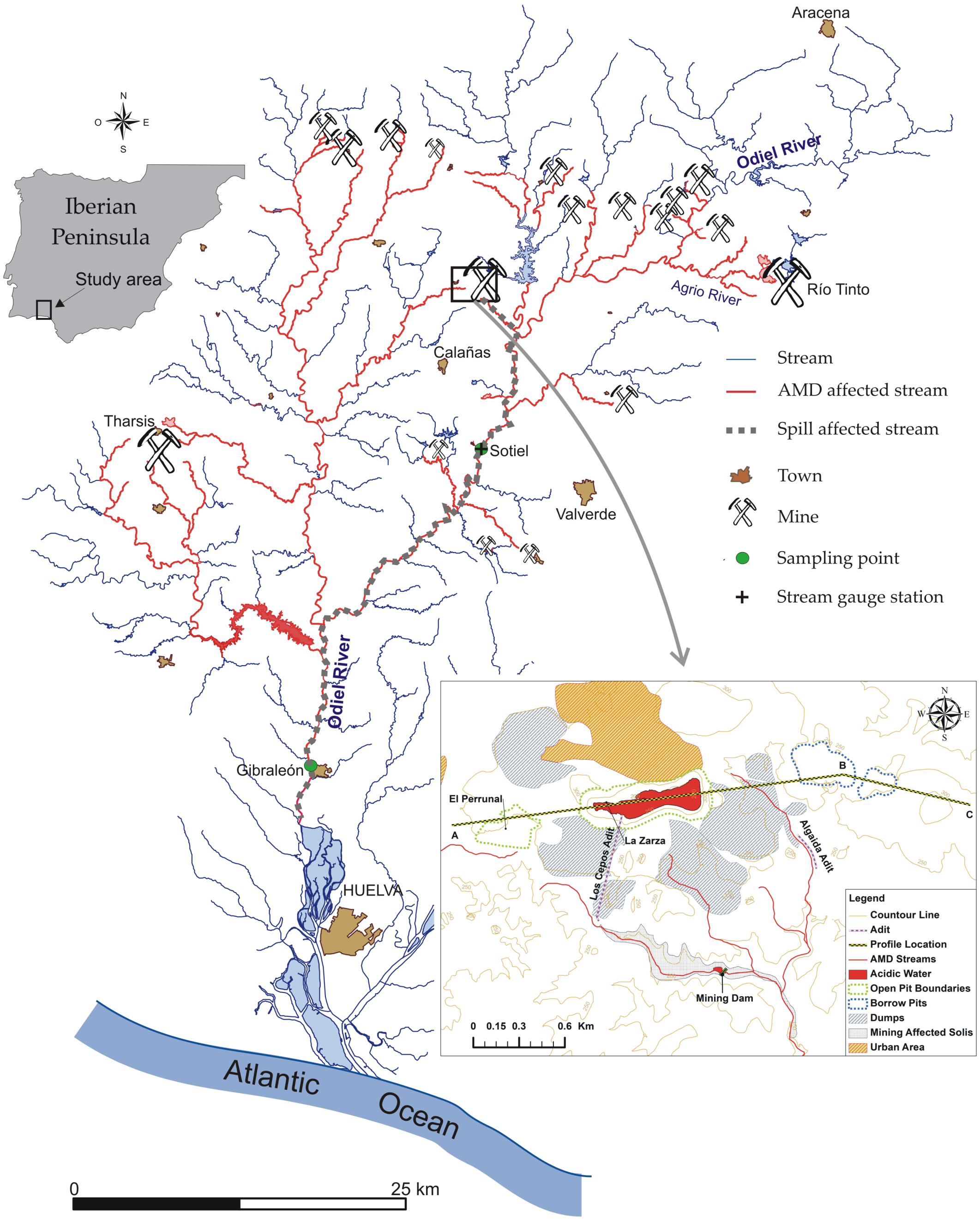

Figure 1. Map of the Odiel River watershed, indicating the area affected by the spill, the sampling points (Sotiel and Gibraleón) and La Zarza mine area.

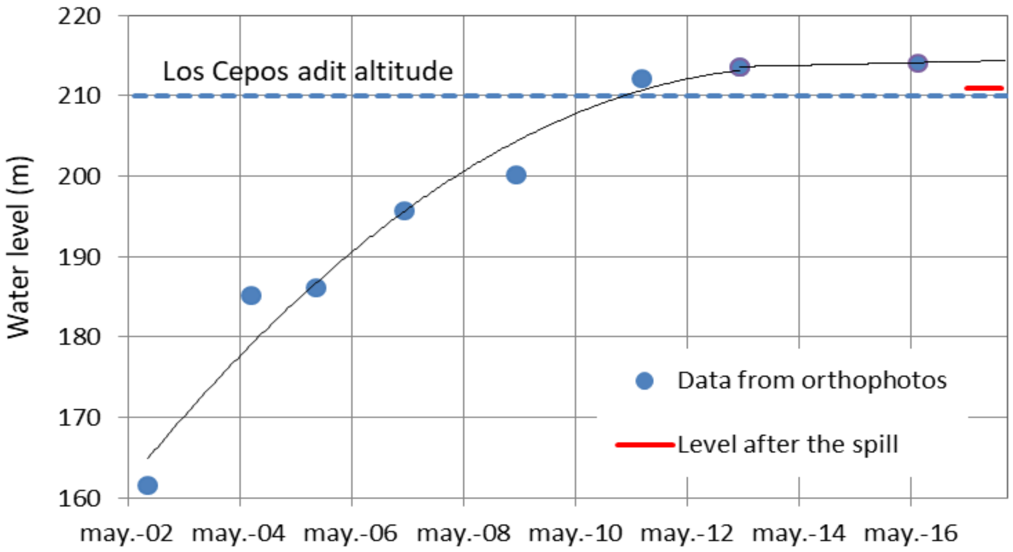

Figure 2. Water level evolution in the pit lake estimated from orthophotographs. The dashed blue line indicates the height of the adit causing the spill.

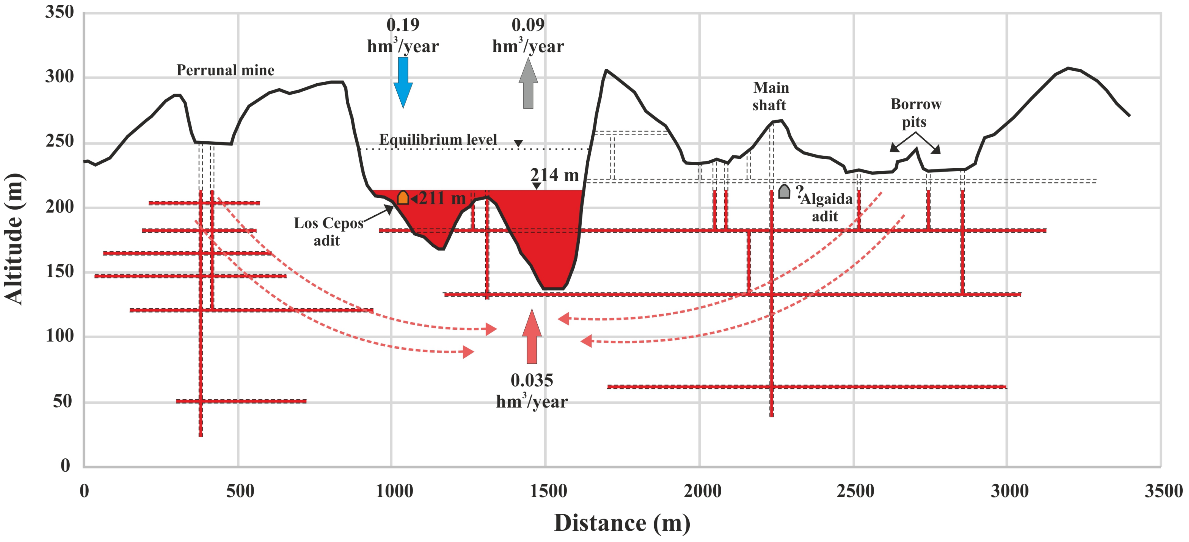

Figure 3. Pit lake section, showing the underground galleries and adits, including Los Cepos and La Algaida, and average water inputs and outputs.

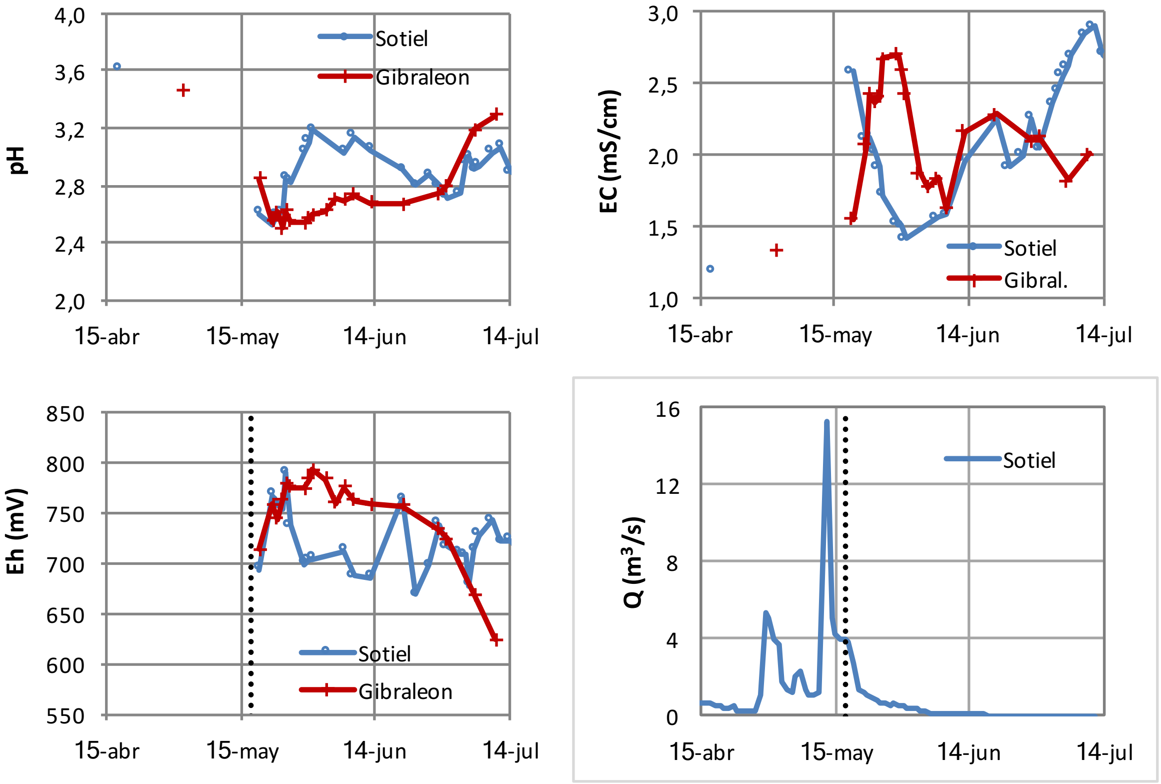

Figure 4. Evolution of pH, EC and Eh at Sotiel and Gibraleón and flow at the gauging station at Sotiel. Vertical point lines indicate the date of the plug break (May 17).

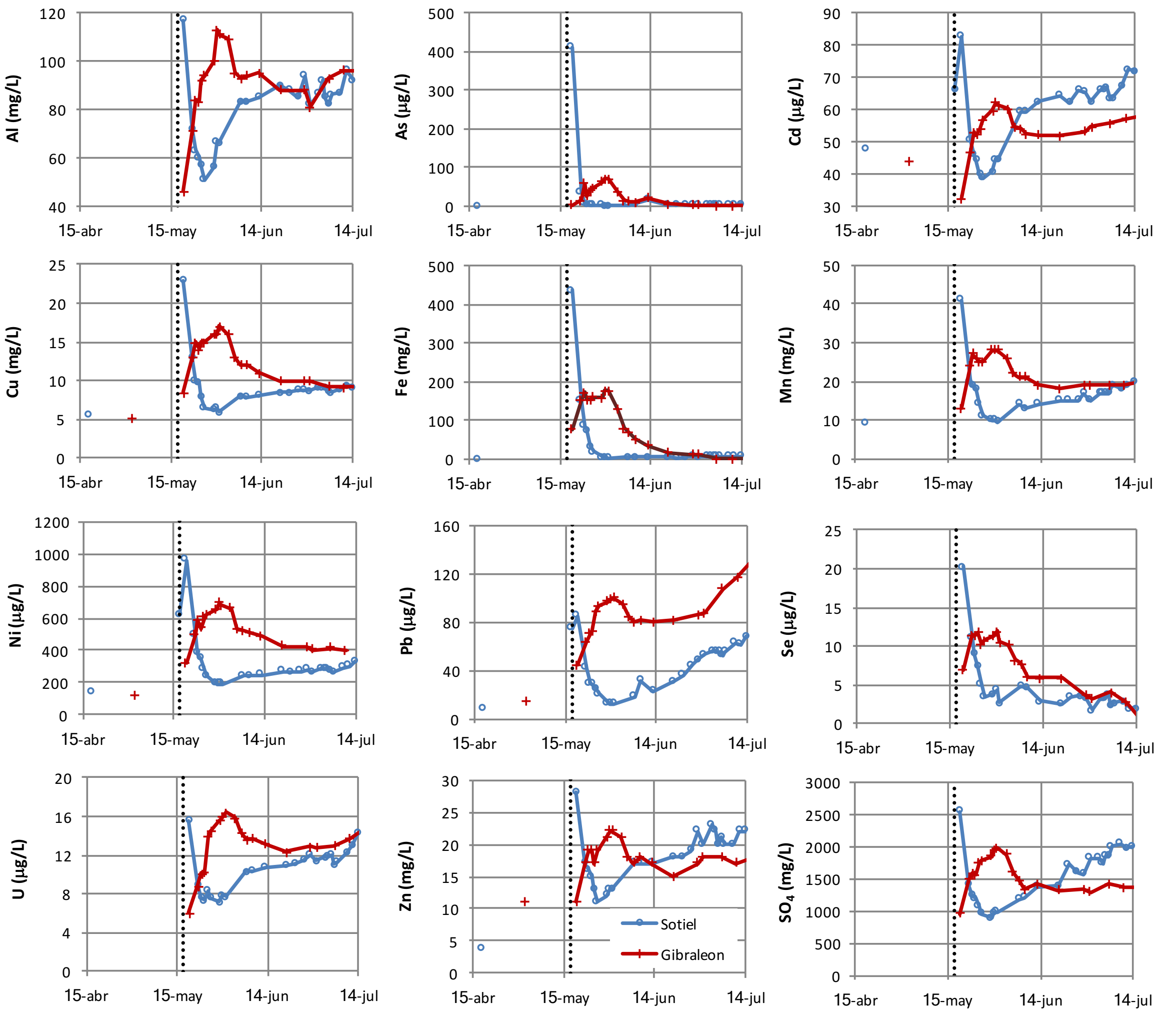

Figure 5. Evolution of the dissolved concentrations of some elements in the Odiel River (Sotiel and Gibraleón sampling points). Vertical point lines indicate the date of the plug break (May 17).

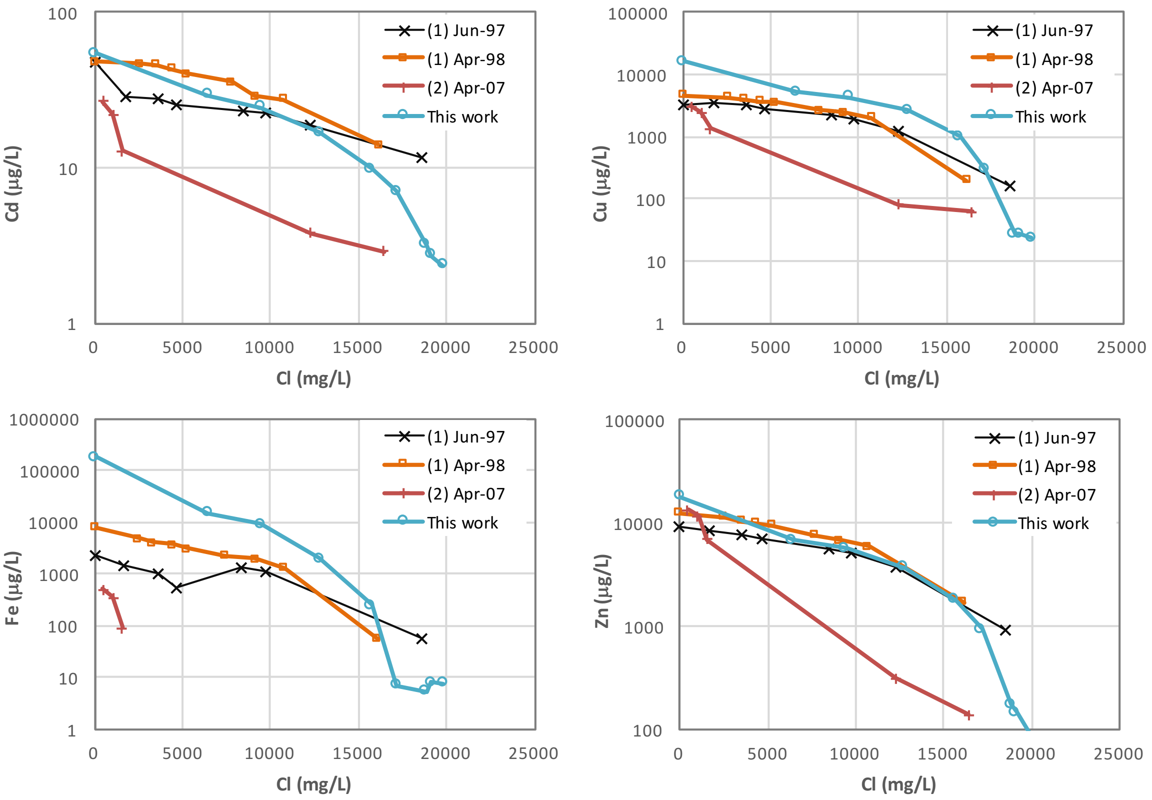

Figure 6. Dissolved concentrations of Fe and Zn in the estuary against chlorinity. (1) Data from Braungardt (2000) and Elbaz-Poulichet et al. (2001); (2) Data from Hierro et al. (2014).