

Surface and Groundwater Quality Evolution in the Agrio and Guadamar Rivers after the Aznalcóllar Mine Spill (SW Spain): Lessons Learned

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Abstract

The failure of the tailing dam at the Aznalcóllar mine (SW Spain) in 1998 released ≈ 6 million m^3 of pyrite sludge and acidic waters, and caused an enormous environmental disaster in the Agrio and Guadamar rivers. A small aquifer formed by recent alluvial materials deposited by both rivers was also affected. The mine closed as a result of the spill but a new project for its reopening is currently being developed. The area covered by the spill (≈ 60 km long) was later transformed into a protected green corridor, which connects two important natural reserves. This work describes the effectiveness of the remediation measures taken and analyzes the evolution of water quality in the area since 1980 (almost 20 years before the accident occurred). The contaminant levels in both surface and groundwater showed a sharp decrease the first years after the spill, followed by a subsequent stabilization of pollution levels. Nowadays, pollutant concentrations in surface waters are even lower than those recorded before the spill, due to the cessation of mining and the effectiveness of the remediation. Despite this fast and outstanding improvement, the alluvial aquifer close to the mining zone is still polluted, with acidic pH values in some areas, probably due to the slow movement of groundwater together with the existence of some areas with polluted soils. As this aquifer feeds the streams, some pollutants (e.g. Al, Cd, and Zn) reach the surface waters. Remediation of the polluted soils as well as the alluvial aquifer in this sector is strongly recommended to achieve the complete rehabilitation of the affected area.

Keywords: tailings dam, sulfides, water pollution, trace elements

Introduction

Large storage facilities built to contain mine tailings can collapse, and have caused many mining-related disasters. Failure of the containment structure around mine tailings is often followed by a fast-moving mudflow, which can run downstream for several miles (Santamarina et al. 2019). This, together with the release of large volumes of toxic water and pollutants, can cause tragic consequences to the populations living downstream of the impoundments, enormous environmental disasters, and compromise the livelihoods of entire communities. Over the last three decades, while the overall number of tailings dam failures has decreased, the number of serious breaches has increased and, due to climate change effects, the likelihood of such incidents could be even more probable nowadays (Roche et al. 2017).

Efforts must be undertaken to improve engineering practices, implement regulations practices, and international collaborative governance to avoid these disasters (Rico et al. 2008; Roche et al. 2017; Santamarina et al. 2019; Schoenberger 2016). In addition, it is important to carry out detailed studies of the environmental effects of the mine spills to assess the best possible remediation measures. Thus, Macklin et al. (2003) studied two tailings dam failures in northwest Romania, which resulted in the release of 200,000 m^3 of contaminated water by cyanide and metals and 40,000 tonnes (t) of tailings into the Tisa River, a tributary of the Danube, resulting in fish deaths not only in Romania, but also downstream in Hungary, Serbia, and Bulgaria. Concentrations decreased rapidly and between 4 and 6 months after the spill, metal contamination in surface water and river sediment affected mainly a reach of 10 km downstream of the spill. However, it was difficult to separate the spill's impacts from the historical problems associated with many decades of largely untreated, industrial, mining, and urban discharges into the rivers (Macklin et al. 2003). Petticrew et al. (2015) reported the effects of the spill at Mount Polley mine (Canada), where 25 million m^3 of tailings and water were released, affecting the receiving stream and Quesnel Lake, located 9.2 km downstream. The surge of material generated an extensive lake bottom deposit, consisting of tailings and eroded overburden. The lake hypolimnion was

modified immediately with a high increase of turbidity (Petticrew et al. 2015). The tailings were not acid-generating and contained generally low levels of trace metals. The swift removal of spilled tailings and river corridor stabilization limited the impacts of the spill, with Cu, and to a lesser extent V, the only elements of concern (Byrne et al. 2018). In November 2015, more than 35 million m³ of mining residues slid down after the Fundão tailing dam (Brazil) failed, causing the deaths of 19 people and affecting more than 650 km of the Doce River (Hatje et al. 2017). The spill caused a substantial increase in suspended sediment loads and significant environmental damages (Silva et al. 2018). Seven months after the spill, arsenic (As) concentrations in the river water were between 10.4 and 50.4 µg/L and the concentration of pollutants in the easily mobilized fractions of the sediments was indicative of high ecotoxicological risk and potential harm to the ecosystems and the health of the local population (Hatje et al. 2017; Silva et al. 2018). The spill reached the Atlantic Ocean, seriously affecting coastal environments and marine ecosystems (Coimbra et al. 2019). A new disaster at the same area of Brazil (at Brumadinho tailings dam) occurred in January 2019 (Thompson et al. 2020). The rupture released ≈12 million m³ of mining waste that reached the Paraopeba River (Vergilio et al. 2020). The mudwave killed more than 250 people and devastated huge forest and agricultural areas (Silva Rotta et al. 2020). The water and sediments were toxic to different trophic levels, from algae to microcrustaceans and fishes, emphasizing the necessity of long-term monitoring in the affected area (Vergilio et al. 2020).

Another important failure took place at the Aznalcóllar mine, located in the Iberian Pyrite Belt (IPB), one of the largest concentrations of massive sulfide deposits in the world, extending from SW Spain to the Portuguese Atlantic coast. The dam failed on April 25th 1998, resulting in a huge spill of metal-rich pyrite sludge and acidic waters. Detailed information about the causes of this failure can be seen in other works within this special issue (Alonso Pérez de Ágreda 2020; Martín et al. 2020). The volumes of sludge and acidic waters released were 1.3 and 5.5 million m³, respectively, according to Feasby et al. (1999), and 2 and 4 million m³, according to Grimalt et al. (1999). The spill caused a flood that moved rapidly downstream by the Agrio and Guadiamar rivers, with a peak flow of 811 m³/s (Ayala-Carcedo 2004), reaching the Guadalquivir River in a few hours (Drake et al. 1999; Gómez-Parra et al. 2000; Palanques et al. 1999; van Geen et al. 1999) and approaching the limits of the Doñana National Park, a wetland zone of great ecological importance in Europe due to its unique biodiversity (Grimalt et al. 1999; Green et al. 2016). The pyritic sludge and the acidic waters were transported 40 and 60 km downstream from the tailings dam, respectively.

A mud layer ≈ 1.7 m thick was left near the mine, with the greatest thickness accumulated in old, abandoned gravel pits, whereas at the final portion of the affected reach was a few centimeters thick (Grimalt et al. 1999). In contact with the atmosphere and water, the pyrite and other accessory sulfides in the tailings started to oxidize very quickly, releasing acidity, sulfate, and metal/loids such as Fe, As, Cu, Zn, Cd, and Pb. The spill constituted a great environmental disaster; the pH in the river waters decreased down to around 3 and the depletion of the dissolved oxygen led to mass mortality of aquatic organisms. A total of ≈ 37 t of fish died (Feasby et al. 1999) and 60 km of the river were defaunated (Grimalt et al. 1999). Additionally, the social impact was also remarkable, due to the job losses after the mine closure, and the inability of using these soils for agriculture or cattle activities (Guerrero et al. 2008).

Most research on environmental consequences of tailings dam failures focuses on the immediate and more dramatic effects (e.g. Grimalt et al. 1999; Hatje et al. 2017; Macklin et al. 2003; Petticrew et al. 2015; Silva et al. 2018; Silva Rotta et al. 2020). Nevertheless, long-term detailed studies are needed to understand the fluvial recovery evolution and the effectiveness of the implemented remediation measures. Therefore, the main goals of this work were to analyze the current status of the Guadiamar spill-affected area and the evolution of the surface and ground water quality, and evaluate the success of the remediation measures adopted. Lessons learned from this case study could be of great interest in other similar cases worldwide.

Study Area

The Aznalcóllar mine is located in the eastern part of the IPB, within the Sevilla province (SW Spain). The area is characterized by a Mediterranean climate, with annual average rainfall close to 650 mm, though with high variability. The average temperature in the study area is about 18 °C, having cold and humid winters, and summers characterized by high temperatures and very little rainfall. The mine is located in the middle reach of the Guadiamar River, which arises from the north, in the foothills of Sierra Morena, flows to the south, and empties into the wetlands of the Doñana

National Park. However, channeling works were performed in the 1950s, at the lower reach of the river ('Entremuros' sector; Fig. 1), for agricultural purposes; thus, the Guadiamar River now directly joins the Guadalquivir River. In the case of the Aznalcóllar mine, the Agrío River was channeled during the 1970s, close to the mine area and a reservoir for water supply was built upstream (Agrío dam in Fig. 1).

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Geology and Hydrogeology

The Aznalcóllar mine drains Paleozoic rocks belonging to the IPB, mainly shales and subvolcanic rocks, with Neogene sediments belonging to the Guadalquivir depression (Fig. 2). Neogene formations, discordantly deposited over the Paleozoic rocks, include: 1) conglomerates and calcarenites of Upper Miocene age, 2) Upper Miocene-Lower Pliocene marls, 3) sandy silts from the medium Pliocene, 4) Plio-Quaternary sands and, in the Doñana area, and 5) marsh clays deposited during the Holocene (Salvany et al. 2004). Finally, recent alluvial deposits, mainly constituted of pebbles, gravels, and sands, were deposited over all of them.

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Regarding hydrogeology, in the mining area there are two aquifers: 1) conglomerates and calcarenites from the Upper Miocene, which is confined by overlying marls, and 2) alluvial terraces form the alluvial aquifer of the Guadiamar River (including the alluvium of the Agrío River), which is under study (Fig. 3A and B). To the south, Plio-Quaternary sands form other important aquifers (Manzano et al. 1999). In the mining area, the recharge of the alluvial aquifer comes only from rainfall infiltration. The discharges are mainly produced by pumping for irrigation and through natural recharge to the rivers. Thus, the Agrío and Guadiamar are gaining rivers. There are remarkable variations in the aquifer thickness (from some meters to tens of meters). In the Agrío River zone, the hydraulic conductivity is close to 600 m/day and the storage coefficient between 0.08 and 0.23 (Ayora et al. 2001).

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Mining at Aznalcóllar

The exploitation of the Aznalcóllar mine dates back to the Phoenicians or even before, with increased activity during the Roman Empire (Amores et al. 2014). More recently, mining began in 1876 by means of underground galleries and continued over the 20th century (Pinedo Vara 1963). Large-scale extractions started in the 1970s at the Aznalcóllar open pit (Fig. 1). During this period, a flotation plant was built for ore processing and production of Zn, Pb, and Cu concentrate. The waste generated by this process necessitated a dam to deposit the tailings generated. The tailings storage, kept under water to avoid sulfide oxidation, began in 1979. In 1987, some environmental improvements of the site were carried out, including the construction of a neutralizing plant to treat the acidic waters generated (Feasby et al. 1999). In 1996, the Aznalcóllar open pit was mined out and abandoned, while extraction began in a closely located deposit: the Los Frailes open pit (Fig. 1). Mining there stopped in 2001 because of the 1998 spill.

During the period of open pit mining, large mine dumps were produced, which, together with the open pits and mining facilities, cover an area of around 8 km² (Fig. 2). Currently, a new project to reopen the mine has been initiated to exploit the ore below the Los Frailes open pit by underground mining.

Remediation Measures after the Spill

The first remediation measures taken after the spill were 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, called the Entremuros zone, to hold the acidic water and prevent acidic water from entering Doñana. The acidic waters accumulated in this zone, though a portion reached the Guadalquivir River (Drake et al. 1999; Grimalt et al. 1999). However, the impact on the Guadalquivir estuary was low (García-Luque et al. 2003; Gómez-Parra et al. 2000; Palanques et al. 1999; van Geen et al. 1999). Two neutralizing plants were constructed to treat the acidic water, one mobile and another built in the Entremuros zone. In addition, the affected crops, fauna, and vegetation were removed (Grimalt et al. 1999).

Pyritic sludge removal was carried out from May to December 1998 using heavy machinery. The toxic muds were deposited in the Aznalcóllar open pit. In the summer of 1999, the small remnant amounts of sludge not withdrawn during the first campaign, were removed. Afterwards, the height of the tailings dam embankments was lowered to ensure stability, the dam was sealed with a layer of clay, and its tightness was improved by the construction of an impermeable screen in the east embankment next to the Agrio River. Recently, the most contaminated mine dumps have also been isolated.

The acidic water entered the soils flooded by the spill. In general, soil alkalinity was sufficient to neutralize the acidity and so the pollutants remained immobile in the soil (Simón et al. 1999). In some sandy areas with low carbonate content, the affected soils were acidified and pH values had to be increased using alkaline materials. Iron-rich clayey materials were also added in some areas to fix As (Aguilar et al. 2007). In addition, the more contaminated surface horizons were mixed with deeper layers to decrease toxic element concentrations (Galán et al. 2002; Simón et al. 2009). Nevertheless, toxic element levels in soils are still high compared to background values and, in some areas near the mine, small patches of soil with pyritic sludge without any vegetation can be seen (Domínguez et al. 2016; Madejón et al. 2018; Fig. 3C and D). According to recent data (García-Carmona et al. 2019), concentrations of trace elements exceeded the background concentrations, with maximum values exceeding 19- and 10-fold for As and Pb, respectively, and 3, 2, and 2.5-fold for Cu, Zn, and Cd, respectively. Domínguez et al. (2016) found concentrations up to 650 mg/kg of As and 2920 mg/kg of Pb, well above the established levels used for declaring a soil as contaminated according to the guidelines from the Andalusia Regional Government (36 and 275 mg/kg, respectively).

Regarding groundwater, large-diameter wells located in the alluvial aquifer were flooded by the slurry. These wells were intensely pumped to remove the pyritic sludge and limed to neutralize the acidity (Ayora et al. 2001). Nevertheless, some of them became acidic again, which meant that the process had to be repeated. An area with low pH values and high concentrations of toxic elements in the Agrio River alluvial aquifer, close to the tailings dam, was detected (Alcolea et al. 2001). In an attempt to improve the groundwater quality in this area, a permeable reactive barrier (PRB) was built in 2000. This barrier was 120 m long, 1.4 m wide, and on average, 6 m deep. The system was divided into several parts with different proportions of filling material (i.e. limestone, vegetal-gardening compost, sewage sludge, and zero-valent iron). More information on the PRB can be found in Gibert et al. (2011).

Since the trace element concentrations in the soils of the area were high, the land could not be used for farming or pastures, so the Andalusian regional government acquired the surface covered by the toxic sludge to create the “Guadiamar Green Corridor”. This corridor was intended to allow public use of the affected area and to connect two important protected natural spaces: Sierra Morena area to the north and Doñana to the south. The ecological restoration was performed through an investigation program following the recommendations of scientific and technical experts, based on limited interventions to remove the factors that prevented the natural recovery of natural systems.

Methodology

The methodology followed in this study can be seen in Fig. 4. A detailed sampling of surface and groundwater was performed during October 2019 in the areas most affected by the spill (Fig. 1), from the tailings dam to 16 km downstream. In total, 9 piezometers located in the alluvial aquifer of the Agrio River and 7 wells in the alluvial aquifer of the Guadiamar River were sampled (Fig. 2) using a PVC bailer sampler. The Agrio River was sampled upstream of the tailings dam (A0 sampling point; Fig. 2), close to the tailings pond embankment (A1), and downstream (A2). However, the Guadiamar River could not be sampled because most of its course was dry.

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Filtered samples (0.45 mm pore size Millipore filters) were collected in high-density polyethylene (HDPE) bottles, acidified to pH < 2 with nitric acid 65% Merck Suprapur®, and refrigerated until analysis. In addition, filtered, non-acidified samples were collected for anions determination. All bottles used during the sampling were acid-washed (10% HNO₃) for 24 h, rinsed in Milli-Q water (18.2 MΩ, Millipore), and stored in sterile plastic bags prior to use.

Different physico-chemical variables, such as temperature, pH, electrical conductivity (EC), and oxidation-reduction potential (ORP) were measured in situ (Fig. 4) using HANNA HI 98190 and 98192 portable meters. A three-point calibration was performed for both EC (147 $\mu\text{S}/\text{cm}$, 1,413 $\mu\text{S}/\text{cm}$, and 12.88 mS/cm) and pH (4.01, 7.00, and 9.21), while ORP was controlled at two points (240 and 470 mV) using standard solutions. Major elements and trace metals was determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES) and inductively coupled plasma mass spectrometry (ICP-MS) at the R+D laboratories of the University of Huelva. Detection limits were 200 $\mu\text{g}/\text{L}$ for Al, Ca, Mg, and Na; 100 $\mu\text{g}/\text{L}$ for K, Cu, and Fe; 50 $\mu\text{g}/\text{L}$ for Zn and Mn, and 0.5 $\mu\text{g}/\text{L}$ for As, Cd, Co, and Ni. The quality of analysis was checked against analysis of NIST-1640 certified reference materials. Anion concentrations (i.e. Cl^- , Br^- , F^- , NO_3^- and NO_2^-) were determined by ion chromatography (Dionex DX-120), while total alkalinity was determined by CHEMetrics® Total Titrets®.

The information obtained was completed with data from the Regional Environmental Authority database (Fig. 4) for the river monitoring stations “El Guijo” and “Vado del Quema” (Fig. 2) to study the evolution of the river quality, and the results obtained in this study were compared with those reported in previous studies (Alcolea et al. 2001; Cabrera et al. 1984, 1987; Manzano et al. 1999; Olías et al. 2005, 2006, 2012).

Results

Table 1 shows basic statistics of results obtained during the sampling of groundwater in the alluvial aquifers of both the Agrio and Guadiamar rivers. The piezometric level was close to the topographic surface, with depths of the water table ranging from 3 to 7 m. The pH ranged from 3.0 to 7.1, while EC varied from 0.64 to 2.21 mS/cm , with a mean value of 1.23 mS/cm . The dominant hydrochemical facie was calcium sulfate, except at the most northern piezometer, located upstream of the tailing dam, which exhibited calcium bicarbonate facie.

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Concentrations of mining-associated elements in groundwater were low (< 0.1 mg/L for Al, Cu, Fe, Mn, and Zn, and < 10 $\mu\text{g}/\text{L}$ for As, Cd, Co, Ni, and Pb.) except in 3 piezometers from the Agrio alluvial aquifer and 2 isolated wells from the Guadiamar alluvial aquifer (W19 and W32; Fig. 2), with acid pH values (<4.5) and concentrations of Fe and Al of up to 27 and 20 mg/L , respectively (Fig. 5).

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Rainfall before the sampling was low; only 24 mm were collected in September and October at the Sanlúcar La Mayor rainfall station (Fig. 1); therefore, the Agrio river flow was noticeably low in October 2019 (around 5-10 L/s). The Guadiamar River could not be sampled because it was dry, with only some pools of stagnant waters observed along its course. The pumping of waters from several wells in the Guadiamar alluvial for agricultural purposes may have lowered the water table, preventing the natural recharge from the aquifer to the river.

Table 2 shows the results obtained for the Agrio River (samples A0, A1 and A2; Fig. 2). Values of pH close to neutrality (pH of 6.78), low EC values (0.25 mS/cm) and sulfate (42 mg/L) and Zn concentrations (0.18 mg/L) were recorded upstream of the tailing dam (sample A0; Fig. 6). However, pH values decrease and sulfate and Zn concentrations increase in the surroundings of the tailing dam (sample A1). Downstream (sample A2), the water quality even worsens except for Zn, which concentration is lower than in A1.

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Figure 7 shows the evolution of some water quality parameters since 1980 at the ‘El Guijo’ quality monitoring station, located after the confluence of the Guadiamar and Agrio rivers (Fig. 1). There are some gaps, and the data must be cautiously considered as analytical techniques and detection limits have noticeably improved since 1980. There is a seasonal pattern with higher concentrations in the summer and lower ones in the winter due to the higher river flows and, consequently, the effect of dilution by runoff. The worst water quality conditions in the Guadiamar River were recorded at the beginning of the 1980s, with pH values close to 2 and Fe concentrations around 100 mg/L . The spill (indicated by the vertical red line in Fig. 7) caused a decrease of pH values and an increase in concentrations of some

toxic elements, such as Cu and As, until about 2002. Afterwards, a progressive decrease in the concentration of Cd, Cu, Fe, and Zn can be observed (Fig. 7), as well as for other mine-related pollutants. In the 'Vado del Quema' water quality monitoring station, located farther from the mining area (Fig. 1), information is only available since 1994, and data are especially scarce from 2009 on (Fig. 8). The pH values at this point are higher than upstream, while the concentrations of mine-related pollutants are lower, except for As.

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Discussion

The low pH values in two isolated wells of the Guadiamar aquifer (W19 and W32, Fig. 2) was probably due to pyritic materials that flowed into the well (Olías et al. 2012). Figure 9 shows the evolution of some large diameter wells with more complete data series also located in the Guadiamar alluvial aquifer that were contaminated during the tailings spill. One of these wells (W22), suffered from frequent acidification episodes for several years after the spill (Fig. 9), despite pumping and cleaning operations, which indicate a higher level of pollution by the spill in this sector, probably due to the lower carbonate materials content in the aquifer. Consequently, Zn concentrations were > 10 mg/L. Since 2005, the pH has been close to 7 and Zn concentrations have been below 1 mg/L, with a notable decreasing tendency observed over time. The W33 sampling point also suffered from acidification after the spill but, unlike W22, the pH quickly increased and Zn concentrations have remained < 50 $\mu\text{g/L}$ since 2006. The furthest point from the mine (W35) also exhibited moderate Zn concentrations until 2002, along with a decreasing trend in sulfate concentrations over time (Fig. 9).

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Acidic values were detected in piezometers drilled in the Agrio alluvial aquifer after the spill, indicating more widespread groundwater pollution in this area. Nonetheless, the concentrations were much less than those recorded immediately after the spill. The evolution of the water quality in the Agrio alluvial aquifer can be seen in Fig. 10, which represents the Zn concentration distribution in three different periods. Although the sampling points were not exactly the same on the three dates, it can be appreciated that Zn concentrations in the aquifer after the spill (1999-2000) were > 50 mg/L in several piezometers (mean value of 20 mg/L), reaching maximum values of up to 300 mg/L. By 2009, the concentrations had remarkably decreased, with a mean value of 2.9 mg/L. This decreasing trend of Zn concentrations, although at a lower rate, was also confirmed in the 2019 sampling, with a mean value of 0.5 mg/L. Concentrations of trace metals strongly decrease when the pH values rise (Fig. 5) due to the precipitation of Fe and Al oxyhydroxides/hydroxysulfates (Nordstrom et al. 2015), together with the sorption/coprecipitation of Cd, Mn, Ni, Zn, and other trace elements (Olías et al. 2012).

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As the groundwater of the alluvial aquifer feeds the streams, there are acidic discharges into the Agrio River, causing a decrease in pH and increase of EC and pollutant concentrations along its course (Table 2 and Fig. 6). Regarding the water quality evolution of the Guadiamar River since 1980 (Fig. 7), as previously indicated, the worst conditions were reached at the beginning of the 1980s (Fe concentrations ≈ 100 mg/L). These conditions were attributed to acidic discharges from the mine (Cabrera et al. 1984 and 1987), favored by more permissive regulations in Spain for mine discharges in this period. Some remediation measures were adopted in 1987, including the building of a neutralization plant for acid water treatment (Feasby et al. 1999), which led to improvement of the Guadiamar River water quality (Fig. 7). The immediate effect of the 1998 spill is not evident from this data because the first sample was taken 3 weeks after the spill, when river conditions had improved. Nevertheless, after the spill, the river exhibited acidic pH values, an absence of dissolved oxygen, and high concentrations of toxic elements and suspended solids (up to 450 mg/L of Zn; Ayora et al. 2001). Dissolved oxygen and pH values were back down to normal, and element concentrations sharply decreased, during a period ranging from a few days to weeks (Ayora et al. 2001; Olías et al. 2006), although the recovery of the aquatic biodiversity was much slower (Prat et al. 1999). From 1999 to 2002, concentrations of Cd, Zn, and other elements remained high and pH values low. From 2003 on, a progressive decrease in Cd, Cu, Fe, and Zn was observed, and nowadays the metal concentrations are better than before the spill. This improvement must be linked to the remediation measures performed in the area together with in-stream natural

attenuation processes (Hudson-Edwards et al. 2003; Turner et al. 2008). In this sense, the swift removal of the pyritic sludge was a key factor, as observed at other tailings spills (Byrne et al. 2018). In addition, the construction of an impermeable screen at the base of the tailings impoundment and the isolation of sulfide-rich dumps in the mining area must have notably reduced the delivery of pollutants into the Agrio River.

At the 'Vado del Quema' quality station, element concentrations were less, except for As, due to more intense dilution by clean tributaries (Fig. 8). As exhibits a behavior completely different from most other mine-related elements because of its affinity to co-precipitate and/or be sorbed onto Fe minerals at pH values below 7. Thus, although the As content in the river sediments of the Guadiamar reaches close to the mine were very high, the As concentrations in the water were very low (Fig. 7). Nevertheless, above pH 7.5, As is desorbed, being transferred again to the dissolved phase (Olías et al. 2006). Thus, an increase in As concentrations is observed in the southern part of the Guadiamar River catchment, where pH values are more alkaline than near the mine. Nonetheless, it can be clearly seen that As concentrations notably decreased after 2003, although the pH remained almost constant or even increased (Fig. 8), reflecting a progressive decrease of As concentrations in the riverbed sediments.

Compared to other rivers from the IPB affected by acid mine drainage (AMD), the Guadiamar River has much less pollution (Grande et al. 2018). However, despite the improvement of river water quality, the concentrations of Zn and Cd still exceed the threshold values established by Spanish regulations for rivers (between 0.45 and 1.5 µg/L for Cd and 30 to 500 µg/L for Zn, depending on the water hardness).

River recovery has been recorded in several studies dealing with the biota in the area. After 6 months of cleaning operations, typical riverine macroinvertebrate species had not recolonized the fluvial system due to the intense transformation of the river into a series of artificial ponds by the cleaning activities, together with the large habitat disturbance associated with the spill (Prat et al. 1999). Solà et al. (2004) studied the macroinvertebrate communities of the Guadiamar River two years after the spill and found poorer communities in the zone close to the mine, whereas downstream from the mine, biodiversity increased. High concentrations of Cu, Cd, and other elements in the larvae of caddisflies were also detected in the Agrio zone.

However, the affected reaches harboured fish after the main cleaning work ceased and the first large flood took place (two years after the spill), although exotics were favored by the kill event (De Miguel et al. 2016a). Also, otters reoccupied the Guadiamar River less than a year after the spill, although the concentrations of As, Pb, and Zn in their faeces were high (Delibes et al. 2009). De Miguel et al. (2016b) stated that the richness and diversity of the Guadiamar fish communities seemed more affected by other anthropogenic impacts, like urban sewage, agricultural pollution, or exotic fish species. In the same sense, Ferreras-Romero et al. (2009) found that the Odonata species assemblage was especially poor in lower river reaches of the Guadiamar, which has experienced permanent, diffuse, urban and agricultural pollution.

Regarding terrestrial fauna, Márquez-Ferrando et al. (2009) found higher concentrations of As, Tl, Sn, Pb, Cd, and Cu in lizards from the affected area eight years after the mine accident, indicating the continued presence of these contaminants in the terrestrial food chain. On the other hand, only five years after the mine accident, bird communities in the affected area were similar in species richness, abundance, and diversity to an unaffected reference site, due to the rapid restoration of habitat and the resilience of the birds (Ontiveros et al. 2013).

In the Guadalquivir River, the environmental impact was much less. Nevertheless, metal concentration in aquatic organisms (i.e. mollusks, crustaceans, and fish species) collected at several stations (from April to September 1998) showed relatively high levels of toxic metals (i.e. Cd, Cu, and Zn), in some cases exceeding the Spanish statutory limits in aquatic organisms. Toxicological studies performed to assess the impact of the spill, as part of a monitoring program between 1998 and 2001, showed no significant negative effects on tested bivalves (Riba et al. 2004). Although moderate and localized acute toxic responses were observed for amphipods, Riba et al. (2004) reported a recovery of the system. Tornero et al. (2014) studied metal concentrations in sediment, clams, and worms from the Guadalquivir estuary 10 years after the spill and reported a significant decrease of Zn content in sediments and clams compared to levels observed after the spill.

In summary, environmental conditions showed a remarkable improvement approximately five years after the spill, and at present, are even better than before the spill. Nevertheless, the Agrio alluvial aquifer is still polluted, releasing toxic elements directly to the Agrio River and finally to the Guadamar River. Discrimination between the impact caused by mining dam accidents and historic mining contamination is often a difficult task (Hatje et al. 2017; Macklin et al. 2003; Silva et al. 2018). Feasby et al. (1999) claimed that background metal concentrations in the Guadamar area may be high due to oxidation of sulfide minerals that outcrop in the area and sulfide-rich wastes inherited after \approx 5000 years of mining. However, the evolution of the Guadamar River quality, nowadays better than before the spill, indicates that the remediation measures carried out reduced the AMD input from the mine to the Agrio River and the underlying aquifer. This pre-spill pollution of the Agrio and Guadamar waters by mine effluent has been previously reported (Cabrera et al. 1984 and 1987; Grimalt et al. 1999). In addition, López-Pamo et al. (1999) and Martín et al. (2000) concluded that soils and sediments along the Guadamar valley were already contaminated by mining before the accident. Ayora et al. (2001) and Alcolea et al. (2001) also pointed out that groundwater pollution in the Agrio alluvial area probably had a mining origin prior to the 1998 spill. Hudson-Edwards et al. (2003) found that current fluvial sediments not affected by the spill had significantly higher concentrations of As, Cd, Pb, and Zn than sediments dated to the 11th–13th centuries, indicating pollution by recent mining. In brief, a mining origin for the contaminant concentrations in the Agrio River aquifer seems probable, together with the influence of the 1998 spill. In this sense, Olías and Nieto (2015) found that pollutant concentrations in other AMD-affected rivers in the IPB are mainly due to the large-scale mining that has taken place since the second half of the 19th century, while the influence of natural sulfide oxidation processes was negligible.

Additional remediation measures should be taken for complete recovery of the area. In particular, acidic and metal-rich soils (Fig. 3C and D), mainly located in the Agrio River watershed (Domínguez et al. 2016; García-Carmona et al. 2019; Madejón et al. 2018), should be cleaned since these metals and acidity may be transferred from the affected soils to the saturated zone of the aquifer during rainfall infiltration. Complete decontamination of affected soils will also improve vegetation and groundwater quality. Another potential measure to be taken would be a tracer test in the Agrio River to identify the zones where the aquifer recharges the river with polluted groundwater. Once located, these contaminant sources could be treated using passive treatment systems such as PRBs or anoxic alkaline drains (Skousen et al. 2017).

Conclusions

The impact caused by the spill on the Guadamar alluvial aquifer was moderate due to the soil's neutralizing capacity. An increase in sulfate and trace elements, especially those more mobile (e.g. Zn), was observed until about five years after the spill. The Agrio alluvial aquifer, close to the mining area, still shows pollution, although the concentration of toxic elements is much less than after the spill. This situation may be explained by inherited mining pollution that was aggravated by the spill. Therefore, additional remediation measures are needed in this area for complete restoration.

Concerning surface waters, the concentrations of toxic elements remained elevated until about 2003. Afterwards, a progressive decrease in mine-related metal concentrations was observed, so at present, the conditions are much better than before the spill. However, the concentrations of some toxic metals in the river, such as Cd and Zn, still exceed the threshold values established by Spain's environmental regulations

In brief, the main lessons learned from the gained experience are that the environmental quality improvement was due to the success of remediation measures performed after the spill (above all, the swift removal of spilled tailings), increased environmental controls in the mine area, and the self-cleaning capacity of the water courses. In this sense, the ecological restoration performed in the area and the creation of the Guadamar Green Corridor was successful, as evidenced by the river's improved biodiversity. Notwithstanding, there is remnant pollution in the Agrio River from groundwater. The pollution of alluvial aquifers, where water movement (and the benefits of remediation measures) is much slower than in surface water, is an important factor to consider in the long-term recovery of rivers affected by tailings spills.

Nowadays, modern mining uses the best technologies and is more environmental friendly than the mining that operated in this area a long time ago. In this sense, the reopening of Los Frailes mine should not present a threat to water quality but an opportunity to complete the restoration of environmental liabilities.

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Figure Captions

Figure 1. Location map showing the area covered by pyritic mud (in orange) and the river water quality monitoring stations.

Figure 2. Hydrogeological map of the Agrio and Guadiamar alluvial aquifers indicating sampling points of surface water and large diameters wells. The inner rectangle is the sector represented in Figure 10.

Figure 3. Photographs of the zone: A) The Agrio River at point A1, with the tailings dam wall on the left (picture looking northward), B) Sampling piezometer downstream the permeable reactive barrier (alluvial materials forming the aquifer can be observed), C) Polluted soil spot close to point A1 with grey color and scarce vegetation due to sulfide sludge remains, D) Detail of picture C showing soluble sulfate salts formed from sulfide oxidation.

Figure 4. Flow chart of the methodology followed in this study.

Figure 5. Relationship between pH and concentrations of Al, Fe, Cd and Zn in groundwater.

Figure 6. Evolution of pH, electrical conductivity (EC), sulfate and Zn along the Agrio River in October 2019.

Figure 7. Evolution of pH values and concentrations of As, Cd, Cu, Fe and Zn at 'El Guijo' monitoring station. The vertical red lines indicate the spill (April 98).

Figure 8. Evolution of pH values and concentrations of As, Cd, Cu, Fe and Zn at 'Vado del Quema' monitoring station. The vertical red lines indicate the spill (April 98).

Figure 9. Evolution of pH, sulfate and Zn in some wells flooded with pyritic muds (data from Manzano et al. 1999, Olías et al. 2012 and this study).

Figure 10. Comparison of Zn concentrations in the Agrio River alluvial aquifer in 1999/2000 (data from Alcolea et al. 2001), 2009 (data from Olías et al. 2012) and October 2019 (this study). Concentrations are expressed in mg/L. PRB: permeable reactive barrier.

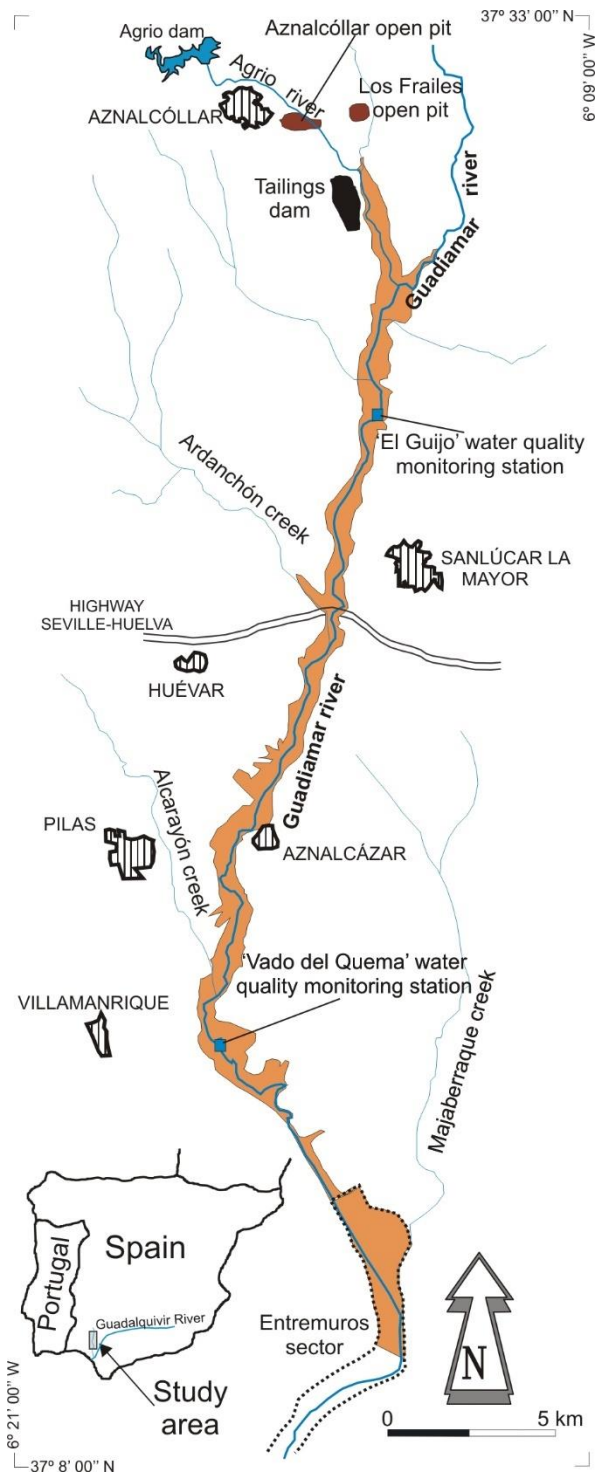


Figure 1. Location map showing the area covered by pyritic mud (in orange) and the river water quality monitoring stations.

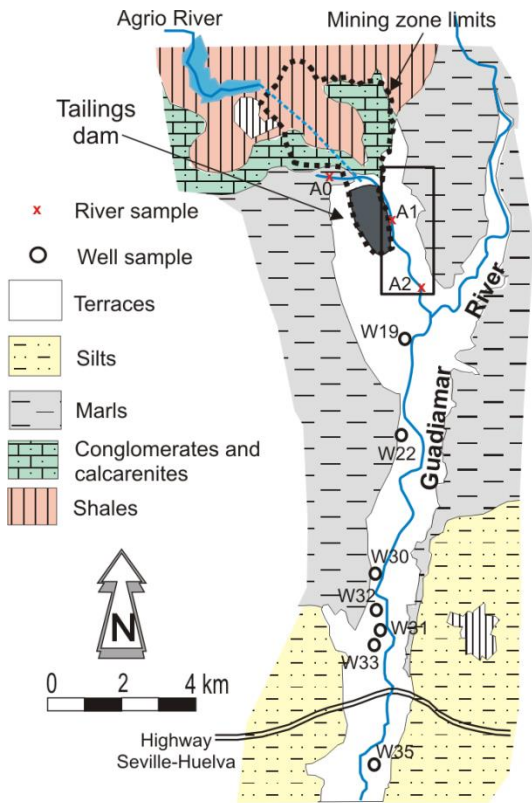


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METHODOLOGY

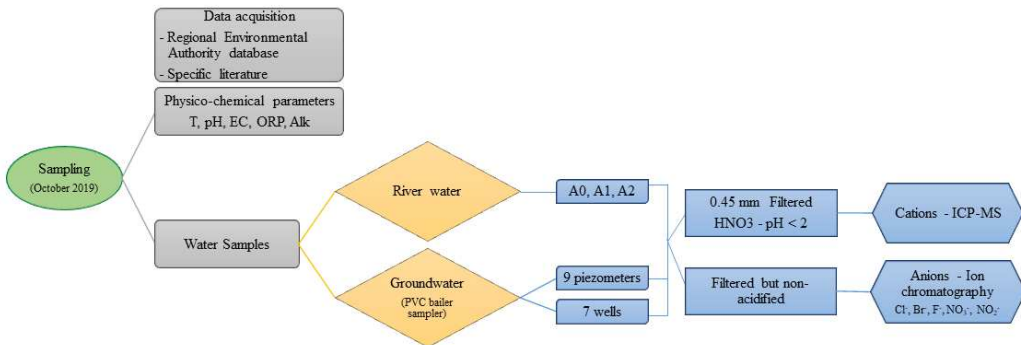


Figure 4. Flowchart of the methodology followed in this study

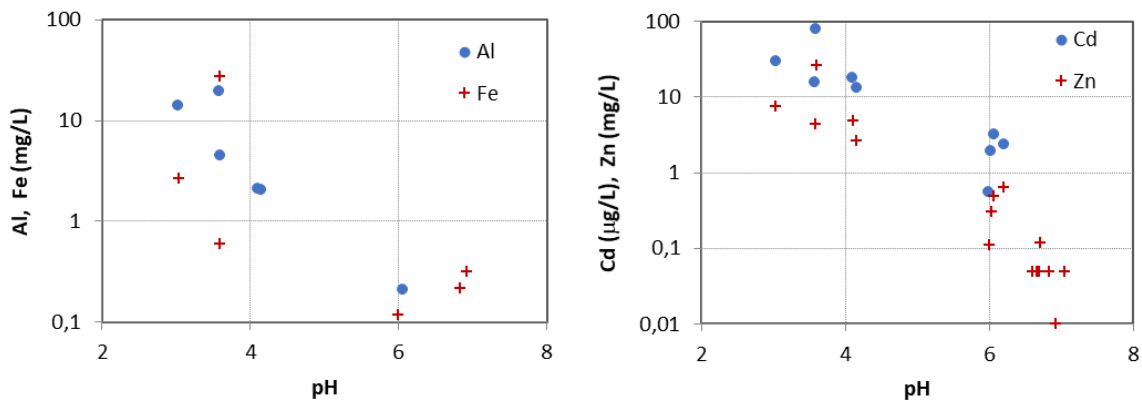


Figure 5. Relationship between pH and concentrations of Al, Fe, Cd, and Zn in groundwater.

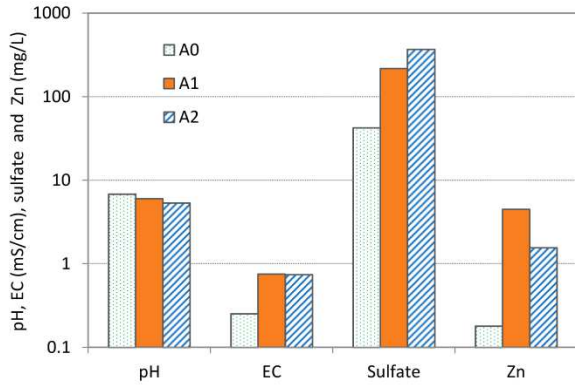


Figure 6. Evolution of pH, electrical conductivity (EC), sulfate, and Zn along the Agrio River in October, 2019

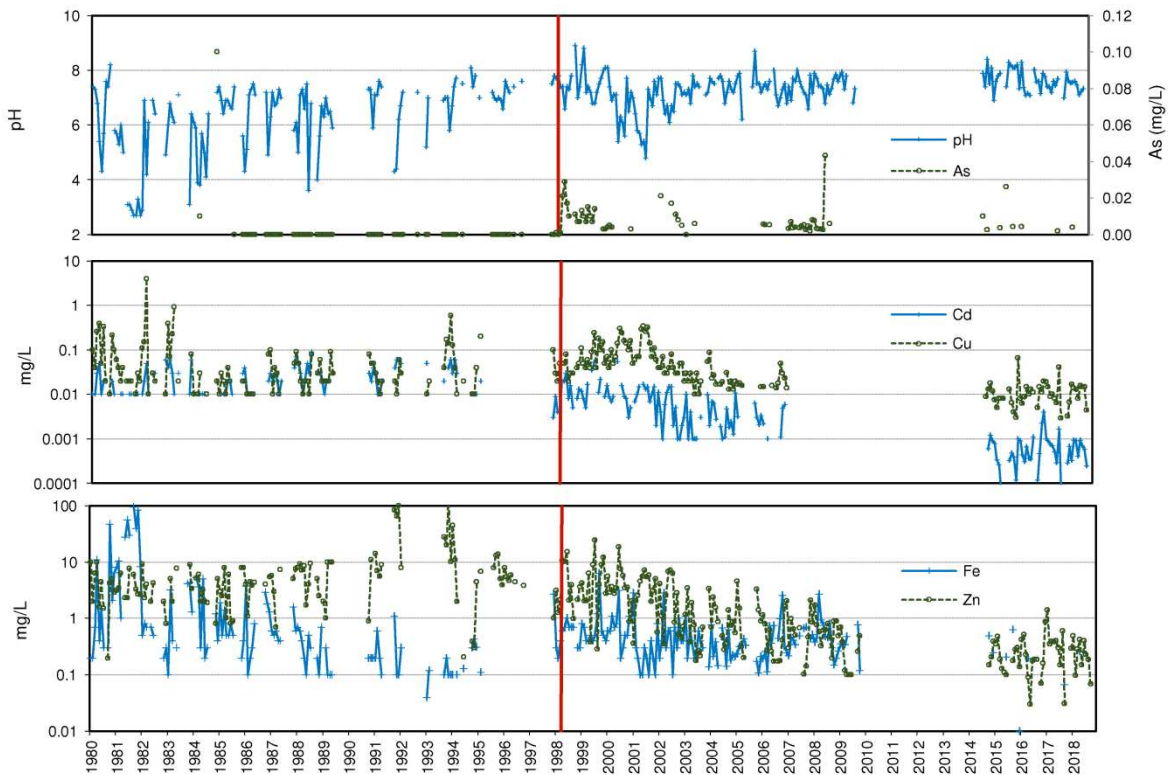


Figure 7. Evolution of pH values and concentrations of As, Cd, Cu, Fe, and Zn at the 'El Guijo' monitoring station. The vertical red lines indicate the spill (April, 1998).

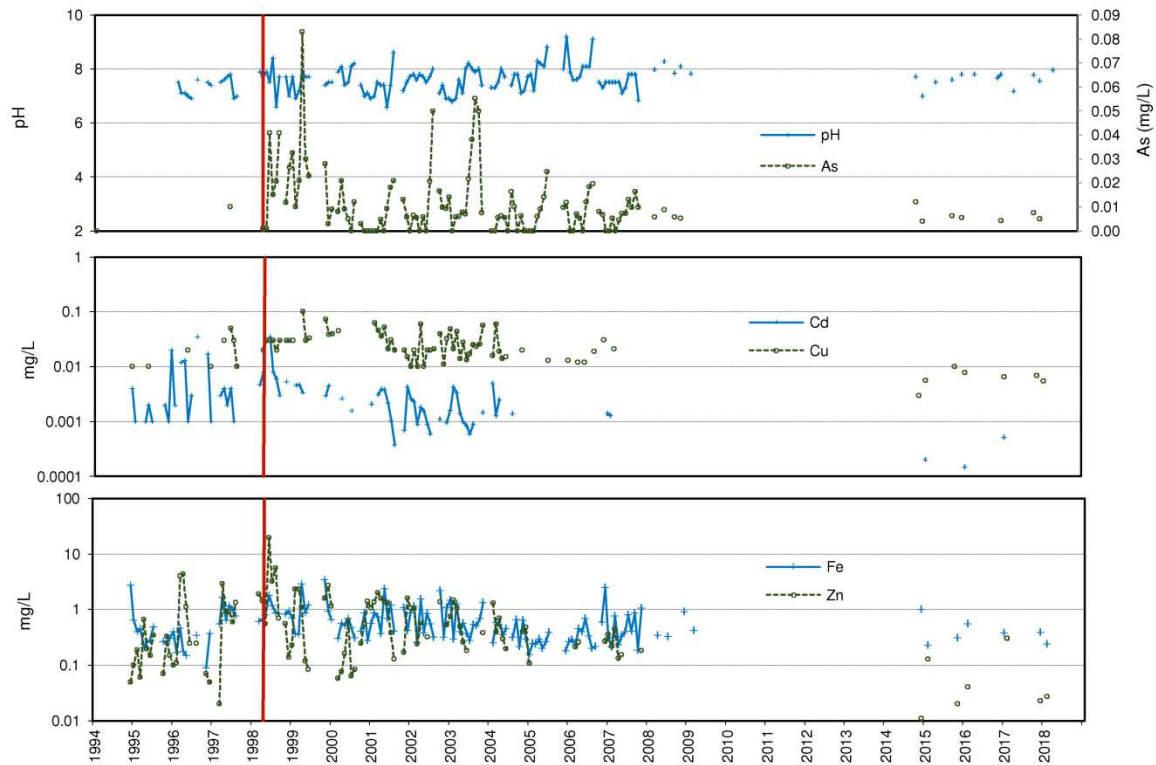


Figure 8. Evolution of pH values and concentrations of As, Cd, Cu, Fe, and Zn at the 'Vado del Quema' monitoring station. The vertical red lines indicate the spill (April, 1998).

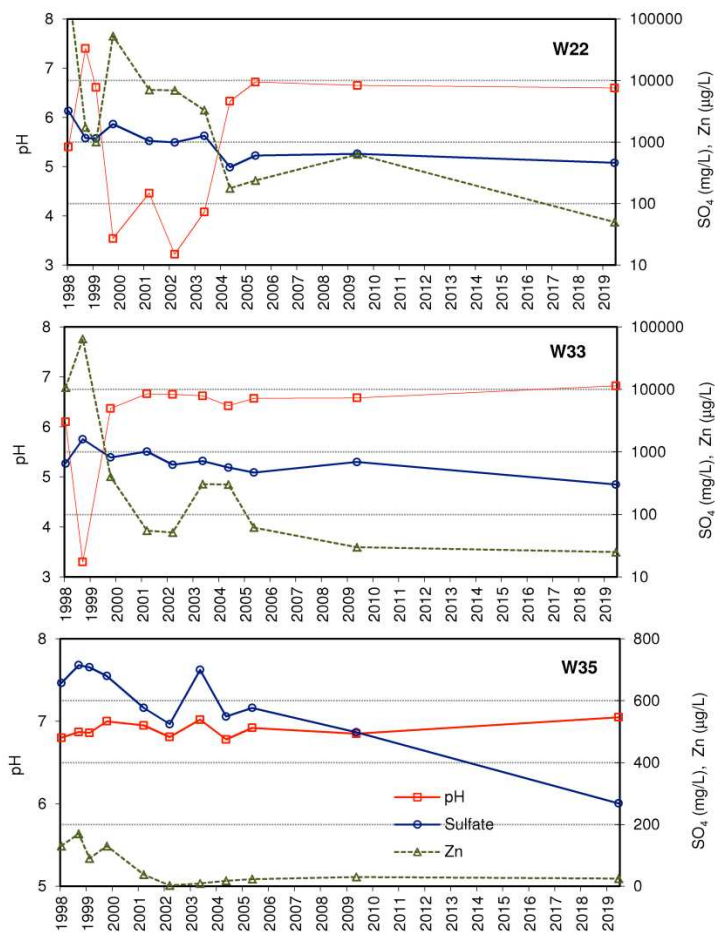


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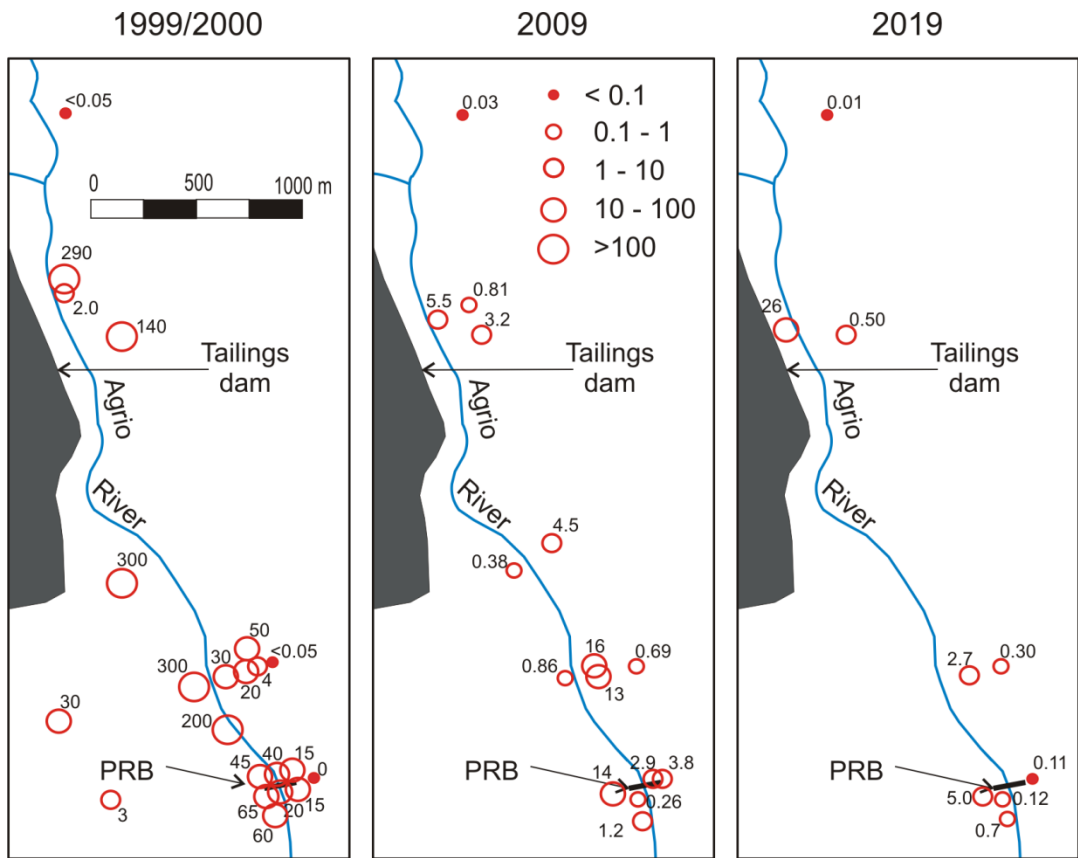


Figure 10. Comparison of Zn concentrations in the Agrio River alluvial aquifer in 1999/2000 (data from Alcolea et al. 2001), 2009 (data from Olías et al. 2012), and October 2019 (this study). Concentrations are expressed in mg/L. PRB: permeable reactive barrier.

Table 1. Basic statistics of some variables measured during the groundwater sampling.

	pH	EC mS/cm	HCO₃	Cl	SO₄	Ca	Mg	Na	K
			mg/L						
Mean	5.63	1.23	104	70	564	152	43	48	4.1
Median	6.13	1.11	58	72	397	137	37	48	3.4
Perc. 25	4.14	0.90	0	42	307	121	33	31	2.2
Perc. 75	6.69	1.38	183	89	693	164	44	55	5.2
Min.	3.03	0.64	0	30	41	68	29	21	1.0
Max.	7.05	2.21	427	143	1425	324	111	104	10.5

	Al	Cu	Fe mg/L	Mn	Zn	As	Cd	Co	Ni
			µg/L						
Mean	7.1	0.24	5.2	3.4	3.0	1.9	18.3	67.8	48.1
Median	3.3	0.26	0.5	1.9	0.2	1.4	13.1	52.0	24.9
Perc. 25	2.1	0.22	0.2	0.6	0.1	1.0	2.4	20.2	9.7
Perc. 75	11.6	0.27	2.1	4.9	3.1	2.0	17.8	92.3	72.8
Min.	<0.2	<0.1	<0.1	<0.05	<0.05	<0.5	<0.5	<0.5	<0.5
Max.	19.8	0.34	27.3	9.7	26.5	5.7	80.4	182.9	166.8

Table 2. Results obtained in the Agrio River upstream the tailings dam (A0), next to the tailings dam (A1) and downstream (A2).

	pH	EC mS/cm	HCO₃	Cl	SO₄	Ca mg/L	Mg	Na	K
A0	6.78	0.25	49	28	42	18	11	17	1.4
A1	5.98	0.75	37	65	217	55	20	47	6.3
A2	5.33	0.74	0	43	369	88	31	32	1.8

	Al	Cu	Fe mg/L	Mn	Zn	As	Cd	Co	Ni
			µg/L						
A0	<0.2	<0.1	<0.1	0.1	0.2	1.5	<0.5	<0.5	<0.5
A1	0.2	0.1	0.4	1.9	4.5	0.5	18	30	27
A2	<0.2	<0.1	<0.1	0.9	1.6	0.7	7.1	9.8	14