**River banks and channels as hotspots of soil pollution after large-scale remediation
of a river basin**

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Abstract

Riparian areas are highly dynamic systems where the control of soil pollution might be particularly challenging. Limited accessibility to river banks and bed sediments makes reclamation operations particularly difficult in these topographical positions, in comparison to floodplains. This usually leads to the large-scale spread of pollutants following pollution episodes in riparian areas. Here, we aimed to evaluate the persistence of trace-element pollution in the soils of Guadiamar River Valley (SW Spain), a large-scale remediation after a mine-spill. We monitored topsoil along the river basin, and in different topographical positions across the river section (river channel, river banks and floodplain), 16 years after a pollution episode and subsequent remediation program. River channels and banks were identified as hotspots of soil pollution, where soluble concentrations of As, Cd and Zn were significantly higher than in floodplains. Along the basin, soil pH and carbonate content was highly variable as a result of contrasted geological background, differential loads of sulphide deposition after the accident and irregular effectiveness of the applied amendments. Cadmium

and Zn showed the highest levels of long-term re-distribution from the pollution source. The results suggests that the stabilization and remediation of soil pollution in river banks and channels, often overlooked when achieving remediation works, should be a priority for land managers.

Highlights

- The persistence of trace-element pollution was analyzed across river sections in a remediated river basin
- River channels and banks were identified as hotspots of soil pollution 16 years after remediation
- The long-term immobilization of pollution was influenced by the background soil texture and pH conditions
- Cd and Zn were identified as the elements with the highest long-term re-distribution along the basin
- Land manager should focus on the stabilization of soil pollution in river channels and banks

Keywords: soil contamination; remediation; heavy metals; river bank; Guadiamar

1. Introduction

Soil pollution is one of the main environmental problems at the global scale. Within the European Union (EU), it is estimated that more than 2.5 million sites are potentially polluted, a 60% of them affected either by hydrocarbons or by trace elements (Panagos et al., 2013; EEA, 2014). The estimated cost of remediating these polluted

sites at the EU scale would be equivalent to 6 billion € per year (Panagos et al., 2013). On average, EU countries expend 10 € per capita annually to remediate part of these polluted sites (EEA, 2014). Besides these remediation costs, there are other indirect costs derived from the reduction in the provision of ecosystem services in polluted soils, which are rarely evaluated (Robinson et al., 2012). The increasing recognition of soil pollution as both an environmental and an economical problem at the European scale has resulted in the inclusion of soil pollution as a priority in the EU environmental agenda (Virto et al., 2015). It is recognized as one of the main seven types of soil degradation within the EU, and the diagnosis and prevention of soil pollution is currently one of the priority tasks for implementing the European Soil Thematic Strategy (European Commission, 2012).

Riparian areas are highly dynamic systems where the control of soil pollution might be particularly challenging (Macklin et al., 2002). Pollutants contained in soil and sediment particles can be easily mobilized and transported by runoff waters following the natural hydrological cycles, therefore reaching downstream areas (see Macklin et al. (2006) for a review on metal dispersion processes in rivers). These processes are particularly important in Mediterranean environments, characterized by an irregular distribution of rainfall around the year and by the occurrence of highly erosive rainstorm episodes (Panagos et al. 2015). In addition, limited accessibility to river banks and bed sediments makes reclamation operations particularly difficult in the riparian sites, in comparison to other landscape units. This usually leads to the large-scale spread of pollutants following spillage episodes in riparian areas, such as the accidents occurred at the Danube river basin in 2010 (Mayes et al., 2011) and at the

Guadamar river basin in 1998 (Grimalt et al., 1999), considered to be two of the most significant pollution events in Europe in the last decades.

In order to optimize the costs of remediating polluted river banks and floodplains, the mobility of the pollutants should ideally be minimized shortly after their release, which would prevent their spread to distant areas. Trace element mobility in soils is determined by a sort of physico-chemical conditions, including pH, redox potential, organic matter content and soil texture, all of them highly variable across river sections, and potentially exposed to seasonal variations following the hydrological cycles (Benito et al., 2001; Macklin et al., 2006). In addition, trace element mobility in alluvial soils might be critically affected by soil management practices (Nikolic et al., 2011; Nikolic and Nikolic, 2012). Therefore, the intrinsic heterogeneity of soil conditions across riparian zones might result in a high spatial variability in the bioavailable concentrations along the river basin, which further complicates soil management.

The processes of natural attenuation should be promoted to achieve a feasible and cost-effective soil remediation in such heterogeneous and large-scale areas (Adriano et al., 2004). Thus the environmental heterogeneity should be taken into account, assisting the natural immobilization with the appropriated measures to each microenvironment. Those techniques that aim to assist the natural attenuation processes involve the addition of soil amendments to promote the establishment of vegetation and to minimize the leaching and spread of contaminants at the long-term, with or without a minimal assistance (Burgos et al., 2013; Madejón and Lepp, 2007).

93

94 There are very few cases of application of assisted natural remediation techniques to
95 real, large-scale pollution problems. The Guadiamar River basin is one of these few
96 cases (Domínguez et al., 2008). After a huge mine spill in 1998 affecting about 55 km²
97 of land, a large scale remediation project was launched, with included the removal of
98 the polluted sludge and the underlying soil, the application of soil amendments, and
99 the plantation of native woody plant species. The pollution episode and subsequent
100 remediation program received much attention from the scientific community during
101 the first years after the spill (Aguilar et al. 2004; Alastuey et al. 1999; Cabrera et al.
102 1999; Cabrera et al. 2008; Clemente et al., 2003; Domínguez et al., 2008; Galán et al.
103 2002; López-Pamo et al. 1999; Simón et al. 1999), although most of these studies were
104 restricted to the river floodplain. However, the zone just near the river bed, including
105 the bank, was more affected by the sludge deposition and less accessible for cleaning-
106 up operations, so it would be expected that soil pollution was differently distributed
107 among different zones across the river section, and that the long-term fate of soil
108 pollutants in the river bank and the floodplain has followed different patterns. In
109 particular, it could be expected that the higher deposition of sludge in the river bank
110 and channel, together with the lower amendment application in these positions, had
111 led to more intensive processes of sulphide oxidation in the soils from river banks and
112 channels, resulting in a higher mobility of trace elements in comparison to the
113 floodplain.

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115 Here, we aimed to evaluate the persistence of soil pollution in this large-scale
116 remediation case study. We studied topsoil along the river basin, 16 years after the

pollution episode and subsequent remediation program. We determined the total and soluble concentrations of the main pollutants along the basin (in two sectors with contrasted background soil properties) and across the river section (topographical factor), to evaluate the effectiveness of the remediation program in the long-term. As exposed above, we expected that river banks are more contaminated than adjacent floodplain because they were less accessible for cleanup and remediation operations. In addition, we expected a different long-term fate for different pollutants, with a higher redistribution from the source, both along the basin and across the river section, of those labile trace elements (Cd and Zn).

2. Material and methods

2.1. Study site

The Guadiamar River is located in SW of Spain, within the Iberian Pyrite Belt, the most important massive sulfide province in Western Europe (López-Pamo et al. 1999). It has a typical Mediterranean pluvial regime, with high values from January to March (mean value of $13 \text{ m}^3 \text{ s}^{-1}$) and low values from June to October ($3 \text{ m}^3 \text{ s}^{-1}$, Gallart et al., 1999).

The lower part of the river basin was affected by one of the largest pollution episodes in Europe, which occurred in 1998 due to the failure of the Aznalcóllar mine's dam.

This accident produced the release of ca. 6 hm^3 of trace element-polluted waters and sludge into the Agrio and Guadiamar rivers, and the resulting flood covered 55 km^2 of the basin southwards to Doñana National Park, where Guadiamar River drains (further details in Grimalt et al., 1999). More than 30,000 kg of dead fish were removed and the habitats of many other animal species were destroyed or degraded. Soils were

severely polluted with several trace elements, mainly As, Cd, Cu, Pb, Tl and Zn (Cabrera et al. 1999).

After the accident, sludge and soil surface were removed by using heavy machinery, and soil remediation was carried out by adding organic matter and calcium-rich amendments. Sugar beet-lime, one of the most used amendments with 70-80 % CaCO_3 , was applied at doses ranging from 20 to 60 Mg ha^{-1} depending on pollution levels. Fe-rich amendments (red soil) were applied ranging from 500 to 900 Mg ha^{-1} , depending on the soil As concentrations, and compost or manure was applied throughout the affected soils at a rate of 15-20 Mg ha^{-1} (Antón-Pacheco et al., 2001). These amendments were mixed within the ploughed depth (20-25 cm) by disc harrowing.

The affected lands were purchased by the Regional Administration, and then afforested using native tree and shrub species (Domínguez et al., 2008). Since 2003, most of the area (2706.8 ha) is protected by the Regional Administration as the Guadiamar Green Corridor. Agricultural activity in the affected area was forbidden and current activities are limited to low-intensity horse grazing for herbaceous control and fuel reduction (Madejón et al., 2009), outdoor sports and ecotourism.

2.1. Soil sampling

Soil sampling was conducted between February and March 2014 (when water level is potentially at its highest) in 20 sites along the Guadiamar Green Corridor, from the Northern limit of the affected area, close to the mine ($37^{\circ} 28.758' \text{N}$, $6^{\circ} 12.956' \text{W}$),

southwards to the Guadalquivir river marshes, where the river drains into ($37^{\circ} 13.040'$ N, $6^{\circ} 14.080'$ W, Fig. 1). The affected area was divided into three geologically-based zones (Northern, Central and Southern), following the same criteria adopted by environmental managers during the emergency cleaning-up operations (Arenas et al., 2003). Typical bedrock types at the Northern zone (sampling sites 1-10) are slate and schist, and the zone is characterized by the presence of naturally acid soils. Potentially, this zone contains the sites with the highest soil pollution levels, due to their proximity to the open-cast mine and the tailings dam (from 1 to 13 km from the dam). Sludge removal in this zone was conducted by the mining company (Boliden-Apirsa S.L.), and included the removal of the topsoil surface using the mining heavy machinery. As a result, soil structure was dramatically affected. The geology at the Central zone (sampling sites 11-20, located from 15 to 30 km from the tailings dam) is characterized by the presence of limestone and calcarenite, developing naturally neutral to calcareous loam soils. Cleaning-up operations in this zone were conducted by the Regional Government, which included the removal of a finer layer of the polluted topsoils, in comparison to the Northern zone. The salt marsh area (Southern zone) was not sampled in this study, as it was basically affected by acid waters but not by the polluting sludge.

In each site, soils were sampled at three different positions across the river section topography: 1) river channel (RC), above the water level, 2) river bank (RB), 2-3 m separated from the channel, and 3) floodplain (FP), 10-30 m separated from the channel, depending of the characteristics of each site (Fig. 1). In each position, a composite soil sample was obtained by mixing three samples (0-20 cm depth),

collected at different sampling points, separated by 3-5 m in the RC and RB zones and by 10 m in the FP. The total number of collected samples was 60.

2.2. Soil preparation and analysis

Samples were oven-dried at 30° C and crushed to pass through a 2 mm sieve, and then a subsample was ground to < 60 µm for S and trace element determination. The < 2 mm subsample was analyzed for pH potentiometrically in a 1:2.5 soil-water suspension. Soil total C and N content was analysed using a Thermo Scientific Flash 2000 analyser. Total carbonate content was determined by the manometric method (Demolon and Leroux, 1952) and size particle distribution by the hydrometer method (Gee and Bauder, 1986). The < 60 µm soil subsamples were digested with 'aqua regia' (1:3 concentration HNO₃: HCl) in a microwave oven (Microwave Laboratory Station Mileston ETHOS 900, Milestone s.r.l., Sorisole, Italy). Quantification of elements Al, As, Cd, Cu, Mn, Pb and Zn was achieved using a Varian ICP 720-ES (simultaneous ICP-OES with axially viewed plasma). 'Aqua regia' digestion does not extract those trace elements associated to silicates (Reimann and Caritat, 1998). Nevertheless, this method is widely accepted to characterize trace element concentrations in soil pollution studies, because the silicate-binding metals have less environmental implications. Such concentrations are referred to as 'pseudo-total' concentrations. The quality of the analysis was assessed using the reference soil sample BCR-143R (sewage sludge amended soil EUR 15284 EN). Obtained recoveries ranged from 96.7 % (Mn) to 103 % (Zn). Available concentrations of trace elements were also quantified by ICP-OES after extracting the samples (< 60 µm) with a 0.1 M Ca₂Cl solution (except for As). A sub-sample (N=24, 12 for each of the geological zones) was selected to measure As

availability, by using an extraction with 0.5 M NaHCO₃ and further determination by ICP-OES, using a hydride-vapour generator system (Varian VGA 77P). Pseudo-total and available concentrations of trace elements are given on a dry weight basis.

2.3. Statistical analysis

Two-way ANOVAs were applied to test for differences in soil variables between topographical positions across the river section (river channel, river bank and floodplain), and to test whether these differences were consistent between sectors along the basin (Northern and Central). Previously, variables were log-transformed. For some variables (pH, and the soluble concentrations of Cd, Cu, Fe, S and Zn) a generalized mixed model (GLZ) was applied using a gamma distribution as a link function, since the normality assumption was not met. A Principal Component Analyses was applied to analyze the overall pattern of covariation of the studied variables (log-transformed). All these analyses were performed using Statistica 10 (Statsoft Inc., Tulsa, OK, USA).

3. Results and discussion

3.1. General soil properties

The topographical location across the river section did not have an influence on general soil properties (texture, carbonate, organic C and N), with the exception of pH, for which the type of position had a marginally significant effect (Table 1, Fig. 2). However, those soil properties with a potentially highest influence on trace element solubility (pH, carbonate content and texture) highly varied between the two sectors

along the river basin. At the Northern zone some extremely acid soils ($\text{pH} < 3.5$) could be found in the river channel (RC) and river banks (RB), while the pH in the soils from the floodplain (FP) was always around neutrality (Fig. 2). A 27 % of the soils at this zone had pH values lower than 4 (in RC and RB), which resulted in a remarkable solubilization of some trace elements (see below). This suggests that the effect of the soil amendments (mainly sugar beet lime with $\text{pH} > 9$) has completely attenuated in this zone. The dose of the applied amendment in these soils was therefore insufficient to buffer against the changes in pH in the long-term, considering that their proximity to the pollution source and the acidic nature of the soils from this zone increases the risk of high leaching of sulphates from sludge oxidation. While amendments were systematically applied to the whole affected area, including those locations in the Central zone, soil pH after the accident has dramatically decreased in the soils from the Northern zone, if compared to soils from the same zone, but not affected by the accident (data available from our previous surveys, Domínguez et al. 2008). In the central zone, however, affected and unaffected soils have similar pH values, suggesting that amendment application was successful in this area. Previous works in the area also reported the presence of extremely acid soils in this Northern sector just after two years after amendment application (Vanderlinden et al., 2006), so it is quite likely that at the time of our sampling (15 years after soil remediation) there is no remaining amendment in the soils from this Northern zone.

At the Central zone, soil pH was more homogenous across the river section, and soils were neutral to slightly alkaline. Carbonate content was associated with soil pH, with those extremely acidic soils having less than 2.5 % of CaCO_3 , although differences in CaCO_3 across the river section were not statistically significant (Tables 1 and 2). At the

Northern zone, soils from the FP had highly variable CaCO_3 content, despite relatively homogeneous pH values. This could be related to the irregular application of the soil amendments during the reclamation works, which could be easily accomplished in the floodplain but not in river banks and channel, leading to an irregular restoration of the pollution buffering capacity in the soils from these two scenarios.

Texture was similar among the three studied topographical locations in both zones. Sandy soils were more frequently found at the Northern zone, with the 50% of cases having a sandy loam texture, and only 5 cases with a clay loam texture. In contrast, at the Central zone, ca. of 45% of the sampled soils had a sandy clay loam, clay loam or even a clayey texture (Table 2). Therefore, soil texture at the Central zone might promote a greater immobilization of trace-elements, in comparison to soils at the Northern zone.

3.2. Total and soluble concentrations of S and trace elements (TE)

As with the general soil properties, total concentrations of “low mobility” trace elements (As, Pb, Domínguez et al., 2009) were not particularly different among positions across the river section, but highly differed between sectors along the basin (Table 1). The total concentrations of more mobile elements such as Cd, Cu and Zn were more different among topographical locations than between zones along the basin. Finally, soluble concentrations were very different both among the topographical positions and between zones (Table 1). In general, soil conditions in the RC and RB enhanced the solubility of the studied trace elements, particularly in the Northern zone.

Sulphur was one of the main components of the sludge (up to 40%; Alastuey et al., 1999; Grimalt et al., 1999), and 16 years after the accident total S concentrations were still remarkably high. At the Northern zone, S pseudo-total concentrations were particularly high in the RC (Fig. 3a), where a maximum concentration of 88386 mg kg⁻¹ (ca. 9 % w/w) was recorded. Such concentrations are found in some spots of bare soil, where vegetation has not established 16 years after the accident due to the high soluble trace element concentrations, which can be observed in the river banks and floodplains from the Northern zone, representing a 7 % of the land surface in this zone (Martín-Peinado et al., 2015). At the Central zone, the maximum S concentrations were clearly lower (11464 mg kg⁻¹, 1.1 % w/w, recorded in the RB). As expected from the pH values (Fig.2), S soluble concentrations (CaCl₂-extracted) were also greater in the Northern zone, and significantly varied across positions in the river section in both zones (Fig. 3d; Table 1). There was a clear negative relationship between soil pH and total S concentrations (Fig. 4), suggesting that the periodical oxidation of the sulphides contained in the remnants of sludge has led to soil acidification (Kraus and Wiengand, 2006), especially at the RC and the RB. The fraction of soluble to total S concentrations was clearly higher in the Northern than in the Central zone, illustrating that soil conditions in this Northern soil promote S mobilization (Fig. 5).

Concentrations of “low mobility” trace elements, such as As and Pb were also very high in the sludge, up to 0.5 and 0.8 % w/w respectively (Grimalt et al., 1999). In our survey, maximum total Pb and As concentrations were up to 2920 mg kg⁻¹ and 650 mg kg⁻¹, respectively, which were recorded in some of the Northern soils (Fig. 3b, c). Soluble As

concentrations were always below 5 mg kg^{-1} , and were greater in the RC than in RB or FP within each zone (Fig. 3e). The higher As mobility recorded in the RC position could be due to the higher frequency of waterlogging episodes in this microsite, given that anaerobic conditions might dramatically increase As solubility (Moreno-Jiménez et al., 2013). When comparing between zones, solubility in the RB and FP tended to be greater in the basic and alkaline soils from the Central zone. Soluble Pb concentrations were one order of magnitude greater in the RC and the RB from the Northern zone (maximum values up to 34.8 and 22.9 mg kg^{-1} , respectively) than those in the corresponding scenarios of the Central zone (Fig. 3f).

In contrast to S, As and Pb, the total Cd concentrations in the FP were significantly greater in the Central than in the Northern zone (Table 1, Fig. 6a). In the river banks and floodplains, Cu concentrations were similar in both zones (Fig. 6b). As with Cd, a trend for greater Zn concentrations in the Central zones was observed (Fig. 6c), although differences were not statistically significant. This suggests that these elements have been progressively leached downstream from the Northern locations, given that the conditions of soil acidity and sandy texture that prevail in those locations enhance the mobility of these heavy metals. Soluble concentrations of Cd, Cu and Zn differed across scenarios and between geological zones, being particularly high in the RC from the Northern zone (Fig. 6d-f, Table S1). In the Central zone, soluble concentrations of Cd, Cu and Zn were well below 1 mg kg^{-1} , indicating that soil conditions in these soils (high pH and clay content) promote the immobilization and accumulation of the elements that are leached from upstream locations. Copper mobility seems to be limited (Table S1), likely because this element has a high affinity

for the solid phase and can be easily retained by soil organic matter (McBride, 1989), particularly by interacting with humic acids (Plaza et al., 2005; Soler-Rovira et al. 2010).

The principal component analysis confirmed that Cd and Zn followed a different pattern of covariation than the rest of trace elements contained in the sludge (Fig. 4). The first factor, explaining a 52 % of the variance, revealed a close negative relationship between pH and total As, S and Pb concentrations, as well between pH and the soluble concentrations of the cationic trace- elements (Cu, Cd, Pb and Zn). Total Cd and Zn concentrations, however, defined the second factor, which was not related to soil pH, but rather positively associated to soil clay content and total C and N (Fig. 4). This confirms that the long-term fate of the pollution would be dependent on the element type, with those “low mobility” elements (As, Pb) showing the lowest level of re-distribution from the pollution source, and agrees with previous studies on the area that showed that, after the remediation works, the highest concentrations of the less mobile elements were located within the first 15 km downstream the tailings dam (Cabrera et al., 2008).

The solubility of some trace elements (Cd, Cu, Pb and Zn) is greatly influenced by soil pH (Greger, 1999). An increase in soil pH reduces the availability of these metals through precipitation and by increasing adsorption on soil colloids (Selin and Amacher, 1997). While Cd, Cu and Zn solubility increases exponentially under pH values below 6, Pb solubility usually shows a non-linear relationship to soil pH, with large increases in solubility in extremely acid soils (pH < 3) and a relative immobilization above that value (Domínguez et al., 2009). Therefore, within the range of soil pH found in this study the

solubility of Pb would be relatively high in only a few of the studied locations. Arsenic, in contrast, is more soluble at alkaline pH (Greger 1999), thus its mobility in the Northern locations and re-distribution downstream was much reduced by the acidic soil conditions in the vicinity of the pollution source. At longer times-scales, even poorly soluble elements could be transported downstream. Studies on metal content in soils of this area conducted before the mining accident showed that waters of Guadamar River had comparatively high heavy metal contents, due to the transport of heavy metal-rich solids precipitated upstream in distant mining sites (Arambarri et al., 1996; Cabrera et al., 1987). The analysis of some plant species from the marshes in Doñana National Park, where the Guadamar River drains, indicated residual As contamination derived from historic mining activities in distant locations within the region (Madejón et al., 2006).

The results found in this study indicate that the extent of the contamination in the soils deserves, at least, further assessment. In both zones most of the recorded As concentrations, including those in the FP, exceeded the intervention value of 50 mg kg⁻¹ reported for Andalusian soils (Aguilar et al., 1999), as well as the toxicity threshold for plants of 20 mg kg⁻¹ (Singh and Steinnes, 1994), and the maximum tolerable level for agricultural soils in some European countries, like Germany (NIPHE, 2001). Indeed, for most of the studied soils As concentrations were greater than the critical range of 20-50 mg kg⁻¹ above which toxicity is considered to be possible (Alloway, 1990; Kabata-Pendias and Pendias, 1992). In the case of Pb, a few samples from the Northern zone (9 out of 30) exceeded the regional intervention value (500 mg kg⁻¹; Aguilar et al., 1999), and 10 out of the 60 samples collected throughout the river basin exceeded the

phytotoxic range of 100-400 mg kg⁻¹ (Alloway, 1990). Furthermore, 35 samples (more than half) exceeded the maximum tolerable level for agricultural soils in some European countries, like Germany (100 mg kg⁻¹, NIPHE, 2001). Therefore further cleaning operations in some of the most contaminated spots would be desirable.

While As and Pb concentrations clearly exceeded the regional intervention levels, the Cd concentration never exceeded the regional intervention level of 10 mg kg⁻¹, and only a few cases were above the permissible level of 3 mg kg⁻¹ (Aguilar et al., 1999). Nevertheless, attending its potential toxicity, a periodical monitoring of this metal in the Guadiamar Green Corridor is recommended (Madejón et al., 2009; Pérez de Mora et al., 2010). Maximum Cd concentrations of 9 and 4 mg kg⁻¹ in the RC and RB at the Northern zone clearly exceed the normal range in soils (0.01-2 mg kg⁻¹, Bowen, 1979) and were into or exceeding the range of 3-8 mg kg⁻¹ above which toxicity is considered to be possible (Alloway, 1990; Kabata Pendias and Pendias, 1992). As certain plant species in the area are able to tolerate and accumulate comparatively high concentrations of Cd in their aboveground biomass (Domínguez et al., 2008; Madejón et al., 2004, 2013), Cd traslocation into plant biomass should be periodically monitored and identified, in order to determine the risk of transfer of this element into the local food web. Previous reports highlighted Cd as one of the most problematic elements for the trophic web in the affected area (Domínguez et al., 2009; Madejón et al., 2009; Madejón et al., 2012; Pérez de Mora et al., 2010).

For Zn, only few of the sampled soils (5 out of 60, collected in the river channel and bank) exceeded the regional intervention value of 1000 mg kg⁻¹, although in 20 of

them concentrations were in the range 500-1000 mg kg⁻¹ which requires obligatory investigation (Aguilar et al., 1999). More than a half of the sampled soils exceeded the regional permissible level of 300 mg kg⁻¹ (Aguilar et al., 1999). Therefore, a periodical soil monitoring for this element is also necessary, even though its potential toxicity is lower than that of Cd.

3.3. Implications for the management of contaminated river basins

Our study illustrates the complexity of managing contaminated river basins. Besides the geological factors that determine the nature of the soil properties, and consequently the capacity of soils to buffer against changes in pH and in trace element concentrations, the topographical factor (position across the river section) may further compromise the cleaning-up operations which determines the long-term persistence of pollution along the basin. Moreover, river channels and banks are subjected to flooding which causes periodical redox processes and changes in soil pH, leading to the potential mobilization of certain metals (Moreno-Jiménez et al., 2013). In our work, we show that the solubility of the most mobile trace elements (Cd and Zn) is different across the river section, being more soluble in the river channel and banks. Achieving a complete removal of the sludge and a regular application of amendments to soils in these scenarios should be a priority for managers. Otherwise, trace elements could be re-located downstream during the seasonal floods.

Indeed, we found evidences that there was a redistribution of Cd and Zn along the basin. Fortunately, the soil conditions at the Central zone (basic and alkaline soils with clayey texture) promoted the immobilization of these potentially toxic elements,

preventing their further re-distribution downstream. Although we did not study the vertical migration of trace elements through the soil profile, it is likely that in those extremely acid soils in the river channel and banks a vertical re-distribution of these labile elements have also occurred, with a potential risk of contamination of groundwaters. This issue should be certainly addressed by the land managers.

Our work also illustrates the need to consider the geological background properties when planning a remediation program. The geological differences along the basin had a critical role in determining the long-term fate of trace elements more than a decade after the pollution episode. In the Northern zone the capacity of the soils to buffer against changes in soil pH and trace element concentrations was much lower due to the acidic nature of the soils, with low carbonate content. In these soils the applied amendments were not enough to neutralize the acids produced by the progressive sulphide oxidation over the years. Maintaining neutral to basic soil pH should be an integral part of any remediation program that involves trace element-contaminated soils (Domínguez et al., 2008). Therefore, the application of new amendments in these extremely acid soils should be a priority for land managers. Besides soil pH correction, appropriate afforestation and revegetation of the river banks is critical to ensure a physical stabilization of the soil, and to reduce the losses of soil through water erosion.

4. Conclusions

The persistence of soil pollution in the studied river basin, 16 years after a pollution episode, depended on the geological background (determining the capacity of the soil to buffer against changes in soil pH) and the topographical location (river channels and

banks remaining more contaminated due to the limited accessibility for cleaning-up operations and amendment application). The long-term fate was different among trace-elements, Cd and Zn being easily re-distributed downstream due to their high solubility, and As and Pb remaining at shorter distances from the pollution source. The application of assisted natural attenuation techniques can be a feasible alternative to achieve large-scale soil remediation goals, but the design and monitoring of the operations should consider the geological background, particularly at adjusting the amendment doses to maintain neutral pH conditions over time in order to immobilize trace-elements.

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649

Table 1. Results of the two-way ANOVAs to test for differences in soil variables between zones and across topographical position in the river section. (*) for these variables, a generalized mixed model (GLZ) was applied using a gamma distribution as a link function, since the normality assumption was not met. The statistic column refers to the F statistic (ANOVA) or the Wald statistic (GLZ).

Variable	Topographical position		Zone		Scenario × Zone	
	statistic	p	statistic	p	statistic	p
pH (*)	6.4	0.041	24.4	<0.001	4.9	0.088
CaCO ₃	0.6	0.575	24.9	<0.001	1.2	0.312
Clay	0.8	0.443	7.8	0.007	2.9	0.066
Sand	0.0	0.981	6.2	0.016	1.8	0.182
Silt	0.7	0.493	0.2	0.626	1.9	0.154
organic C	1.5	0.225	18.4	<0.001	0.4	0.691
organic N	0.7	0.507	0.8	0.374	0.7	0.496
<i>Pseudo-total concentrations:</i>						
As	1.1	0.337	9.8	0.003	0.8	0.460
Cd	5.0	0.010	8.2	0.006	0.6	0.550
Cu	3.0	0.058	3.5	0.068	0.6	0.532
Pb	1.5	0.239	14.1	<0.001	1.7	0.201
S	1.8	0.180	8.4	0.005	1.5	0.242
Zn	5.0	0.010	4.2	0.046	0.6	0.577
<i>Soluble concentrations:</i>						
As	5.7	0.012	2.58	0.126	2.0	0.162
Cd (*)	12.4	0.002	50.6	<0.001	5.2	0.074
Cu (*)	7.5	0.024	96.4	<0.001	3.2	0.198
Pb	23.2	<0.001	59.2	<0.001	25.0	<0.001
S (*)	23.2	<0.001	59.2	<0.001	25.0	<0.001
Zn (*)	16.3	<0.001	137.7	<0.001	1.6	0.452

659 Table 2. General soil properties across the river section at the Northern and Central zones. Mean values $\pm$ standard error and ranges (in
660 parenthesis) on a dry soil basis. RC = river channel; RB = river bank; FP = floodplain.

661

Zone	Topographical position	Organic C (%)	CaCO ₃ (%)	Soil particle size (mm)			
				2.0 – 0.2 (%)	0.2 – 0.05 (%)	0.05 – 0.002 (%)	< 0.002 (%)
Northern	RC	1.91 ± 0.70	5.3 ± 1.6	27.7 ± 5.4	25.2 ± 2.0	28.0 ± 1.9	19.2 ± 3.2
		(0.48 – 7.93)	(1.1 – 14.5)	(2.5 – 50.7)	(17.1 – 36.9)	(18.2 – 37.3)	(8.4 – 30.3)
	RB	1.26 ± 0.21	5.3 ± 1.6	27.9 ± 5.1	24.2 ± 1.7	31.3 ± 3.7	16.6 ± 2.6
		(0.39 – 2.18)	(1.0 – 13.5)	(5.5 – 53.4)	(18.1 – 30.9)	(17.7 – 52.3)	(8.4 – 28.8)
	FP	1.00 ± 0.08	2.4 ± 0.3	34.1 3.4	24.9 ± 0.8	25.9 ± 2.2	15.1 ± 1.8
		(0.45 – 1.30)	(0.6 – 16.1)	(16.9 – 49.8)	(22.3 – 30.3)	(14.6 – 37.0)	(8.8 – 25.5)
Central	RC	1.90 ± 0.21	10.0 ± 1.1	23.7 ± 4.4	31.4 ± 2.2	24.3 ± 2.8	20.6 ± 2.6
		(0.93 – 2.88)	(5.4 – 15.2)	(6.1 – 42.7)	(21.8 – 41.4)	(14.3 – 38.5)	(9.8 – 35.0)
	RB	1.65 ± 0.14	9.1 ± 1.1	23.5 ± 3.9	29.3 ± 3.1	27.0 ± 2.3	20.1 ± 1.7
		(0.94 – 2.55)	(5.1 – 16.7)	(8.2 – 43.9)	(17.2 – 45.2)	(16.2 – 37.5)	(10.1 – 26.1)
	FP	1.65 ± 0.26	10.1 ± 1.7	15.9 ± 3.4	25.0 ± 3.1	30.7 ± 2.1	28.4 ± 3.5
		(0.59 – 2.90)	(4.4 – 18.1)	(3.5 – 39.8)	(7.9 – 43.7)	(19.3 – 40.3)	(15.7 – 54.1)

662

Figure captions

Fig. 1. Location of the Guadamar River in SW Spain (A) and sketch of the three scenarios across the river section considered in this study (B).

Fig. 2. Soil pH across the river section at the Northern and Central zones within the Guadamar River basin (mean $\pm$ standard error). RC = river channel; RB = river bank; FP = floodplain.

Fig. 3. Pseudo-total and soluble S, As and Pb concentrations (mean $\pm$ standard error) across the river section at the Northern and Central zones within the Guadamar River basin. RC = river channel; RB = river bank; FP = floodplain.

Fig. 4. Principal component analysis applied to some key general properties (pH, CaCO_3 , total C and N, and clay content), and total (-t, black color) and soluble (-s, grey color) trace element concentrations. The percentage of variance explained by each factor is indicated in their corresponding axis.

Fig. 5. Ratio of soluble to pseudo-total S concentrations across the river section at the Northern and Central zones within the Guadamar River basin. RC = river channel; RB = river bank; FP = floodplain.

685 Fig. 6. Pseudo-total and soluble Cd, Cu and Zn concentrations (mean $\pm$ standard error)
686 across the river section at the Northern and Central zones within the Guadamar River
687 basin. RC = river channel; TB = top bank; FP = floodplain.