1    **River banks and channels as hotspots of soil pollution after large-scale remediation**

2    **of a river basin**

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8    **Abstract**

9    Riparian areas are highly dynamic systems where the control of soil pollution might be

10   particularly challenging. Limited accessibility to river banks and bed sediments makes

11   reclamation operations particularly difficult in these topographical positions, in

12   comparison to floodplains. This usually leads to the large-scale spread of pollutants

13   following pollution episodes in riparian areas. Here, we aimed to evaluate the

14   persistence of trace-element pollution in the soils of Guadiamar River Valley (SW

15   Spain), a large-scale remediation after a mine-spill. We monitored topsoil along the

16   river basin, and in different topographical positions across the river section (river

17   channel, river banks and floodplain), 16 years after a pollution episode and subsequent

18   remediation program. River channels and banks were identified as hotspots of soil

19   pollution, where soluble concentrations of As, Cd and Zn were significantly higher than

20   in floodplains. Along the basin, soil pH and carbonate content was highly variable as a

21   result of contrasted geological background, differential loads of sulphide deposition

22   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

45     sites at the EU scale would be equivalent to 6 billion € per year (Panagos et al., 2013).

46     On average, EU countries expend 10 € per capita annually to remediate part of these

47     polluted sites (EEA, 2014). Besides these remediation costs, there are other indirect

48     costs derived from the reduction in the provision of ecosystem services in polluted

49     soils, which are rarely evaluated (Robinson et al., 2012). The increasing recognition of

50     soil pollution as both an environmental and an economical problem at the European

51     scale has resulted in the inclusion of soil pollution as a priority in the EU environmental

52     agenda (Virto et al., 2015). It is recognized as one of the main seven types of soil

53     degradation within the EU, and the diagnosis and prevention of soil pollution is

54     currently one of the priority tasks for implementing the European Soil Thematic

55     Strategy (European Commission, 2012).

56

57     Riparian areas are highly dynamic systems where the control of soil pollution might be

58     particularly challenging (Macklin et al., 2002). Pollutants contained in soil and

59     sediment particles can be easily mobilized and transported by runoff waters following

60     the natural hydrological cycles, therefore reaching downstream areas (see Macklin et

61     al. (2006) for a review on metal dispersion processes in rivers). These processes are

62     particularly important in Mediterranean environments, characterized by an irregular

63     distribution of rainfall around the year and by the occurrence of highly erosive

64     rainstorm episodes (Panagos et al. 2015). In addition, limited accessibility to river

65     banks and bed sediments makes reclamation operations particularly difficult in the

66     riparian sites, in comparison to other landscape units. This usually leads to the large-

67     scale spread of pollutants following spillage episodes in riparian areas, such as the

68     accidents occurred at the Danube river basin in 2010 (Mayes et al., 2011) and at the

69  Guadiamar river basin in 1998 (Grimalt et al., 1999), considered to be two of the most

70  significant pollution events in Europe in the last decades.

71

72  In order to optimize the costs of remediating polluted river banks and floodplains, the

73  mobility of the pollutants should ideally be minimized shortly after their release, which

74  would prevent their spread to distant areas. Trace element mobility in soils is

75  determined by a sort of physico-chemical conditions, including pH, redox potential,

76  organic matter content and soil texture, all of them highly variable across river

77  sections, and potentially exposed to seasonal variations following the hydrological

78  cycles (Benito et al., 2001; Macklin et al., 2006). In addition, trace element mobility in

79  alluvial soils might be critically affected by soil management practices (Nikolic et al.,

80  2011; Nikolic and Nikolic, 2012). Therefore, the intrinsic heterogeneity of soil

81  conditions across riparian zones might result in a high spatial variability in the

82  bioavailable concentrations along the river basin, which further complicates soil

83  management.

84

85  The processes of natural attenuation should be promoted to achieve a feasible and

86  cost-effective soil remediation in such heterogeneous and large-scale areas (Adriano et

87  al., 2004). Thus the environmental heterogeneity should be taken into account,

88  assisting the natural immobilization with the appropriated measures to each

89  microenvironment. Those techniques that aim to assist the natural attenuation

90  processes involve the addition of soil amendments to promote the establishment of

91  vegetation and to minimize the leaching and spread of contaminants at the long-term,

92  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 km$^2$

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.

114

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

117    pollution episode and subsequent remediation program. We determined the total and

118    soluble concentrations of the main pollutants along the basin (in two sectors with

119    contrasted background soil properties) and across the river section (topographical

120    factor), to evaluate the effectiveness of the remediation program in the long-term. As

121    exposed above, we expected that river banks are more contaminated than adjacent

122    floodplain because they were less accessible for cleanup and remediation operations.

123    In addition, we expected a different long-term fate for different pollutants, with a

124    higher redistribution from the source, both along the basin and across the river

125    section, of those labile trace elements (Cd and Zn).

126

127    **2.   Material and methods**

128

129    *2.1.    Study site*

130    The Guadiamar River is located in SW of Spain, within the Iberian Pyrite Belt, the most

131    important massive sulfide province in Western Europe (López-Pamo et al. 1999). It has

132    a typical Mediterranean pluvial regime, with high values from January to March (mean

133    value of 13 $m^3 s^{-1}$) and low values from June to October (3 $m^3 s^{-1}$, Gallart et al., 1999).

134     The lower part of the river basin was affected by one of the largest pollution episodes

135    in Europe, which occurred in 1998 due to the failure of the Aznalcóllar mine's dam.

136    This accident produced the release of ca. 6 $hm^3$ of trace element-polluted waters and

137    sludge into the Agrio and Guadiamar rivers, and the resulting flood covered 55 $km^2$ of

138    the basin southwards to Doñana National Park, where Guadiamar River drains (further

139    details in Grimalt et al., 1999). More than 30,000 kg of dead fish were removed and

140    the habitats of many other animal species were destroyed or degraded. Soils were

6

141      severely polluted with several trace elements, mainly As, Cd, Cu, Pb, Tl and Zn (Cabrera

142      et al. 1999).

143

144      After the accident, sludge and soil surface were removed by using heavy machinery,

145      and soil remediation was carried out by adding organic matter and calcium-rich

146      amendments. Sugar beet-lime, one of the most used amendments with 70-80 %

147      $CaCO_3$, was applied at doses ranging from 20 to 60 Mg ha$^{-1}$ depending on pollution

148      levels. Fe-rich amendments (red soil) were applied ranging from 500 to 900 Mg ha$^{-1}$,

149      depending on the soil As concentrations, and compost or manure was applied

150      throughout the affected soils at a rate of 15-20 Mg ha$^{-1}$ (Antón-Pacheco et al., 2001).

151      These amendments were mixed within the ploughed depth (20-25 cm) by disc

152      harrowing.

153

154      The affected lands were purchased by the Regional Administration, and then

155      afforested using native tree and shrub species (Domínguez et al., 2008). Since 2003,

156      most of the area (2706.8 ha) is protected by the Regional Administration as the

157      Guadiamar Green Corridor. Agricultural activity in the affected area was forbidden and

158      current activities are limited to low-intensity horse grazing for herbaceous control and

159      fuel reduction (Madejón et al., 2009), outdoor sports and ecotourism.

160

161      *2.1. Soil sampling*

162      Soil sampling was conducted between February and March 2014 (when water level is

163      potentially at its highest) in 20 sites along the Guadiamar Green Corridor, from the

164      Northern limit of the affected area, close to the mine (37$^{o}$ 28.758`N, 6$^{o}$ 12.956' W),

165  southwards to the Guadalquivir river marshes, where the river drains into ($37^o$ 13.040'

166  N, $6^o$ 14.080' W, Fig. 1). The affected area was divided into three geologically-based

167  zones (Northern, Central and Southern), following the same criteria adopted by

168  environmental managers during the emergency cleaning-up operations (Arenas et al.,

169  2003). Typical bedrock types at the Northern zone (sampling sites 1-10) are slate and

170  schist, and the zone is characterized by the presence of naturally acid soils. Potentially,

171  this zone contains the sites with the highest soil pollution levels, due to their proximity

172  to the open-cast mine and the tailings dam (from 1 to 13 km from the dam). Sludge

173  removal in this zone was conducted by the mining company (Boliden-Apirsa S.L.), and

174  included the removal of the topsoil surface using the mining heavy machinery. As a

175  result, soil structure was dramatically affected. The geology at the Central zone

176  (sampling sites 11-20, located from 15 to 30 km from the tailings dam) is characterized

177  by the presence of limestone and calcarenite, developing naturally neutral to

178  calcareous loam soils. Cleaning-up operations in this zone were conducted by the

179  Regional Government, which included the removal of a finer layer of the polluted

180  topsoils, in comparison to the Northern zone. The salt marsh area (Southern zone) was

181  not sampled in this study, as it was basically affected by acid waters but not by the

182  polluting sludge.

183

184  In each site, soils were sampled at three different positions across the river section

185  topography: 1) river channel (RC), above the water level, 2) river bank (RB), 2-3 m

186  separated from the channel, and 3) floodplain (FP), 10-30 m separated from the

187  channel, depending of the characteristics of each site (Fig. 1). In each position, a

188  composite soil sample was obtained by mixing three samples (0-20 cm depth),

189 collected at different sampling points, separated by 3-5 m in the RC and RB zones and

190 by 10 m in the FP. The total number of collected samples was 60.

191

192 *2.2. Soil preparation and analysis*

193 Samples were oven-dried at 30º C and crushed to pass through a 2 mm sieve, and then

194 a subsample was ground to < 60 µm for S and trace element determination. The < 2

195 mm subsample was analyzed for pH potentiometrically in a 1:2.5 soil-water

196 suspension. Soil total C and N content was analysed using a Thermo Scientific Flash

197 2000 analyser. Total carbonate content was determined by the manometric method

198 (Demolon and Leroux, 1952) and size particle distribution by the hydrometer method

199 (Gee and Bauder, 1986). The < 60 µm soil subsamples were digested with 'aqua regia'

200 (1:3 concentration $HNO_3$: HCl) in a microwave oven (Microwave Laboratory Station

201 Mileston ETHOS 900, Milestone s.r.l., Sorisole, Italy). Quantification of elements Al, As,

202 Cd, Cu, Mn, Pb and Zn was achieved using a Varian ICP 720-ES (simultaneous ICP-OES

203 with axially viewed plasma). 'Aqua regia' digestion does not extract those trace

204 elements associated to silicates (Reimann and Caritat, 1998). Nevertheless, this

205 method is widely accepted to characterize trace element concentrations in soil

206 pollution studies, because the silicate-binding metals have less environmental

207 implications. Such concentrations are referred to as 'pseudo-total' concentrations. The

208 quality of the analysis was assessed using the reference soil sample BCR-143R (sewage

209 sludge amended soil EUR 15284 EN). Obtained recoveries ranged from 96.7 % (Mn) to

210 103 % (Zn). Available concentrations of trace elements were also quantified by ICP-OES

211 after extracting the samples (< 60 µm) with a 0.1 M $Ca_2Cl$ solution (except for As). A

212 sub-sample (N=24, 12 for each of the geological zones) was selected to measure As

9

213    availability, by using an extraction with 0.5 M $NaHCO_3$ and further determination by

214    ICP-OES, using a hydride-vapour generator system (Varian VGA 77P). Pseudo-total and

215    available concentrations of trace elements are given on a dry weight basis.

216

217    *2.3. Statistical analysis*

218    Two-way ANOVAs were applied to test for differences in soil variables between

219    topographical positions across the river section (river channel, river bank and

220    floodplain), and to test whether these differences were consistent between sectors

221    along the basin (Northern and Central). Previously, variables were log-transformed. For

222    some variables (pH, and the soluble concentrations of Cd, Cu, Fe, S and Zn) a

223    generalized mixed model (GLZ) was applied using a gamma distribution as a link

224    function, since the normality assumption was not met. A Principal Component

225    Analyses was applied to analyze the overall pattern of covariation of the studied

226    variables (log-transformed). All these analyses were performed using Statistica 10

227    (Statsoft Inc., Tulsa, OK, USA).

228

229    **3. Results and discussion**

230

231    *3.1. General soil properties*

232    The topographical location across the river section did not have an influence on

233    general soil properties (texture, carbonate, organic C and N), with the exception of pH,

234    for which the type of position had a marginally significant effect (Table 1, Fig. 2).

235    However, those soil properties with a potentially highest influence on trace element

236    solubility (pH, carbonate content and texture) highly varied between the two sectors

237 along the river basin. At the Northern zone some extremely acid soils (pH < 3.5) could

238 be found in the river channel (RC) and river banks (RB), while the pH in the soils from

239 the floodplain (FP) was always around neutrality (Fig. 2). A 27 % of the soils at this zone

240 had pH values lower than 4 (in RC and RB), which resulted in a remarkable

241 solubilization of some trace elements (see below). This suggests that the effect of the

242 soil amendments (mainly sugar beet lime with pH > 9) has completely attenuated in

243 this zone. The dose of the applied amendment in these soils was therefore insufficient

244 to buffer against the changes in pH in the long-term, considering that their proximity

245 to the pollution source and the acidic nature of the soils from this zone increases the

246 risk of high leaching of sulphates from sludge oxidation. While amendments were

247 systematically applied to the whole affected area, including those locations in the

248 Central zone, soil pH after the accident has dramatically decreased in the soils from the

249 Northern zone, if compared to soils from the same zone, but not affected by the

250 accident (data available from our previous surveys, Domínguez et al. 2008). In the

251 central zone, however, affected and unaffected soils have similar pH values, suggesting

252 that amendment application was successful in this area. Previous works in the area

253 also reported the presence of extremely acid soils in this Northern sector just after two

254 years after amendment application (Vanderlinden et al., 2006), so it is quite likely that

255 at the time of our sampling (15 years after soil remediation) there is no remaining

256 amendment in the soils from this Northern zone.

257 At the Central zone, soil pH vas more homogenous across the river section, and soils

258 were neutral to slightly alkaline. Carbonate content was associated with soil pH, with

259 those extremely acidic soils having less than 2.5 % of $CaCO_3$, although differences in

260 $CaCO_3$ across the river section were not statistically significant (Tables 1 and 2). At the

11

261　Northern zone, soils from the FP had highly variable $CaCO_3$ content, despite relatively

262　homogeneous pH values. This could be related to the irregular application of the soil

263　amendments during the reclamation works, which could be easily accomplished in the

264　floodplain but not in river banks and channel, leading to an irregular restoration of the

265　pollution buffering capacity in the soils from these two scenarios.

266

267　Texture was similar among the three studied topographical locations in both zones.

268　Sandy soils were more frequently found at the Northern zone, with the 50% of cases

269　having a sandy loam texture, and only 5 cases with a clay loam texture. In contrast, at

270　the Central zone, ca. of 45% of the sampled soils had a sandy clay loam, clay loam or

271　even a clayey texture (Table 2). Therefore, soil texture at the Central zone might

272　promote a greater immobilization of trace-elements, in comparison to soils at the

273　Northern zone.

274

275　*3.2. Total and soluble concentrations of S and trace elements (TE)*

276　As with the general soil properties, total concentrations of "low mobility" trace

277　elements (As, Pb, Domínguez et al., 2009) were not particularly different among

278　positions across the river section, but highly differed between sectors along the basin

279　(Table 1). The total concentrations of more mobile elements such as Cd, Cu and Zn

280　were more different among topographical locations that between zones along the

281　basin. Finally, soluble concentrations were very different both among the

282　topographical positions and between zones (Table 1). In general, soil conditions in the

283　RC and RB enhanced the solubility of the studied trace elements, particularly in the

284　Northern zone.

285

286     Sulphur was one of the main components of the sludge (up to 40%; Alastuey et al.,

287     1999; Grimalt et al., 1999), and 16 years after the accident total S concentrations were

288     still remarkably high. At the Northern zone, S pseudo-total concentrations were

289     particularly high in the RC (Fig. 3a), where a maximum concentration of 88386 mg kg$^{-1}$

290     (ca. 9 % w/w) was recorded. Such concentrations are found in some spots of bare soil,

291     where vegetation has not established 16 years after the accident due to the high

292     soluble trace element concentrations, which can be observed in the river banks and

293     floodplains from the Northern zone, representing a 7 % of the land surface in this zone

294     (Martín-Peinado et al., 2015).  At the Central zone, the maximum S concentrations

295     were clearly lower (11464 mg kg$^{-1}$, 1.1 % w/w, recorded in the RB). As expected from

296     the pH values (Fig.2), S soluble concentrations ($CaCl_2$-extracted) were also greater in

297     the Northern zone, and significantly varied across positions in the river section in both

298     zones (Fig. 3d; Table 1). There was a clear negative relationship between soil pH and

299     total S concentrations (Fig. 4), suggesting that the periodical oxidation of the sulphides

300     contained in the remnants of sludge has led to soil acidification (Kraus and Wiengand,

301     2006), especially at the RC and the RB. The fraction of soluble to total S concentrations

302     was clearly higher in the Northern than in the Central zone, illustrating that soil

303     conditions in this Northern soil promote S mobilization (Fig. 5).

304

305     Concentrations of "low mobility" trace elements, such as As and Pb were also very high

306     in the sludge, up to 0.5 and 0.8 % w/w respectively (Grimalt et al., 1999). In our survey,

307     maximum total Pb and As concentrations were up to 2920 mg kg$^{-1}$ and 650 mg kg$^{-1}$,

308     respectively, which were recorded in some of the Northern soils (Fig. 3b, c). Soluble As

13

309 concentrations were always below 5 mg kg$^{-1}$, and were greater in the RC than in RB or

310 FP within each zone (Fig. 3e). The higher As mobility recorded in the RC position could

311 be due to the higher frequency of waterlogging episodes in this microsite, given that

312 anaerobic conditions might dramatically increase As solubility (Moreno-Jiménez et al.,

313 2013). When comparing between zones, solubility in the RB and FP tended to be

314 greater in the basic and alkaline soils from the Central zone. Soluble Pb concentrations

315 were one order of magnitude greater in the RC and the RB from the Northern zone

316 (maximum values up to 34.8 and 22.9 mg kg$^{-1}$, respectively) than those in the

317 corresponding scenarios of the Central zone (Fig. 3f).

318

319 In contrast to S, As and Pb, the total Cd concentrations in the FP were significantly

320 greater in the Central than in the Northern zone (Table 1, Fig. 6a). In the river banks

321 and floodplains, Cu concentrations were similar in both zones (Fig. 6b). As with Cd, a

322 trend for greater Zn concentrations in the Central zones was observed (Fig. 6c),

323 although differences were not statistically significant. This suggests that these

324 elements have been progressively leached downstream from the Northern locations,

325 given that the conditions of soil acidity and sandy texture that prevail in those

326 locations enhance the mobility of these heavy metals. Soluble concentrations of Cd, Cu

327 and Zn differed across scenarios and between geological zones, being particularly high

328 in the RC from the Northern zone (Fig. 6d-f, Table S1). In the Central zone, soluble

329 concentrations of Cd, Cu and Zn were well below 1 mg kg$^{-1}$, indicating that soil

330 conditions in these soils (high pH and clay content) promote the immobilization and

331 accumulation of the elements that are leached from upstream locations. Copper

332 mobility seems to be limited (Table S1), likely because this element has a high affinity

333     for the solid phase and can be easily retained by soil organic matter (McBride, 1989),

334     particularly by interacting with humic acids (Plaza et al., 2005; Soler-Rovira et al. 2010).

335

336     The principal component analysis confirmed that Cd and Zn followed a different

337     pattern of covariation than the rest of trace elements contained in the sludge (Fig. 4).

338     The first factor, explaining a 52 % of the variance, revealed a close negative

339     relationship between pH and total As, S and Pb concentrations, as well between pH

340     and the soluble concentrations of the catonic trace- elements (Cu, Cd, Pb and Zn).

341     Total Cd and Zn concentrations, however, defined the second factor, which was not

342     related to soil pH, but rather positively associated to soil clay content and total C and N

343     (Fig. 4). This confirms that the long-term fate of the pollution would be dependent on

344     the element type, with those "low mobility" elements (As, Pb) showing the lowest

345     level of re-distribution from the pollution source, and agrees with previous studies on

346     the area that showed that, after the remediation works, the highest concentrations of

347     the less mobile elements were located within the first 15 km downstream the tailings

348     dam (Cabrera et al., 2008).

349

350     The solubility of some trace elements (Cd, Cu, Pb and Zn) is greatly influenced by soil

351     pH (Greger, 1999). An increase in soil pH reduces the availability of these metals

352     through precipitation and by increasing adsorption on soil colloids (Selin and Amacher,

353     1997). While Cd, Cu and Zn solubility increases exponentially under pH values below 6,

354     Pb solubility usually shows a non-linear relationship to soil pH, with large increases in

355     solubility in extremely acid soils (pH < 3) and a relative immobilization above that value

356     (Domínguez et al., 2009). Therefore, within the range of soil pH found in this study the

357    solubility of Pb would be relatively high in only a few of the studied locations. Arsenic,

358    in contrast, is more soluble at alkaline pH (Greger 1999), thus its mobility in the

359    Northern locations and re-distribution downstream was much reduced by the acidic

360    soil conditions in the vicinity of the pollution source.  At longer times-scales, even

361    poorly soluble elements could be transported downstream. Studies on metal content

362    in soils of this area conducted before the mining accident showed that waters of

363    Guadiamar River had comparatively high heavy metal contents, due to the transport of

364    heavy metal-rich solids precipitated upstream in distant mining sites (Arambarri et al.,

365    1996; Cabrera et al., 1987). The analysis of some plant species from the marshes in

366    Doñana National Park, where the Guadiamar River drains, indicated residual As

367    contamination derived from historic mining activities in distant locations within the

368    region (Madejón et al., 2006).

369

370    The results found in this study indicate that the extent of the contamination in the soils

371    deserves, at least, further assessment. In both zones most of the recorded As

372    concentrations, including those in the FP, exceeded the intervention value of 50 mg kg$^{-1}$

373    $^{1}$ reported for Andalusian soils (Aguilar et al., 1999), as well as the toxicity threshold for

374    plants of 20 mg kg$^{-1}$ (Singh and Steinnes, 1994), and the maximum tolerable level for

375    agricultural soils in some European countries, like Germany (NIPHE, 2001). Indeed, for

376    most of the studied soils As concentrations were greater than the critical range of 20-

377    50 mg kg$^{-1}$ above which toxicity is considered to be possible (Alloway, 1990; Kabata-

378    Pendias and Pendias, 1992).  In the case of Pb, a few samples from the Northern zone

379    (9 out of 30) exceeded the regional intervention value (500 mg kg$^{-1}$; Aguilar et al.,

380    1999), and 10 out of the 60 samples collected throughout the river basin exceeded the

16

381     phytotoxic range of 100-400 mg kg$^{-1}$ (Alloway, 1990). Furthermore, 35 samples (more

382     than half) exceeded the maximum tolerable level for agricultural soils in some

383     European countries, like Germany (100 mg kg$^{-1}$, NIPHE, 2001). Therefore further

384     cleaning operations in some of the most contaminated spots would be desirable.

385

386     While As and Pb concentrations clearly exceeded the regional intervention levels, the

387     Cd concentration never exceeded the regional intervention level of 10 mg kg$^{-1}$, and

388     only a few cases were above the permissible level of 3 mg kg$^{-1}$(Aguilar et al., 1999).

389     Nevertheless, attending its potential toxicity, a periodical monitoring of this metal in

390     the Guadiamar Green Corridor is recommended (Madejón et al., 2009; Pérez de Mora

391     et al., 2010). Maximum Cd concentrations of 9 and 4 mg kg$^{-1}$ in the RC and RB at the

392     Northern zone clearly exceed the normal range in soils  (0.01-2 mg kg$^{-1}$, Bowen, 1979)

393     and were into or exceeding the range of 3-8 mg kg$^{-1}$ above which toxicity is considered

394     to be possible (Alloway, 1990; Kabata Pendias and Pendias, 1992). As certain plant

395     species in the area are able to tolerate and accumulate comparatively high

396     concentrations of Cd in their aboveground biomass (Domínguez et al., 2008; Madejón

397     et al., 2004, 2013), Cd traslocation into plant biomass should be periodically monitored

398     and identified, in order to determine the risk of transfer of this element into the local

399     food web. Previous reports highlighted Cd as one of the most problematic elements

400     for the trophic web in the affected area (Domínguez et al., 2009; Madejón et al., 2009;

401     Madejón et al., 2012; Pérez de Mora et al., 2010).

402

403     For Zn, only few of the sampled soils (5 out of 60, collected in the river channel and

404     bank) exceeded the regional intervention value of 1000 mg kg$^{-1}$, although in 20 of

405    them concentrations were in the range 500-1000 mg kg$^{-1}$ which requires obligatory

406    investigation (Aguilar et al., 1999). More than a half of the sampled soils exceeded the

407    regional permissible level of 300 mg kg$^{-1}$ (Aguilar et al., 1999). Therefore, a periodical

408    soil monitoring for this element is also necessary, even though its potential toxicity is

409    lower than that of Cd.

410

411    *3.3. Implications for the management of contaminated river basins*

412    Our study illustrates the complexity of managing contaminated river basins. Besides

413    the geological factors that determine the nature of the soil properties, and

414    consequently the capacity of soils to buffer against changes in pH and in trace element

415    concentrations, the topographical factor (position across the river section) may further

416    compromise the cleaning-up operations which determines the long-term persistence

417    of pollution along the basin. Moreover, river channels and banks are subjected to

418    flooding which causes periodical redox processes and changes in soil pH, leading to the

419    potential mobilization of certain metals (Moreno-Jiménez et al., 2013). In our work, we

420    show that the solubility of the most mobile trace elements (Cd and Zn) is different

421    across the river section, being more soluble in the river channel and banks. Achieving a

422    complete removal of the sludge and a regular application of amendments to soils in

423    these scenarios should be a priority for managers. Otherwise, trace elements could be

424    re-located downstream during the seasonal floods.

425

426    Indeed, we found evidences that there was a redistribution of Cd and Zn along the

427    basin. Fortunately, the soil conditions at the Central zone (basic and alkaline soils with

428    clayey texture) promoted the immobilization of these potentially toxic elements,

429 preventing their further re-distribution downstream. Although we did not study the

430 vertical migration of trace elements through the soil profile, it is likely that in those

431 extremely acid soils in the river channel and banks a vertical re-distribution of these

432 labile elements have also occurred, with a potential risk of contamination of

433 groundwaters. This issue should be certainly addressed by the land managers.

434

435 Our work also illustrates the need to consider the geological background properties

436 when planning a remediation program. The geological differences along the basin had

437 a critical role in determining the long-term fate of trace elements more than a decade

438 after the pollution episode. In the Northern zone the capacity of the soils to buffer

439 against changes in soil pH and trace element concentrations was much lower due to

440 the acidic nature of the soils, with low carbonate content. In these soils the applied

441 amendments were not enough to neutralize the acids produced by the progressive

442 sulphide oxidation over the years. Maintaining neutral to basic soil pH should be an

443 integral part of any remediation program that involves trace element-contaminated

444 soils (Domínguez et al., 2008). Therefore, the application of new amendments in these

445 extremely acid soils should be a priority for land managers. Besides soil pH correction,

446 appropriate afforestation and revegetation of the river banks is critical to ensure a

447 physical stabilization of the soil, and to reduce the losses of soil through water erosion.

448

449 **4.    Conclusions**

450 The persistence of soil pollution in the studied river basin, 16 years after a pollution

451 episode, depended on the geological background (determining the capacity of the soil

452 to buffer against changes in soil pH) and the topographical location (river channels and

453 banks remaining more contaminated due to the limited accessibility for cleaning-up

454 operations and amendment application). The long-term fate was different among

455 trace-elements, Cd and Zn being easily re-distributed downstream due to their high

456 solubility, and As and Pb remaining at shorter distances from the pollution source.

457 The application of assisted natural attenuation techniques can be a feasible alternative

458 to achieve large-scale soil remediation goals, but the design and monitoring of the

459 operations should consider the geological background, particularly at adjusting the

460 amendment doses to maintain neutral pH conditions over time in order to immobilize

461 trace-elements.

462

469

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649

650    Table 1. Results of the two-way ANOVAs to test for differences in soil variables

651    between zones and across topographical position in the river section. (*) for these

652    variables, a generalized mixed model (GLZ) was applied using a gamma distribution as

653    a link function, since the normality assumption was not met. The statistic column

654    refers to the F statistic (ANOVA) or the Wald statistic (GLZ).

655

| 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 |
| *Pseudo-total concentrations:* | | | | | | |
| 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 |
| *Soluble concentrations:* | | | | | | |
| 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 |

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659   Table 2. General soil properties across the river section at the Northern and Central zones. Mean values ± 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 (0.48 – 7.93) | 5.3 ± 1.6 (1.1 – 14.5) | 27.7 ± 5.4 (2.5 – 50.7) | 25.2 ± 2.0 (17.1 – 36.9) | 28.0 ± 1.9 (18.2 – 37.3) | 19.2 ± 3.2 (8.4 – 30.3) |
| | RB | 1.26 ± 0.21 (0.39 – 2.18) | 5.3 ± 1.6 (1.0 – 13.5) | 27.9 ± 5.1 (5.5 – 53.4) | 24.2 ± 1.7 (18.1 – 30.9) | 31.3 ± 3.7 (17.7 – 52.3) | 16.6 ± 2.6 (8.4 – 28.8) |
| | FP | 1.00 ± 0.08 (0.45 – 1.30) | 2.4 ± 0.3 (0.6 – 16.1) | 34.1  3.4 (16.9 – 49.8) | 24.9 ± 0.8 (22.3 – 30.3) | 25.9 ± 2.2 (14.6 – 37.0) | 15.1 ± 1.8 (8.8 – 25.5) |
| Central | RC | 1.90 ± 0.21 (0.93 – 2.88) | 10.0 ± 1.1 (5.4 – 15.2) | 23.7 ± 4.4 (6.1 – 42.7) | 31.4 ± 2.2 (21.8 – 41.4) | 24.3 ± 2.8 (14.3 – 38.5) | 20.6 ± 2.6 (9.8 – 35.0) |
| | RB | 1.65 ± 0.14 (0.94 – 2.55) | 9.1 ± 1.1 (5.1 – 16.7) | 23.5 ± 3.9 (8.2 – 43.9) | 29.3 ± 3.1 (17.2 – 45.2) | 27.0 ± 2.3 (16.2 – 37.5) | 20.1 ± 1.7 (10.1 – 26.1) |
| | FP | 1.65 ± 0.26 (0..59 – 2.90) | 10.1 ± 1.7 (4.4 – 18.1) | 15.9 ± 3.4 (3.5 – 39.8) | 25.0 ± 3.1 (7.9 – 43.7) | 30.7 ± 2.1 (19.3 – 40.3) | 28.4 ± 3.5 (15.7 – 54.1) |

662

**Figure captions**

Fig. 1.  Location of the Guadiamar 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 Guadiamar River basin (mean ± standard error). RC = river channel; RB = river bank; FP = floodplain.

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

685 Fig. 6. Pseudo-total and soluble Cd, Cu and Zn concentrations (mean ± standard error)

686 across the river section at the Northern and Central zones within the Guadiamar River

687 basin. RC = river channel; TB = top bank; FP = floodplain.