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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 sulfide 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.

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 Guadiamar 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).

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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).

There are very few cases of application of assisted natural remediation techniques to real, large-scale pollution problems. The Guadiamar River basin is one of these few cases (Domínguez et al., 2008). After a huge mine spill in 1998 affecting about 55 km^2 of land, a large scale remediation project was launched, with included the removal of the polluted sludge and the underlying soil, the application of soil amendments, and the plantation of native woody plant species. The pollution episode and subsequent remediation program received much attention from the scientific community during the first years after the spill (Aguilar et al., 2004; Alastuey et al., 1999; Cabrera et al., 1999, 2008; Clemente et al., 2003; Domínguez et al., 2008; Galán et al., 2002; López-Pamo et al., 1999; Simón et al., 1999), although most of these studies were restricted to the river floodplain. However, the zone just near the river bed, including the bank, was more affected by the sludge deposition and less accessible for cleaning-up operations, so it would be expected that soil pollution was differently distributed among different zones across the river section, and that the long-term fate of soil pollutants in the river bank and the floodplain has followed different patterns. In particular, it could be expected that the higher deposition of sludge in the river bank and channel, together with the lower amendment application in these positions, had led to more intensive processes of sulfide oxidation in the soils from river banks and channels, resulting in a higher mobility of trace elements in comparison to the floodplain.

Here, we aimed to evaluate the persistence of soil pollution in this large-scale 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 water flow values from January to March (mean value of 13 $m^3\ s^{-1}$) and low values from June to October (3 $m^3\ s^{-1}$, 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 plowed depth (20–25 cm) by disk 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.

2.2. 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° 28.758′ N, 6° 12.956′ W), southwards to the Guadalquivir River marshes, where the river drains into (37° 13.040′ N, 6° 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.

2.3. 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 analyzed using a Thermo Scientific Flash 2000