HEAVY METAL AND AS TRANSPORT UNDER LOW AND HIGH FLOWS IN THE RIVER GUADIAMAR THREE YEARS AFTER THE AZNALCÓLLAR TAILINGS DAM FAILURE: IMPLICATIONS FOR RIVER RECOVERY AND MANAGEMENT

J. N. TURNER (1)
P. A. BREWER (1)
M. G. MACKLIN (1)
K. A. HUDSON-EDWARDS (2)
T. J. COULTHARD (1)
A. J. HOWARD (3)
H. E. JAMIESON (4)

(1) Institute of Geography and Earth Sciences, University of Wales, Aberystwyth, Wales SY23 3DB, UK
(2) School of Earth Sciences, Birkbeck College, University of London, Malet Street, London WC1E 7HX, UK
(3) School of Geography, University of Leeds, Leeds LS2 9JT, UK
(4) Department of Geological Sciences, Queen’s University, Kingston, Ontario, K7L3N6, Canada

ABSTRACT: This paper presents work from an on-going research programme examining the recovery of the Guadiamar River following the April 1998 Aznalcóllar tailings dam failure. Analysis of heavy metal (Cd, Cu, Pb and Zn) and As in surface waters, valley floor alluvium, overbank and suspended sediments are compared between six study reaches downstream of the dam, over five sampling periods. The principal aims of the paper are to examine the distribution of contaminants in sediments and river waters and their delivery downstream under low and high flows, and the implications for river channel recovery and management three years after the tailings dam failure.

Results from a survey of Guadiamar alluvium carried out in January 1999 showed that, although clean-up operations were largely successful in restoring the affected area to pre-spill conditions, sediments continued to exceed intervention thresholds for the region. Residual contaminant levels were highest near the spill source, with isolated 'hotspots' of elevated contamination throughout the affected area, superimposed on a general downstream decline in concentrations. In terms of contaminant mobility, surface water samples taken in May 99, under very low flows, have dissolved Cd, Cu and Zn concentrations which fail EC directive thresholds for surface water abstraction. Element concentrations are significantly lower for waters in January 1999, when controlled discharge from the Agrio reservoir was taking place. Under high flow conditions, sediment-associa
ted contaminant transport is dominant for all elements discussed, accounting for between 91% (Cu) and 99% (Pb) of export yields. This has lead to the remobilisation of significant quantities of contaminants, particularly Pb and Zn, during post-spill floods. Overbank deposits, however, show a fall in contaminant concentrations, following successive flood events. This has been due to sediment mixing of contaminated and “clean” material. Dilution has so far maintained contaminant concentrations below intervention threshold limits in the lower reaches, thereby offering a cautiously optimistic prognosis for the sensitive wetlands of Doñana.

RESUMEN: Este trabajo estudia la recuperación del río Guardiamar después de la ruptura de una presa en Aznalcóllar en abril de 1998. Se han realizado análisis de metales pesados (Cd, Cu, Pb y Zn) y arsénico en las aguas superficiales y llanura aluvial, y sedimento en suspensión en seis tramos aguas abajo de la presa, durante cinco periodos de muestreo. Los principales objetivos del estudio son examinar la distribución de contaminantes en los sedimentos y en las aguas fluviales, y su liberación aguas abajo con caudales bajos y altos, así como las implicaciones para la recuperación y gestión del cauce tres años después de la ruptura de la presa.

Los resultados obtenidos en el río Guardiamar en enero de 1999 demuestran que, aunque las operaciones de limpieza han tenido mucho éxito en la recuperación del área afectada, los sedimentos están por encima de los umbrales admisibles. Los niveles de contaminación residual fueron más elevados cerca de la presa, con áreas aisladas de contaminación elevada a lo largo del cauce superponiéndose a una tendencia decreciente de aguas abajo. En términos de movilidad de contaminantes, los muestras en agua superficial en mayo de 1999, con caudal muy bajo, tienen concentraciones de Cd, Cu y Zn disueltos que no cumplen con la directiva de la Unión Europea. La concentración de elementos es significativamente menor en enero de 1999, cuando se soltó agua desde el embalse de Agrio. Con caudal elevado el transporte de contaminantes representa el 91% de Cu, el 99% de Pb, lo que conduce a la remobilización de grandes cantidades de contaminantes, particularmente Pb y Zn. La sedimentación en la llanura aluvial muestra un descenso en la concentración de contaminantes después de sucesivas avenidas. La dilución ha mantenido la concentración de contaminantes por debajo de los límites de umbral en el curso bajo, lo que ofrece una perspectiva moderadamente optimista para las áreas húmedas de Doñana.

**Key-words:** Dam failure, Contamination, Heavy metals, Sediments, Wetlands, Andalucía, Spain.

**Palabras clave:** Ruptura de presa, Contaminación, Metales pesados, Sedimentos, Humedales, Andalucía, España.

1. Introduction

More than three years have passed since the Aznalcóllar tailings dam failure and the flooding of the Agrio-Guadiamar River in April 1998. Over this period major clean-up operations have been carried out on the channel, floodplain and valley floor. Studies undertaken shortly after the tailings dam failure emphasised the high toxicity of the heavy metal-bearing residues and the persistent threat these contaminants pose to the natural environment (Grimalt and Macpherson, 1999). However, little work has been pre-
Heavy metal and As transport under low and high flows in the river Guadiamar three years after the Aznalcóllar tailings dam failure

This paper presents water and sediment quality data which show how the Guadiamar is recovering both physically and chemically. Heavy metal (Cd, Cu, Pb and Zn) and As levels in river water are presented for low and high flows, as well as for suspended and overbank sediment to assess the medium to long-term fate of these contaminants and the risks they pose to the environmentally sensitive lower reaches of the Doñana nature reserve.

2. The Guadiamar basin: physiography, geology and mining

The Guadiamar catchment is located in the Province of Sevilla, southern Spain (Figure 1) and drains an area of 1,879 km². The river rises in the Ossa-Morena Zone, 24 km to the north of the town of Aznalcóllar and flows for 78 km until it joins the River Guadalquivir via the Brazo de la Torre. The climate in the region is typically Mediterranean, characterised by very dry summers and intermittent autumn-winter rains. The mean annual precipitation varies within the catchment between 800 mm in the headwaters to 500 mm downstream (CMA, 1999). Rainfall is often very intense, and the mean annual rainfall can be concentrated in a few torrential storms. As a consequence, the hydrological regime is characterised by low flows with infrequent flood events (Gallart et al., 1999; CHG,

![Figure 1. The Guadiamar catchment, showing the location of the six study reaches (after Macklin et al., 1999)](image)

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The northern part of the basin is underlain by Upper Devonian – Lower Carboniferous Volcano-Sedimentary Complex (Almodóvar et al., 1998). These are associated with the Iberian Pyrite Belt (IPB), formed of massive sulphide deposits which have long been exploited for base and precious metals. The southern part of the basin is underlain by Miocene silts and calcarenites, which are overlain by Eocene marls and Late-Quaternary sands and gravels. Early mining activity in the Aznalcóllar region dates back over 4 millennia and reached a peak during the Roman period (Boliden-Apirsa, 1999). The present phase of mining began in 1979 at Aznalcóllar, first by Andaluza de Piritas SA (Apirsa) and then by Boliden, who acquired Apirsa in 1987. The Aznalcóllar reserves were exhausted in 1996 and operations were transferred to the adjacent Los Frailes deposit in February 1997 (McDermott and Sibley, 2000). The tailings facility, that was breached in April 1998, was constructed in 1978 and was used for sub-aqueous storage of mine wastes (Sassoon, 1998). Land-use in the lower Guadiamar valley before the spill was dominated by agriculture. According to the Spanish authorities, the initial losses in production exceeded $10 million (CMA, 1999). Along with providing an important water source for irrigation of agricultural land, the Guadiamar delivers fresh water to the wetlands of the Doñana nature reserve on the Atlantic coast. This region comprises several distinct and fragile ecosystems and provides refuge to more than 70% of European bird species (Grimalt et al., 1999). It is largely the threat of contamination to this unique national heritage that has driven the rehabilitation programmes.

3. The tailings dam failure

The breach in the Aznalcóllar tailings dam at Boliden-Apirsa’s Aznalcóllar/Los Frailes Zn-Pb-Cu mine occurred on the 25 April 1998. An estimated 5.5 million m$^3$ of acidic water and 1.98 million m$^3$ of pyritic tailings were discharged into the Agrio River (CMA, 1999), 2 km upstream of its confluence with the Guadiamar. According to UN statistics, this was the second largest mine spillage to have occurred worldwide in the last decade (WISE, 2001) and was by far the worst environmental pollution disaster recorded in Spanish history (Grimalt et al., 1999). Approximately 4600 ha along both sides of the river was flooded, with 2616 ha directly affected by tailings. More than 60% of the solid wastes were deposited in the first 13 km downstream of the breach, reaching depths of 4 m close to the impoundment and a few mm at the spill margins (CMA, 1999; López-Pamo et al., 1999; Eriksson and Adamek, 2000; McDermott and Sibley, 2000). The residues were largely composed of pyrite (>80%) and other sulphide minerals, and contained Pb (0.8 – 1.1%); Zn (0.5 – 0.8%); As (0.2 – 0.5%) and Cu (0.1 – 0.2%), with smaller proportions (<0.1%) of Sb, Co, Tl, Cd, Ag, Hg and Se (Simón et al., 1999).

4. The clean-up operations

Clean-up operations began on 3 May 1998, under the auspices of Boliden-Apirsa, the Confederación Hidrográfica del Guadalquivir (CHG) and the Consejería de Medio Ambiente (CMA). Work was undertaken in two phases, with all contaminated material transported to the former Aznalcóllar open pit for sub-aqueous storage. The first phase,
completed in December 1998, was carried out without any consideration for metal concentrations in the soil (Eriksson and Adamek, 2000). During this phase, most of the deposited tailings and approximately 4.7 million m$^3$ of contaminated soil were removed. The second phase was carried out during the summer of 1999 and targeted areas where residual contaminant concentrations exceeded intervention criteria for the region laid down in the Law of Wastes 10/1998 (González-Aurioles, 1999). A further 200 ha, confined mostly to the river channel and areas around upstanding trees, were cleaned and an additional 1 million m$^3$ of material was removed (Eriksson and Adamek, 2000).

With such vast quantities of soil and sediment removed during the clean-up, the impacts on the river channel and valley floor morphology were considerable. Channelisation, involving dredging, re-sectioning and realignment of the river, was undertaken from the dam downstream to reach 6 (Figure 1), and all in-channel and most riparian vegetation (in the upper reaches) was removed. Channel banks and valley floor soils and sediments were left extremely vulnerable to erosion, increasing the risk of channel instability and the remobilisation of residual contaminants.

5. Methodology

In comparison to other research on the Agrio-Guadiamar this study is unique by providing an integrated geomorphological-geochemical approach to the assessment of river channel recovery. The scientific basis for this approach is that the deposition and storage patterns of sediment-associated contaminants can be related to floodplain geomorphology and river regimes in a predictable way (Lewin and Macklin, 1987; Graf, 1994; Macklin, 1996).

5.1. Geomorphological mapping

In January 1999 six study reaches were selected, representative of the principal river channel and floodplain environments affected by the spill (Table 1). At each reach a total station survey was carried out to establish a monumented local coordinate system and a detailed geomorphological map of channel and valley floor topography. Five further surveys have been carried out following flood events and/or further management intervention (Table 1). All topographical information has been geo-referenced and is stored in an Arc/Info™ GIS.

5.2. Sediment analysis

Physical and chemical data for three types of sediment were collected:

1. valley floor alluvium was collected from each study reach to establish heavy metal and As concentrations in the Guadiamar following the clean-up;

2. suspended sediments sampled at reach 2 (El Guijo gauging station) during a flood in October 1999 and;

3. overbank sediments deposited during post-spill flood events.
All sediment sample sites have been spatially referenced and linked to the geomorphic maps of the channel, floodplain and valley floor.

Surface samples (100-200g) were collected over a c. 10 m² area by combining 10 random surface sub-samples from a depth of 3 – 5 cm. The sub-samples were homogenised and a disaggregated portion was air-dried, passed through a 2 mm screen and milled for four minutes. Samples were digested using either HNO₃-HF-HClO₄ (valley floor alluvium, February 1999 and October 1999 overbank sediments, October 1999 suspended sediments), or using concentrated (70%) HNO₃ (October 1999, March 2000, and May 2000 overbank sediments). A comparison between the two digestion methods shows a good correlation ($R^2 > 0.9$ at 95% significance level) for all elements reported. The HNO₃-HF-HClO₄ procedure removed, on average, 5% less As, 5% less Cd, 20% more Cu, 15% more Pb and 10% less Zn than the (70%) HNO₃ method. Analyses were carried out by ICP-MS (VG Elemental Plasma Quad II+) at the Institute of Geography and Earth Sciences (IGES), University of Wales, Aberystwyth. Analytical precision was determined by inserting blind duplicates to approximately 10% of the total number of samples analysed. Analytical accuracy was determined using Chinese reference standards for stream sediments (GSD5; GSD7; GSD12). Both precision and accuracy were within 10%, except for Cd under very low concentrations (<0.1 mg/kg).

### Table 1. Description and location of study reaches (after Macklin et al., 1999)

| Reach | Location (Lat, Long) | Length (m) | Distance downstream from the mine environment (km) | Survey dates and environment |
|-------|----------------------|------------|--------------------------------------------------|-----------------------------|
| 1     | River Agrio-River Guadiamar confluence (37°28’N, 6°13’W) | 1300       | 2.5                                              | Jan 1999; May 1999; Oct 99; April 00; Sept. 00; April 01; Active wandering gravel bed |
| 2     | El Guijo gauging station (37°27’N, 6°13’W) | 350        | 7.0                                              | Jan 1999; May 1999; Oct 99; Sept. 00; April 01; Active low sinuosity gravel bed |
| 3     | Upstream of Sanlúcar road bridge (37°24’N, 6°14’W) | 340        | 11.3                                             | Jan 1999; May 1999; Oct 99; Sept. 00; April 01; Active low sinuosity gravel/sand bed |
| 4     | Upstream of Aznalcázar railway bridge (37°18.5’N, 6°15’W) | 500        | 23.1                                             | Jan 1999; May 1999; Oct 99; Sept. 00; April 01; Stable low sinuosity sand/gravel bed |
| 5     | La Tiésa (37°13.5’N, 6°14’W) | 930        | 38.4                                             | Jan 1999; May 1999; Oct 99; Sept. 00; April 01; Stable straight silt/sand bed (tidal) |
| 6     | Puente San Simone (37°11.5’N, 6°13’W) | 640        | 43.5                                             | Jan 1999; May 1999; Oct 99; Sept. 00; April 01; Stable straight silt/sand bed (tidal) |
5.3. Water sampling and analysis

River water samples were taken from the Guadiamar and the Agrio at reaches 1 to 5 in January 1999, May 1999 and October 1999. Samples were filtered in the field through 0.45 µm cellulose nitrate screens and those destined for cation analysis were acidified with 2 ml of concentrated HNO$_3$. Analyses were carried out by ICP-MS at the Department of Geological Sciences, Queen’s University Kingston, Canada and at IGES University of Wales, Aberystwyth. Analytical accuracy, measured with a reference water (SLRS-4) from the National Research Council of Canada and an in-house standard at IGES, Aberystwyth, was generally within 10%. Analytical precision of field and laboratory duplicates was also generally within 10%.

6. Results

6.1. Post clean-up conditions in the affected area

Table 2 summarises the January 1999 and May 1999 geochemical data and shows that, following the clean-up operations, the reaches closest to the failed tailings dam had the highest heavy metal and As concentrations. Although concentrations generally declined downstream, these were not uniform and contaminant concentrations increased between reach 1 to 2 (Zn, Cd), reach 2 to 3 (Cu), reach 3 to 4 (As, Pb) and reach 5 to 6 (Zn). There was also considerable spatial variability in contaminant concentration at all six reaches (Table 2). High heavy metal and As concentrations found in individual samples very often reflected the patchy distribution of residual tailings following the clean-up and even as recently as April 2001 raw tailings were still evident in several of the reaches. Given the long history of metal mining in the region, however, elevated levels may also reflect historic pollution prior to the spill. Hudson-Edwards et al. (in press) compared metal levels in studies undertaken during the modern mining era (post-1979) with pre-spill alluvium, and showed that mining activity during the 1980s and 1990s had already increased the contaminant loadings (González et al., 1990; Ramos et al., 1994; Martín et al., 2000). The January 1999 heavy metal and As levels were generally lower than those reported in the earlier studies, suggesting that the clean-up operations were effective in removing the majority of contaminated sediment released by the tailings dam failure. However, mean concentrations in post-spill alluvium still represent a quantifiable risk to human and ecosystem health. Intervention thresholds for the Guadiamar were drawn up in December 1998, following extensive sampling and analysis of catchment soils and sediments (González-Aurioles, 1999). These values are shown in Table 2, along with Dutch interventions limits that are generally more stringent. When compared to the non-sensitive intervention thresholds for non-agricultural landuse, heavy metal and As levels in the upper reaches continue to be remediation concern.

6.2. Low flow water quality

Dissolved heavy metal and As concentrations in Agrio-Guadiamar river water samples taken in January and May 1999 are summarised in Figure 2. Background element levels
were established in the Guadiamar waters by sampling upstream and outside of the affected area in January 1999. The horizontal lines show European Union directive values for the abstraction of drinking water (75/440/EEC). The long-dashed lines denote imperative thresholds (As 50 µg/l; Cd 5 µg/l; Cu 50 µg/l; Pb 50 µg/l; Zn 3000 µg/l) and the short-dashed lines denote guideline thresholds (As 10 µg/l; Cd 1 µg/l; Cu 20 µg/l; Zn 500 µg/l).

In January 1999, water samples had higher pH values and lower dissolved concentrations for all elements measured, with the single exception of As in the Agrio at reach 1, than water samples collected in May 1999 (Hudson-Edwards et al., in press). This is believed to be due, in part, to the controlled discharge of water from the Agrio reservoir during January 1999 following an unseasonably dry winter. A second factor maintaining low concentrations in the January water samples is thought to be the reduced rates of sulphide oxidation and contaminant dissolution during the relatively cooler winter months.
Contaminant concentrations in May 1999 water samples decreased downstream from reach 1 to reach 5, and were probably related to a combination of precipitation/adsorption processes and dilution (Hudson-Edwards et al., in press). The increase in As concentrations between reaches 4 and 5 is attributed to either differences in the anionic behaviour of As compared to Cd, Cu, Pb and Zn or to an alternative source of As (such as lead arsenate pesticides) in the catchment. In terms of EU directives, the May 1999 waters all exceeded imperative thresholds for Cd, Cu and Zn in the upper three reaches, and for As at reach 5.

It is possible to calculate a low flow dissolved contaminant yield in May 1999 waters at reach 2 (El Guijo gauging station) using a mean daily discharge of 1 m$^3$/s (measured base flow; CHG, 1999) and element concentration data reported in Hudson-Edwards et al. (in press). Dissolved contaminant yields vary considerably between the elements described here: As (0.5 kg/day), Cd (2.5 kg/day), Cu (21.3 kg/day) Pb (0.5 kg/day) and Zn (1,296 kg/day). Low flow water quality in the Guadiamar is still poor, especially for Cd, Cu and Zn.
Figure 3 shows total (sediment-associated and dissolved) and sediment-associated yields for Cu at El Guijo gauging station (Figure 1, reach 2) during the October 1999 flood. This was the first major flood (>10m³/s) in the Guadiamar River following the tailings dam failure. Sampling began at 12:00 hours on 24th October and continued until 12:15 hours on the 27th October. The graph shows a Cu yield pattern that closely reflects the flood hydrograph. In addition, the total and sediment-associated curves are almost coincident, illustrating the dominant role that suspended sediments play in transporting Cu. The divergence of the total and sediment-associated curves, displayed on the waning limb of the second flood wave, is due to the effect of sediment exhaustion. This is illustrated by the positive hysteresis curve shown in Figure 4. Irregularities in the form of the curve in Figure 4 represent sediment pulses arriving during the flood.

Sediment-associated transport is equally important for As, Cd, Pb and Zn, accounting for up to 99% of contaminants mobilised during the October 1999 flood (Table 3). Total sediment-associated loads indicate the remobilisation of significant quantities of Zn and Pb during the sampling period (Table 3). Almost 22,000 tonnes of suspended sediment passed through the El Guijo gauging station during the sampling period and there was a reduction in mean contaminant concentrations in the suspended sediments compared to those recorded in the baseline alluvium at reach 2 (Table 2) for all elements discussed.
Figure 4. Suspended sediment hysteresis at El Guijo gauging station during the October 1999 flood

As (78%), Cd (66%), Cu (72%), Pb (72%) and Zn (63%). Although the fall in contaminant concentrations could be due to the summer 1999 clean-up campaign, an alternative explanation could be the effect of contaminant dilution due to the mixing of contaminated and “clean” material. A statistical comparison of suspended sediment and Zn concentrations for part of the flood wave (when the influence of particle size is negligible) gives a significant inverse relationship at the 99% significance level. Figure 5 illustrates the effect of sediment mixing by showing how sediment pulses coincide with a fall in Zn

Table 3. Sediment-associated and dissolved yields, and mean heavy metal and As concentrations during high flows: 24/10/99 to 27/10/99

| Sediment-associated load (kg) | Percentage moving with sediment | Mean sediment-associated concentration (mg/kg _ ppm) | Dissolved load (kg) | Percentage moving in aqueous solution | Mean dissolved concentration (µg/l _ ppb) |
|-------------------------------|---------------------------------|------------------------------------------------------|---------------------|--------------------------------------|--------------------------------------------|
| As                            | 1500                            | 97.9                                                 | 71                  | 33                                   | 2.1                                        |
| Cd                            | 41                              | 97.6                                                 | 1.9                 | 1.1                                  | 2.4                                        |
| Cu                            | 1100                            | 91.1                                                 | 52                  | 110                                  | 8.9                                        |
| Pb                            | 4200                            | 99.9                                                 | 190                 | 4.2                                  | 0.1                                        |
| Zn                            | 13000                           | 98.5                                                 | 600                 | 190                                  | 1.5                                        |
|                               |                                 |                                                      |                     |                                      | 27                                         |

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concentration. As a result of dilution, although large quantities of contaminants were mobilised in this flood, the concentrations of heavy metals and As moving towards the sensitive lower reaches did not exceed non-sensitive threshold intervention values shown in Table 2.

In the October 1999 flood waters, dissolved contaminant concentrations are more than an order of magnitude lower than those recorded in May 1999 water samples, and all element concentrations lie within guideline values for water abstraction (Table 3). Although there are a number of factors that could control element solubility, including mineralogy and organic matter content, as the pH of the flood waters varied between pH 7.3 and pH 8.1, alkaline conditions are likely to have impeded dissolution.

6.4. Overbank sediment

The longer term pattern of sediment-associated contaminant export can be evaluated by examining element concentrations in overbank sediment. Figure 6 shows heavy metal and As concentrations in overbank sediments sampled after flood events in March 1999 (10 m$^3$/s), October 1999 (72 m$^3$/s), April 2000 (no discharge information) and May 2000 (75 m$^3$/s). Heavy metal concentrations are given for mean, maximum and minimum values at reach 1 and for reaches 5 and 6. Data for reaches 5 and 6 were combined, as they are both located in the tidal, channelised section of the lower Guadiamar that borders the

Figure 5. A comparison of suspended sediment and Zn concentrations at El Guijo gauging station, during the October 1999 flood.
Heavy metal and As concentrations in overbank sediment deposited during floods in February 1999, October 1999, April 2000 and May 2000.

Figure 6. Heavy metal and As concentrations in overbank sediment deposited during floods in February 1999, October 1999, April 2000 and May 2000.

Doñana Natural Park. Sensitive and non-sensitive intervention thresholds are shown by the long and short dashed horizontal lines, respectively.

Similar to the patterns shown in the valley floor and floodplain geochemical survey (Table 2), all elements show higher concentrations in reach 1 close to the mine, than in the downstream reaches 5 and 6. Element concentrations in overbank sediments have progressively declined over time, particularly following the first major flood in October 1999, when very high suspended sediment concentrations were recorded. The fall in contaminant concentrations after the October flood could be due to i) further mixing of remobilised contaminated material with “cleaner” sediment ii) removal of contaminated material due to minor clean-up works and/or export to the River Guadalquivir iii) transfer of
contaminated material into floodplain and valley floor storage. Our geomorphological surveys show that considerable channel bank erosion and floodplain stripping had occurred at reach 1 and, to a lesser extent, at reach 2, suggesting that contaminated material is still being sourced from the upper reaches. The net results are that sediments in the lower reaches show no evidence for the delivery of a “front” of contamination, as reported by Ramos et al. (1994) and that element concentrations downstream remain below intervention threshold values. Exceptions, however, are As and Pb at reaches 5 and 6, which have remained almost constant over time.

7. Conclusions

Although present day contaminant levels in many parts of the floodplain and valley floor are similar to those before the tailings dam failure, large areas, especially upstream of Sanlúcar Bridge (Figure 1), still have elevated levels of As, Cd, Cu, Pb and Zn. There are isolated “hotspots” of contamination, which pose a specific problem both in terms of a secondary source of contamination and a potential health hazard to the public. In light of the plans to convert the Guadiamar valley into a municipal “Green Corridor” conservation area (CMA, 2000a), residual raw tailings should be removed. Although some re-vegetation of the valley floor has taken place, the river is still under-going major channel change, particularly in the upper reaches. Under conditions of channel re-adjustment there continues to be a high risk of contaminant remobilisation.

Under low flows, Cd, Cu and Zn, display dissolved concentrations in the upper reaches that exceed EU imperative thresholds for surface water abstraction. On the basis that dilution, through the addition of waters with pH > 7, appears to have an ameliorating effect on dissolved heavy metal concentrations, continued controlled discharge from the Agrio reservoir would be advised.

Under high flows, dissolved element concentrations are low, and sediment-associated contaminants dominate heavy metal and As loads. As a consequence, large quantities of remobilised contaminants are moving rapidly downstream, to accumulate in the sedimentation zones of the lower reaches. The implications for this net accumulation is presently offset through the mixing of contaminated and “clean” sediments. As a consequence, there has been a fall in contaminant concentrations in freshly mobilised sediments since the spill and clean-up, which has maintained contaminant levels below regional threshold values in the lower reaches that border the Doñana Natural Park. An exception are As concentrations, which have remained almost constant over time. Given that As also displays anomalously high dissolved concentrations downstream during low flows, the sediment-water interaction of As under predominantly alkaline conditions deserves further consideration. We would also recommend additional research, including an inventory of agricultural inputs (e.g. lead arsenate pesticides) used in the catchment, to determine whether As patterns are linked to an alternative source of As pollution in the Guadiamar.

Declining concentrations in surface sediments throughout the Guadiamar show that the river is recovering. Results from the January 1999 data indicate that if minimum
flows can be maintained dissolved contaminant concentrations under low flows should remain within guideline limits. Although CaCO$_3$ has been widely employed in the upper reaches of the Guadiamar, in order to raise pH levels and help fix contaminants to sediments (CMA 2000b), unnecessary floor disturbance has impeded re-vegetation and prolonged geomorphic instability and accelerated erosion. As the upper reaches are the main source of contaminated material in the Guadiamar, we recommend that they are left to recover. In the downstream reaches, declining metal concentrations in surface sediments during the last three years provide a cautiously optimistic outlook for the management of the Doñana nature reserve. In fact, due to the vast quantities of sediment moving through the system, excessive sedimentation could pose a more significant problem than metal pollution in these lower reaches. Conversely, if valley floor vegetation continues to re-establish in the Guadiamar catchment, decreased erosion would lead to a reduction in sediment supply from “cleaner” sources. If sediment mixing is reduced as a result, the present improvements in sediment quality could be reversed.

Acknowledgments

The authors would like to thank Pavel Adamek and Hugh Blair of Boliden Apirsa s.l. for logistical support and helpful discussions. We would also like to thank the Oficina Técnica for support at reach 6, W Perkins for ICP-MS analysis, V Remenda and S Walker for water sampling and field assistance and the IGES, UW Aberystwyth Graphics Unit for the preparations of diagrams. Funding for this work was provided by NERC (Grant no. GR9/04094, KH-E, MGM), Boliden Apirsa s.l. (MGM, KH-E and HEJ), the Association of Universities and Colleges of Canada (HEJ), and a NERC postgraduate studentship (JNT).

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