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The impact of tailings dam spills and clean-up operations on sediment and water quality in river systems: the Ríos Agrio–Guadiamar, Aznalcóllar, Spain

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Abstract

The Aznalcóllar tailings dam at Boliden Apirsa's Aznalcóllar/Los Frailes Ag–Cu–Pb–Zn mine 45 km west of Seville, Spain, was breached on 25 April 1998, flooding approximately 4600 hectares of land along the Ríos Agrio and Guadiamar with approximately 5.5 million m^3 of acidic water and 1.3×10^6 m^3 of heavy metal-bearing tailings. Most of the deposited tailings and approximately 4.7×10^6 m^3 of contaminated soils were removed to the Aznalcóllar open pit during clean-up work undertaken immediately after the spill until January 1999. Detailed geomorphological and geochemical surveys of the post-clean-up channel, floodplain and valley floor, and sediment and water sampling, were carried out in January and May 1999 at 6 reaches representative of the types of river channel and floodplain environments in the Río Guadiamar catchment affected by the spill. The collected data show that the clean-up operations removed enough spill-deposited sediment to achieve pre-spill metal (Ag, As, Cd, Cu, Pb, Sb, Tl, Zn) concentrations in surface sediment. These concentrations, however, are still elevated above pre-mining concentrations, and emphasise that mining continues to contaminate the Agrio-Guadiamar river system. Dilution by relatively uncontaminated sediment appears to reduce metal concentrations downstream but increases in metal and As concentrations occur downstream, presumably as a result of factors such as sewage and agriculture. River water samples collected in May 1999 have significantly greater dissolved concentrations of metals and As than those from January 1999, probably due to greater sulphide oxidation from residual tailings with concomitant release of metals in the warmer early summer months. These concentrations are reduced downstream, probably by a combination of dilution and removal of metals by mineral precipitation. Single chemical extractions (de-ionised water, $CaCl_2$ 0.01 mol l^{-1}, CH_3COONH_4 1 M, CH_3COONa 1 M and ammonium oxalate 0.2 M) on alluvial samples from reaches 1 and 6, the tailings, pre-spill alluvium and marl have shown that the order of sediment-borne contaminant mobility is generally $Zn > Cd > Cu > Pb > As$. Pb and As are relatively immobile except possibly under reducing conditions. Much of the highly contaminated sediment remaining in the floodplain and channel still contains a large proportion of tailings-related sulphide minerals which are potentially reactive and may continue to release contaminants to the Agrio–Guadiamar river system. Our work emphasises the need for pre-mining geomorphological and geochemical data, and an assessment of potential contributions of contaminants to river systems from other, non-mining sources.

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1. Introduction

Failures of mine tailings dams are often catastrophic events which severely impact water and sediment quality, as well as aquatic life in river systems (e.g. Macklin et al., 1996; Draves and Fox, 1998; Anonymous, 2000). One of the largest, accidental discharges of contaminant metals from a mine tailings dam failure to have occurred in recent years was the breaching of the Aznalcóllar tailings dam at Boliden Apirsa's Aznalcóllar/Los Frailes Ag–Cu–Pb–Zn mine 45 km west of Seville, Spain. On 25 April, 1998, approximately 4600 hectares of land along the Agrio and Guadiamar rivers were flooded with an estimated 5.5×10^6 m^3 of acidic water and 1.3 million m^3 of heavy metal-bearing tailings (Sassoon, 1998). A zone, approximately 400 m wide on each side of these rivers and extending 40 km downstream of the dam, was covered with an approximately 1.7 m thick layer of tailings (Grimalt et al., 1999). Acidic water from the spill continued 20 km further downstream where it was prevented from contaminating Doñana Natural and National Parks, the largest reserves of bird species in Europe (Grimalt et al., 1999), by several temporary walls in the Entremuros area. The main phase of clean-up work by Boliden Apirsa S.L., the Confederacion Hidrografica de Guadalquivir and the Consejería de Medio Ambiente was initiated immediately after the spill and continued until January 1999. Clean-up operations included mechanical excavation and hand cleaning (using shovel, trowel and brush) of most of the deposited tailings and approximately 4.7×10^6 m^3 of contaminated soils, and their storage in the Aznalcóllar open pit.

A considerable number of studies on soil and water quality (van Geen and Chase, 1998; Alastuey et al., 1999; Cabrera et al., 1999; Díaz-Barrientos et al., 1999; López-Pamo et al., 1999; Símon et al., 1999; Vidal et al., 1999) and one on the geomorphology of the Ríos Agrio and Guadiamar (Gallart et al., 1999) were undertaken immediately after the spill and in the early stages of the clean-up. Although these provided invaluable data on the conditions of the catchment at this time, they did not utilise an integrated geomorphological-geochemical approach to assess the long-term fate of contaminants from the spill. Such an approach has proved essential for assessing contaminant storage and remobilisation in other rivers affected by tailings dam spills and metal mining pollution (e.g., Lewin and Macklin, 1987; James, 1989, 1991; Macklin and Lewin, 1989; Knighton, 1991; Macklin et al., 1996; Miller et al., 1998; Hudson-Edwards et al., 2001). The scientific basis of this approach is that sediment-associated metals follow the same transport pathways as other particulate-bound elements, and their deposition and storage patterns can be related in a predictable way to floodplain geomorphology and channel sedimentation styles (Graf, 1994; Macklin, 1996; Miller, 1997). When data on these are combined with geochemical information on the forms of contaminants (e.g. Pirrie et al., 1997; Hudson-Edwards et al., 1998), their long-term impact can be modelled and appropriate remediation strategies implemented.

An interdisciplinary geomorphological-geochemical research programme began in December 1998 (Macklin et al., 1999) to monitor and model the recovery of the river, especially in terms of the geochemical and physical (erosion, sediment reworking, deposition) controls on the distribution of potentially hazardous elements between sediment and waters. One of the major objectives of this project is to define the post-clean-up geomorphology, geochemistry and metal speciation of Río Agrio and Guadiamar channel and floodplain sediment in order to develop predictive models of future sediment-water interactions under various climatic and land-use regimes. This paper presents the results of data for samples collected in January and May 1999 which are used to (1) evaluate the impact of the April 1998 Aznalcóllar tailings dam failure and subsequent clean-up on sediment and water quality in the Agrio–Guadiamar catchment, and (2) assess the long-term behaviour and fate of contaminants in sediments and water of the Agrio-Guadiamar catchment. This information will be of use in evaluating the response of other river systems, in terms of sediment and water quality, and river dynamics, to the effects of tailings dam spills and subsequent clean-up operations.

2. Physiography, geology and mining history of the Guadiamar catchment

The Guadiamar catchment (37°30′N 6°20′W) is located in southern Spain to the west of Sevilla (Fig. 1). It has a catchment area of 1092 km^2 and average annual rainfall of ca. 500 mm. The Río Guadiamar rises 24 km to the north of Aznalcóllar and flows 40 km downstream to its confluence with the Río Agrio (Fig. 1). The Río Agrio originally flowed through the site of an open pit at Aznalcóllar, but was diverted through the construction of a 20 million m^3 upstream dam and a 2 km tunnel (Sassoon, 1998). Downstream of the Agrio/Guadiamar confluence the river flows for another 38 km until it joins the Río Guadalquivir. The upper limit of tidal flows in the Guadiamar is located at Aznalcazar. The upper catchment is underlain by rocks of the Lower Carboniferous Volcano-Sedimentary Complex of the Iberian Pyrite Belt, and south of Aznalcóllar by Miocene silts and calcarenites overlain by Eocene marl beds (Almodóvar et al., 1998). The Los Frailes mine is located at Aznalcóllar at the eastern end of the Iberian Pyrite Belt, 45 km northwest of Sevilla. The region has a long history of mining, dating to the pre-Roman period, with the most recent phase of large-scale mining commencing in 1979 by Andaluza de Piritas SA (APIRSA), and

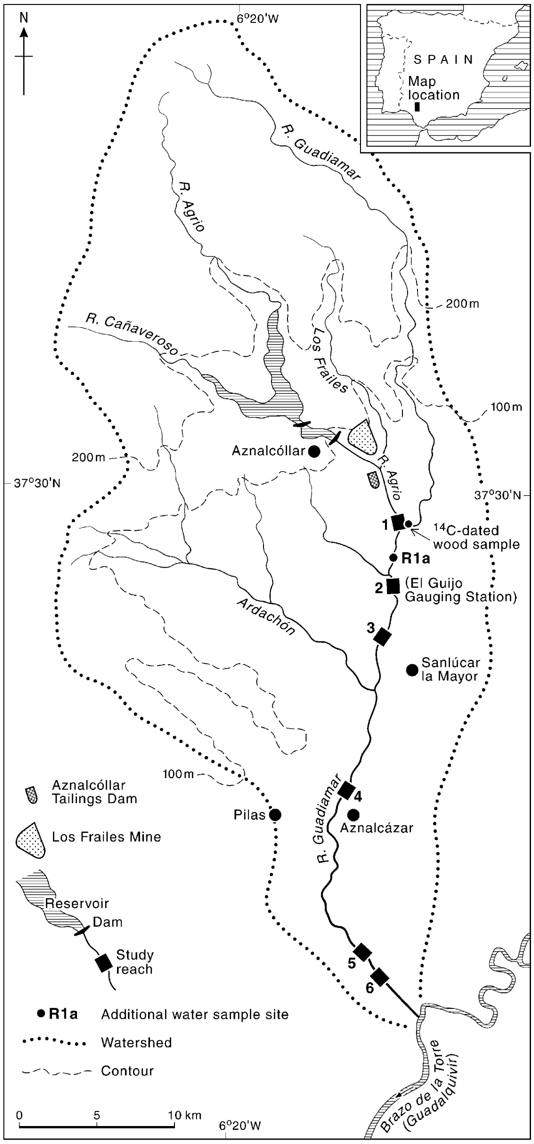

Fig. 1. Location of the Ríos Agrio and Guadiamar, and the village of Aznalcóllar, showing positions of the six study reaches and of the Aznalcóllar tailings dam.

eventually Boliden, who acquired APIRSA in 1987. There are several ore deposits at Aznalcóllar with total massive sulphide reserves of up to 130 Mt and average grades 3.6% Zn, 2% Pb, 0.4% Cu and 65 ppm Ag. The Los Frailes ore deposit is the most recently discovered, consisting of ca. 70 Mt of massive sulphides with average ore grades of 0.35% Cu, 2.21% Pb, 3.87% Zn and 63 ppm Ag (Almodóvar et al., 1998). The tailings dam that was breached in April 1998 was constructed in 1978, and was used for waste materials from orebodies at Aznalcóllar from 1979 to 1997 and from the Los Frailes mine after 1997 (Sassoon, 1998).

3. Methodology

3.1. Geomorphology

Detailed geomorphological surveys of the post-clean-up channel, floodplain and valley floor were carried out in January and May 1999 at six reaches representative of the types of river channel and floodplain environments in the Río Guadiamar catchment affected by the spill (Fig. 1; Table 1). At each reach, a total station survey was used to (1) establish a local coordinate grid system, (2) survey a traverse of fixed control stations, (3) define detail observations of channel and valley floor topography, and (4) document monumented valley floor cross profiles. Sediment and water samples (see below) were spatially referenced and integrated within a GIS (ARC/INFO™). This spatial referencing will allow detailed repeat surveys to be undertaken.

3.2. Water sampling and analysis

Water sampling was carried out at the same time as the geomorphological surveying in January and May 1999. Surface water samples were taken from the Río Guadiamar and the Río Agrio at reaches 1 to 5 (Fig. 1), as well as field blanks and duplicates. An extra sampling site, which has been named 'R1a' (Fig. 1; Table 1) was added midway between reaches 1 and 2. Water samples were filtered in the field through 0.45 μm filters and those destined for cation analysis were preserved with HNO_3 to pH less than 2. Field blanks were opened and acidified in the same manner as samples. Cations were analysed by ICP-MS in the Department of Geological Sciences at Queen's University, Ontario. Field and lab duplicates indicate a relatively high degree of reproducibility (within 10%). Measured values of all elements reported for the waters in our study are within the margin of error for certified values for SLRS-4, a reference water from the National Research Council of Canada, with the exception of Cd, which is consistently low due to a mass interference. Thus, reported Cd concentrations may be considered a minimum value. Anions were analysed by ion chromatography. Field and lab duplicates are very close in concentration and the difference between measured and expected values for the laboratory standard solutions is less than 10%.

3.3. Sediment sampling and analysis

In January and May 1999, sediment samples were taken from the channel bed and banks, the floodplain and higher river terraces to establish levels of metals in material that is likely to form sources of river sediment. All samples taken were spatially referenced and tied into the geomorphological surveys. Each sample was collected over a 12 m^2 area by combining 10 random

Table 1
Description and location of study reaches (after Macklin et al., 1999, p. 273)

Reach	Location (latitude, longitude)	Distance downstream of mine (km) (from mid-point of reach)	Nos. of survey points	Length (m)	Channel type and environment
1	Río Agrio-Río Guadimar confluence (37°28′N, 6°13′W)	2.6	2731	1300	Active wandering gravel bed
1a	Extra sampling site for river water (37°27′N, 6°13′W)	5.0	NA	NA	NA
2	El Guijo gauging station (37°27′N, 6°13′W)	7.0	536	350	Active low sinuosity gravel bed
3	Upstream of Sanlucar road bridge (37°24′N, 6°14′W)	11.3	393	340	Active low sinuosity gravel/sand bed
4	Upstream of Aznacázar railway bridge (37°18.5′N, 6°15′W)	23.1	535	500	Stable low sinuosity sand/gravel bed
5	La Tiesa (37°13.5′N, 6°14′W)	38.4	455	930	Stable straight silt/sand bed (tidal)
6	Puente San Simone (37°11.5′N, 6°13′W)	43.5	294	640	Stable straight silt/sand bed (tidal)

NA: not applicable.

sub-samples to ca. 200–300 g from the upper 5 cm of the sediment surface. Several samples of deposited tailings and 'pre-spill' alluvium were also taken at all of the reaches. Radiocarbon dating was carried out on a sample of wood preserved within channel bank alluvium from the Río Guadiamar in reach 1 (Fig. 1). The analysis was conducted by Beta Analytical, Inc. (Miami, Florida; Beta-130201), and results are reported as both cal. AD and cal. BP.

The 1998/1999 winter was relatively dry with only enough rainfall to allow a small amount of vegetation to re-establish itself on floodplain and terrace surfaces. A small ca. 10 m^3 s^{-1} flood occurred in March 1999 (H. Blair, pers. comm., 2000), and caused up to 4 m of bank erosion and channel widening, and deposition of sand and gravel splays in the Río Guadiamar in reach 1 (Macklin et al., 1999) and fresh overbank sediment in all of the other reaches. Samples of this material were taken from each of the reaches during the May 1999 field campaign.

In the laboratory, the sediment samples were homogenised, and a portion was air-dried, disaggregated and sieved to pass through a 2 mm aperture. A sub-sample of the air-dried material was then ground in an agate tema for four minutes. The samples were digested in $HF–HClO_4–HNO_3$ and analysed by ICP-MS (VG elemental plasma Quad II+) for As, Cd, Cu, Pb, Ni, Sb, Tl and Zn at the Institute of Geography and Earth Sciences, 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 the reference sediment standards GBW07311 and GBW 07312 (Office of Reference Materials, Laboratory of the Government Chemist, UK). Both precision and accuracy were within 10%. Selected samples were analysed by X-ray diffraction (Philips PW1710 instrument fitted with a graphite monochromator, with Cu (K_α) radiation at 40 kV/30 Ma operating conditions) for their mineralogical composition.

Selected alluvial samples from the upstream and downstream reaches (1 and 6), as well as three samples each of tailings, bedrock marl and pre-spill alluvium, were selected for more detailed investigations involving grain-size analysis, total S and C analysis, sediment pH, and select chemical extractions. Grain-size analysis was carried out using a Beckman-Coulter LS 230 fluid module particle size analyser. The <2 mm fraction was mixed to a paste with 5% calgon, and was analysed using a pump speed of 51% for 90 s. Total S and C were determined by dry combustion using a LECO instrument, and sediment pH was measured potentiometrically in a 1:2.5 sediment–deionised water (DIW) suspension. Five single chemical extractions were also applied to the homogenised, untreated sediment samples, as follows:

- Extractions with DIW. One g of sample is shaken at 20 rev/min in 10 ml of DIW for 1 h.
- Extractions with $CaCl_2$. 0.01 mol l^{-1}, 1 g of sample is shaken at 20 rev/min in 10 ml of $CaCl_2$ 0.01 mol l^{-1} for 2 h (Novozamsky et al., 1993).
- Extractions with ammonium acetate. 1 g of sample is shaken at 20 rev/min in 10 ml of 1 M ammonium acetate (CH_3COONH_4) for 2 h (adapted from Tessier et al., 1979).
- Extractions with sodium acetate. 1 g of sample is shaken for 5 h at 20 rev/min in 10 ml of 1 M CH_3COONa (SLR) (adjusted to pH 5 using acetic acid) (adapted from Tessier et al., 1979).
- Extractions with ammonium oxalate. 1 g sample is shaken at 20 rev/min in 20 ml 0.2 M ammonium oxalate adjusted to pH 3 with 0.2M oxalic acid for 2 h (Schwertmann, 1959, 1964).

All the extractions were performed in acid-washed, 25-ml erlenmeyer flasks. After shaking, the solutions were filtered using Whatman no. 42 filter papers, made up to volume and stored in polypropylene bottles in a cold store until analysis, which was undertaken no more than 2 months after extraction. For every 8 samples a duplicate sample and a blank were also extracted. For the first three extractions, two drops of 50% HNO_3 (Aristar) were added to prevent flocculation and sorption of metals onto the bottle walls. Analyses for Cd, Cu, Pb, and Zn were carried out by ICP-AES (Phillips instrument) at the NERC Facility at Royal Holloway College, Egham, and for As using atomic absorption spectrophotometry (Unicam Soker system) in the UCL-Birkbeck Wolfson Laboratory for Environmental Geoscience. Precisions ranged between 10 and 15 percent, except for samples exhibiting very low concentrations (<0.1 mg/kg), for which precisions ranged between 5 and 50%.

4. Results and discussion

4.1. Geomorphology

Descriptions of the geomorphology of reaches 1–6 can be found in Macklin et al. (1999). Reaches 1, 2 and 3 have been totally transformed by the mine tailings spill and cleanup operations, and neither the new channel nor the truncated floodplain are in equilibrium with the runoff or flow regime of the Guadiamar catchment. In reaches 4, 5 and 6, however, cleanup operations involved the removal of ca. 0.5 m of tailings and topsoil material with the preservation of the pre-spill river channel and floodplain morphology. These downstream reaches are likely to be sites where a considerable proportion of contaminated sediment, reworked from the laterally and vertically active upstream parts of the Guadiamar, will be deposited and enter long-term storage.

4.2. Water geochemistry

4.2.1. Comparison of results from January 1999 and May 1999

As shown in Table 2 and Fig. 2, water samples collected in May had lower pH values and higher dissolved concentrations of all elements measured (with the single exception of As in the Río Agrio at reach 1) than water samples collected at the same location in January. This is considered to be, in part, the result of dilution by water released from the reservoir upstream of the mine during the January sampling period to provide increased supply downstream after an extremely dry winter. If dilution were the only mechanism reducing metal contents in river water, however, we would still expect to see the pattern of decreased metal concentrations with increasing distance from the mine that is apparent in the samples collected in May (Fig. 2). Thus, a second factor in maintaining relatively low metal concentrations and high pH values in January may be the reduced rates of sulphide oxidation and metal leaching from residual tailings during the relatively cool winter months. In January, measured river water temperatures ranged from 10 to 18 °C, whereas in May the river was considerably warmer, with temperatures of 21 to 28 °C, and up to 30 °C in standing pools of water adjacent to residual tailings.

4.2.2. Effect of distance from mine site on water chemistry

In the May 1999 river water samples the pH rises from 4.4 in the Río Agrio at reach 1 to 7.4 in the Río Guadiamar at reach 5 (Table 2, Fig. 2). The pH of river water in the Río Guadiamar upstream of the Río Agrio confluence is the highest of those recorded, at 7.9. Only the Río Agrio pH is below that recommended in the EU directive concentrations for surface water intended for abstraction. Dissolved aqueous concentrations of Cd, Cu, Ni, Pb, Fe, Zn and SO_4 show an overall downstream decrease from the tailings dam to reach 5, 33 km downstream of the tailings dam, with concentrations of Cd at reaches 1–3 exceeding EU directive concentrations for surface water intended for abstraction. The downstream trends mirror the increase in pH, and suggest that surface water in the upper reaches of the sampling corridor is affected by acidic, metal- and SO_4-rich water associated with the presence of the mine. Further downstream the water quality is improved, possibly through dilution by tributary streams and recharge of uncontaminated groundwater to the river.

In Fig. 3 the significance of dilution is examined by plotting the concentrations of some of the dissolved constituents versus the concentration of SO_4. Mixing lines represent concentration trends expected through simple dilution of the most SO_4-rich water (R1a) and the most SO_4-poor water (the Guadiamar river sample upstream of the Agrio confluence at R1). The high pH and low metal content of the latter sample suggests that it can be considered a background sample, relatively unaffected by recent or past mining activities. In this analysis, SO_4 is used as a conservative tracer. It is possible that SO_4^- is not behaving completely conservatively, but the SO_4 concentrations are so much higher than those of Fe Zn and Cd that small changes in SO_4 would not really affect the trends depicted (cf., Berger et al., 2000). Speciation modelling of the river waters using MINTEQA2 (Allison et al., 1990) indicates that sulphate minerals are unlikely to precipitate from river waters or, if they do, they remove no more than a very small fraction of the total dissolved sulphate. Water compositions that fall on the mixing lines indicate a mechanism of simple dilution, those that fall above indicate addition of dissolved species through

Table 2

Geochemistry of Ríoo Agrio and Ríoo Guadiamar surface water, January and May 1999. R1 to R5 refers to reach 1 to reach 5. Not all reaches were sampled in Jan 99. Dissolved oxygen was not measured in January; NA—not analysed

Sample	pH		Temperature (°C)		Dissolved oxygen		Na (mg/l)		Mg (mg/l)		Ca (mg/l)		K (mg/l)		Fe (mg/l)		Mn (mg/l)	
	Jan	May	Jan	May	Jan	May	Jan	May	Jan	May	Jan	May	Jan	May	Jan	May	Jan	May
Guadiamar R1	NA	7.9	NA	28.3	NA	11.2	NA	32.0	NA	16.1	NA	66.4	NA	2.51	NA	0.0991	NA	0.0978
Agrio R1	NA	4.4	18.0	26.9	NA	9.28	18.4	31.5	12.2	49.2	67.9	207	2.07	4.03	0.1244	4.01	2.385	7.193
Guadiamar R1a	7.6	5.1	17.5	24.6	NA	NA	19.2	38.4	13.5	93.1	76.1	271	2.50	4.03	0.1300	1.66	1.792	5.862
Guadiamar R2	7.0	6.5	13.8	27.0	NA	8.94	23.4	38.7	17.6	86.4	103	233	2.61	4.24	0.1348	0.2530	2.114	5.958
Guadiamar R3	6.8 7.6	6.1	11.1 10.1	21.4	NA	7.14	20.5 36.1	38.7	14.3 15.9	79.2	72.9 92.3	258	2.26 2.57	4.31	0.1742 .1526	0.1169	2.069 1.851	5.688
Guadiamar R4	7.3	7.1	10.7	21.2	NA	8.85	29.1	63.7	19.1	48.6	101	256	3.81	8.23	0.1100	0.1128	1.809	3.351
Guadiamar R5	NA	7.4	NA	22.6	NA	4.70	NA	119	NA	43.3	NA	191	NA	12.38	NA	0.0914	NA	1.107

Sample	Zn (mg/l)		As (μg/l)		Ba (μg/l)		Cd (μg/l)		Cu (μg/l)		Ni (μg/l)		Pb (μg/l)		Sr (μg/l)	
	Jan	May	Jan	May	Jan	May	Jan	May	Jan	May	Jan	May	Jan	May	Jan	May
Guadiamar R1	NA	0.001	NA	6.95	NA	61.1	NA	0.40	NA	5.27	NA	1.44	NA	0.940	NA	354
Agrio R1	3.02	23.6	6.85	1.04	19.1	31.7	8.33	39.6	31.8	737	13.0	90.1	2.33	20.3	168	500
Guadiamar R1a	3.39	19.0	1.46	1.77	22.5	43.7	11.0	30.2	44.6	459	15.3	58.2	0.92	20.98	253	559
Guadiamar R2	2.68	14.9	1.77	11.18	35.8	45.1	10.4	28.3	22.8	248	13.8	54.5	1.65	7.18	303	560
Guadiamar R3	3.20 3.09	14.2	1.40 1.58	3.52	24.8 22.9	22.9	10.3 10.1	29.6	19.5 23.4	187	15.1 14.4	53.5	1.29 0.94	3.81	284 234	604
Guadiamar R4	2.54	2.82	5.29	7.04	140.5	54.0	10.3	0.71	4.22	3.34	11.8	24.1	0.89	2.38	344	755
Guadiamar R5	NA	0.001	NA	50.7	NA	51.1	NA	0.22	NA	2.36	NA	4.39	NA	3.60	NA	712

Sample	Cl (mg/l)		F (mg/l)		NO_3 (mg/l)		SO_4 (mg/l)	
	Jan	May	Jan	May	Jan	May	Jan	May
Guadiamar R1	NA	39	NA	0.30	NA	3.8	NA	112
Agrio R1	18	33	0.55	<1.0	0.64	0.55	186	833
Guadiamar R1a	23	41	0.59	<1.0	1.2	<0.5	209	1200
Guadiamar R2	29	40	0.86	2.1	1.2	1.2	299	1020
Guadiamar R3	24 28	45	0.80 0.62	<1.0	1.3 1.3	<0.5	257 212	1080
Guadiamar R4	36	76	0.84	2.0	1.8	1.5	271	815
Guadiamar R5	NA	179	NA	<1.0	NA	<0.5	NA	457

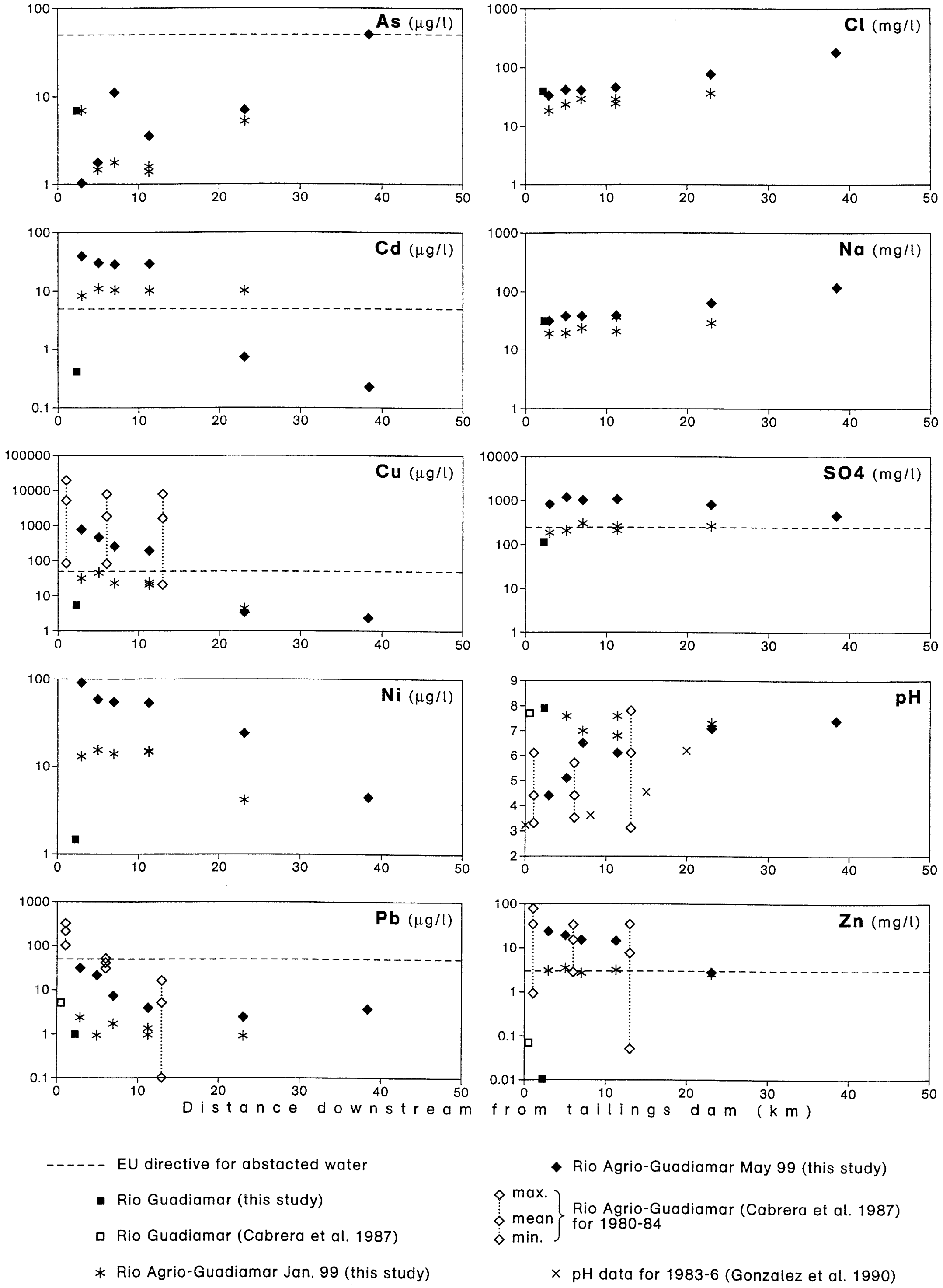

Fig. 2. Dissolved concentrations of selected elements in water samples collected at six sampling locations along the Ríos Agrio and Guadiamar. Dashed lines represent EU/WHO guideline values for drinking water. Cu, Pb, Zn and pH data for 1980–84 is taken from Cabrera et al. (1987), and pH data for 1983–97 from González et al. (1990).

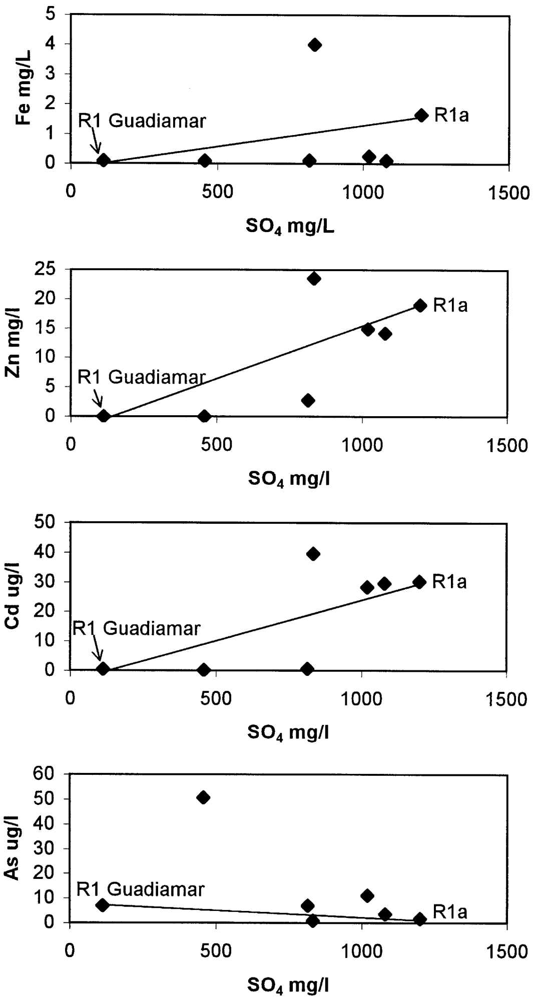

Fig. 3. Dissolved SO_4 (mg/l) versus Fe (mg/l), Zn (mg/l), Cd (μg/l) and As (μg/l) for water samples collected from the Ríos Agrio and Guadiamar in May 1999. Mixing lines join the most SO_4-rich water, sampled at site R1a, to the least SO_4-rich sample, taken from the Río Guadiamar upstream of the confluence with the Río Agrio at R1. See text for discussion.

dissolution or desorption and those that fall below indicate the removal of species through precipitation or adsorption processes (cf. Berger et al., 2000). Fig. 3 shows that most of the downstream trends can be explained by a combination of dilution and removal of metals by mineral precipitation. Iron concentrations fall below the mixing line for all samples downstream of site R1a in the Guadiamar, consistent with positive saturation indices for ferrihydrite and goethite in these waters except for the samples from the Río Agrio. If an iron oxyhydroxide is precipitating directly, it may scavenge metals such as Cu, Zn, Cd, Pb and Ni, resulting in the concentrations of those elements falling below the mixing line. Cadmium and Ni behave in a manner similar to Zn (Fig. 3), falling near the mixing line at reaches 2 and 3, but apparently removed by mineral precipitation/adsorption at reaches 4 and 5. Copper and Pb follow a similar pattern to Fe, indicating that removal of these elements by precipitation/adsorption is significant at reaches 2, 3, 4 and 5. As does not show evidence of simple dilution (Fig. 3).

Water from the Río Agrio sampled in May 1999 is different from the other samples in that it has relatively low pH, high Fe, Cd, Zn, Cu, Ni and Pb but intermediate concentrations of SO_4. Although the measured pH is distinctly lower than those measured in the Río Guadiamar, it is within the lower end of the range of values determined at this location by mine staff in the years before and since the tailings accident (H. Blair, pers. comm., 2000). The origin of this acidic, metal-rich water is probably related to mining activities, but the exact nature of that relation is unclear.

Arsenic concentrations exhibit the most irregular pattern of any element analysed. The May 1999 As concentrations rise from reach 3 to 5, with a steep rise from reach 4 to 5 (where As exceeds the EU surface water abstraction limit). Although the tailings are known to be high in As (Table 3), and this is released to aqueous solution through oxidation of the sulphides (Macklin et al., 1999), there is no simple correlation between the As concentration in water samples and other constituents derived from tailings such as Zn, Cu, Cd or SO_4. This is also consistent with observations made by mine staff monitoring water quality from the mine to the estuary (H. Blair, pers. comm., 2000). The irregular As distribution suggests that either (1) there is another source of As in the Agrio–Guadiamar system, such as lead arsenate pesticides, known to have been used for insect control in deciduous fruit trees in the middle part of the Guadiamar catchment in the mid-20th century, or (2) that the mobility of As, which behaves as an anion, is controlled by factors different to those that control metal cation mobility.

Water samples taken in the lowest reaches have relatively high concentrations of dissolved Na, Cl and Sr compared to those upstream, probably as a result of mixing with seawater enriched in these elements.

4.3. Comparison with other studies

The May 1999 Agrio–Guadiamar pH ranges are no lower than average pH data from 1980 to 1984 (Cabrera et al., 1987) and 1983–1986 (Gonzalez et al., 1990). The 1983–1986 pH values for the Agrio–Guadiamar are, in fact, an order of magnitude lower than the May 1999 pH values, suggesting that the clean-up resulted in an improvement in water acidity compared with the 1980s. The May 1999 dissolved concentrations of Cu and Pb are considerably lower than, and Zn similar to, average concentrations reported by Cabrera et al. (1987) for

Table 3
Mean values and ranges (in mg/kg) of sediment-borne heavy metal and As concentrations for sediment samples from the six Guadiamar catchment reaches, pre-spill alluvium, Eocene marl, tailings, and other mining-affected river basins

Sample/ Area	As	Cd	Cu	Ni	Pb	Sb	Tl	Zn
Río Guadiamar channel and floodplain alluvium (January and May 1999)								
Reach 1 ($n=37$)	320 (20–1200)	4.7 (0.5–12)	260 (17–490)	17 (1.2–69)	990 (50–2700)	35 (1.6–150)	7.4 (0.8–15)	1200 (140–4600)
Reach 2 ($n=10$)	320 (40–860)	5.5 (0.9–11)	190 (50–340)	24 (14–34)	680 (98–1500)	22 (<0.1–55)	5.8 (1.1–12)	1600 (330–3200)
Reach 3 ($n=13$)	220 (36–1000)	4.1 (0.6–9.3)	310 (110–730)	17 (1.9–31)	610 (110–2200)	20 (3.8–90)	4.8 (1.0–16)	1200 (270–3200)
Reach 4 ($n=13$)	280 (46–680)	2.7 (0.1–5.6)	190 (58–370)	18 (5.7–32)	780 (71–1600)	25 (2.2–62)	6.2 (1.4–13)	900 (270–1700)
Reach 5 ($n=11$)	93 (30–180)	2.5 (<0.1–6.9)	150 (28–300)	19 (3.7–70)	300 (66–750)	7.8 (<0.1–21)	2.2 (0.5–5.8)	670 (190–1800)
Reach 6 ($n=9$)	41 (27–37)	4.6 (1.0–6.0)	88 (45–110)	97 (35–530)	120 (67–250)	3.0 (<0.1–10)	2.1 (1.1–2.5)	1100 (680–1400)
Pre-spill alluvium, Eocene marl and tailings								
Pre-spill alluvium ($n=17$)	39 (13–110)	0.1 (0.1–2.6)	78 (9.6–280)	16 (1.0–29)	140 (18–540)	3.7 (0.7–12)	1.4 (0.2–5.0)	220 (70–900)
Pre-cal. AD1025–1255 (cal. BP 925–695) alluvium ($n=1$)	14	0.2	9.6	18	18	0.59	0.7	112
Eocene marl ($n=3$)	20 (14–24)	0.3 (0.3)	17 (15–18)	21 (14–32)	22 (10–30)	0.8 (0.6–1.0)	0.7 (0.4–1.0)	100 (94–110)
Tailings ($n=11$)	2500 (1800–3700)	27 (12–76)	1600 (950–3000)	20 (2.0–82)	8500 (3700–12000)	270 (58–350)	56 (19–76)	7400 (3700–23000)
Fresh overbank sediment splays deposited from floods between January and May 1999								
Reach 1	1200	19	410	41	2100	71	13	5100
Reach 2	1300	16	480	42	2800	89	15	4800
Reach 3	460	11	300	30	1000	33	8.2	3200
Reach 4	60	1.3	54	15	130	<0.1	2.8	750
Reach 5	41	5.4	110	27	180	1.6	1.8	1500
Reach 6	95	4.9	55	29	190	7.2	2.1	960
Alluvium from other mining-affected catchments elsewhere in the world								
Río Tinto, Spain ($n=14$)[a]	370 (110–750)	n.r.	300 (75–1500)	n.r.	2800 (490–3100)	n.r.	n.r.	200 (<20–1200)
Upper Río Pilcomayo, Bolivia ($n=7$)[b]	2500 (210–7200)	62 (6.9–190)	490 (88–1400)	n.r.	960 (230–1700)	17 (<0.5–91)	25 (2.6–64)	8200 (1800–10000)
Lower Río Pilcomayo, Bolivia ($n=2$)[b]	16 (15–18)	<0.5 (<0.5–6)	14 (11–17)	n.r.	21 (20–22)	n.r.	0.5	130 (9–170)

Values in brackets are ranges (minimum to maximum values); *n*—number of samples analysed; n.r.—not reported.

[a] Hudson-Edwards et al. (1999).

[b] Hudson-Edwards et al. (2001).

samples collected in 1980–1984, again suggesting that water quality in the Agrio-Guadiamar has improved considerably since that time.

As described above, the pH values measured in January 1999 are relatively high, and metal and sulphate contents relatively low. The difference between the two sample sets reflect the multiple sources of water in the Agrio–Guadiamar including surface runoff, groundwater discharge to the river, and reservoir releases. Long-term monitoring is required in order to truly evaluate water quality.

4.4. Total sediment-borne metal and As concentrations

Early post-spill research identified a number of elements which were both deleterious to soil, sediment and water quality, and which had been considerably elevated in these media after the spill (Cabrera et al., 1999; Simón et al., 1999; Vidal et al., 1999). Discussions in this paper focus on 7 of these (As, Cd, Cu, Pb, Sb, Tl and Zn), as well as one 'control' element (Ni) whose reported concentrations in 'uncontaminated' soils and sediments were similar to those in the tailings. A summary of the results for total sediment-associated concentrations of these elements for samples from the six reaches sampled in January and May 1999 is presented in Table 3. Also included are average concentrations of these elements in tailings deposited during the spill, Eocene marl bedrock which underlies the Guadiamar catchment, pre-spill alluvium, and fresh sediment splays and overbank sediment deposited during floods between January and May 1999. These are compared to data for other catchments elsewhere in the world affected by mining activity.

4.4.1. Tailings

The tailings samples exhibit similar metal and As concentrations to those described by van Geen and Chase (1998), López-Pamo et al. (1999), Símón et al. (1999) and Vidal et al. (1999). Pb and Zn are the most abundant metals in the tailings, followed by As, Cu, Sb, Tl and Cd (Table 3; Fig. 4). Tailings-borne Zn and Cd show roughly similar average downstream trends (Fig. 4), as do Pb, Sb and Tl. Arsenic, Cu and Ni each show distinct patterns. These trends are probably best explained by the mineralogy of the deposited tailings. Mineralogical analysis for this paper and that reported by other authors (e.g. López-Pamo et al., 1999) has shown that the sulphide component of the tailings is mainly composed of pyrite, with minor sphalerite (hosting Zn and Cd), galena (hosting Pb and possibly Tl), arsenopyrite (hosting As) and buornonite [$PbCuSbS_3$] (hosting Pb, Cu and Sb). Alternatively, the downstream metal and As decreases in the tailings may have been caused by dilution by Guadiamar sediments and soils as they moved downstream. The wide spread variation in tailings concentrations at reach 3 (Fig. 4) suggests that even on a reach scale, sorting, dilution or reaction of the tailings may have also occurred.

4.4.2. Comparisons of January and May 1999 to pre-spill alluvial concentrations

Within the Guadiamar channel and floodplain alluvium collected in January and May 1999, the principal contaminant concentrations decrease in the order: Zn, Pb, As, Cu, Sb, Tl and Cd (Table 3), similar to that reported by Simón et al. (1999), and to that of the tailings except for the order of Zn and Pb. Average elemental concentrations in the January and May 1999 channel and floodplain alluvium are considerably lower than those in the spilled tailings material, with the following ranges: Zn 5–11 times lower, Pb 9–71 times lower, As 8–61 times lower, Cu 6–18 times lower, Sb 8–90 times lower, Tl 8–27 times lower, and Cd 5–11 times lower. This strongly suggests that the clean-up operation significantly reduced the impact of the spill on metal and As concentrations in the Guadiamar alluvial sediments. Nickel concentrations were similar to those in the tailings material, as previously reported by Cabrera et al. (1999) and Simón et al. (1999), but anomalously high Ni values were recorded at reach 6. The cause of these high reach 6 Ni values is unknown, but is unlikely to be due to the spill since the values exceed all reported Ni values for the spilled tailings material.

The long-term environmental significance of the January and May 1999 channel and floodplain concentrations of contaminant elements can be assessed when they are compared to pre-spill concentrations in the Guadiamar system. Because only limited information about pre-spill metal and As levels was available in the literature (González et al., 1990; Ramos et al., 1994; Martín et al., 2000), several samples of 'pre-spill' alluvium (alluvium which was clearly older than, and stratigraphically 0.5 to several m below, the post-clean-up, surface alluvium, and was undisturbed by the incident or the clean-up operations) were analysed for this study (Table 3). One of these samples lay stratigraphically below a sample of wood radiocarbon dated to 1025–1255 cal. AD (925–695 cal. BP; Beta-130201). The variation in pre-spill concentrations is considerable, with the upper ranges being identical to some of the average January and May 1999 channel and floodplain alluvial concentrations at the downstream reaches (Table 3). Work is in progress (Turner, in prep.) to determine if a chemo-stratigraphic sequence can be defined for the pre-spill alluvium, and whether metal peaks at depth in the alluvium are primary or are due to secondary metal remobilisation.

Fig. 5 summarises the ranges and averages of metal and As concentrations for these pre-spill samples, as well as those found in the literature, from 1025–1255 cal. AD to May 1999. Mann–Whitney *U* statistical tests

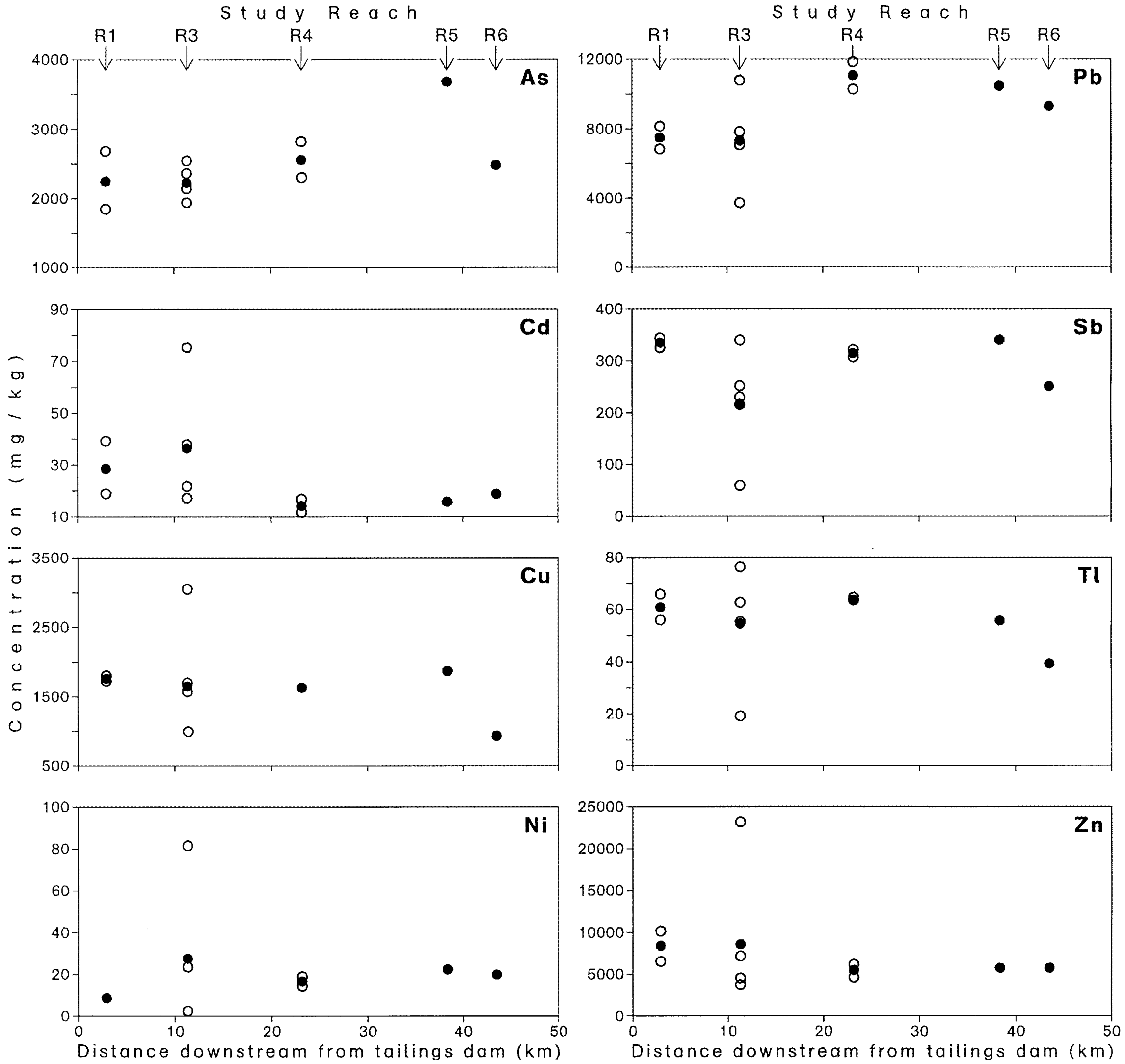

Fig. 4. Metal and As compositional variation in deposited tailings with distance down the Agrio–Guadiamar river system from the Aznalcóllar tailings dam. Open circles represent individual samples, and filled circles average compositions for each reach. Note that at reaches 5 and 6, only single samples were taken.

(Swan and Sandilands, 1995) were also carried out to check if there were significant differences between the pre-spill, tailings, and January and May 1999 channel and floodplain alluvium. Concentrations in the pre-1025–1255 cal. AD alluvium can be assumed to be lower than those in alluvium prior to intensive mining in the 19th and 20th centuries, and are very low compared to, and significantly different than, all of the other pre-spill and the January and May 1999 channel and floodplain alluvium. The other pre-spill alluvial samples, though undated, exhibit metal and As values which are intermediate between the pre-1025–1255 cal. AD sample and the 1983–1986, 1990 and 1996 samples (Ramos et al., 1994; Martín et al., 2000). No pre-spill data exist for Ni, Sb or Tl. In terms of statistical analysis, concentrations of Cd, Cu, Pb and Zn in the undated pre-spill alluvium are significantly lower than the 1983–1986 values (González et al., 1990), and Cd, Cu and Zn values are significantly lower, and Pb significantly higher, than the 1990 values for Guadiamar alluvium (Ramos et al., 1994). This suggests that mining from 1983 up to 1990 may have considerably increased the loadings of Cd, Cu and Zn to the Guadiamar catchment, assuming that most of the pre-spill alluvium sampled for this study is older than 1983. The 1983–1986 data suggest that loadings of Pb were also increased, although a decrease in values is seen in the 1990 data. It should be noted, however, that the 1990 data show the average and range for only three samples, and may not be fully representative. The averages and ranges of As, Cd, Cu and

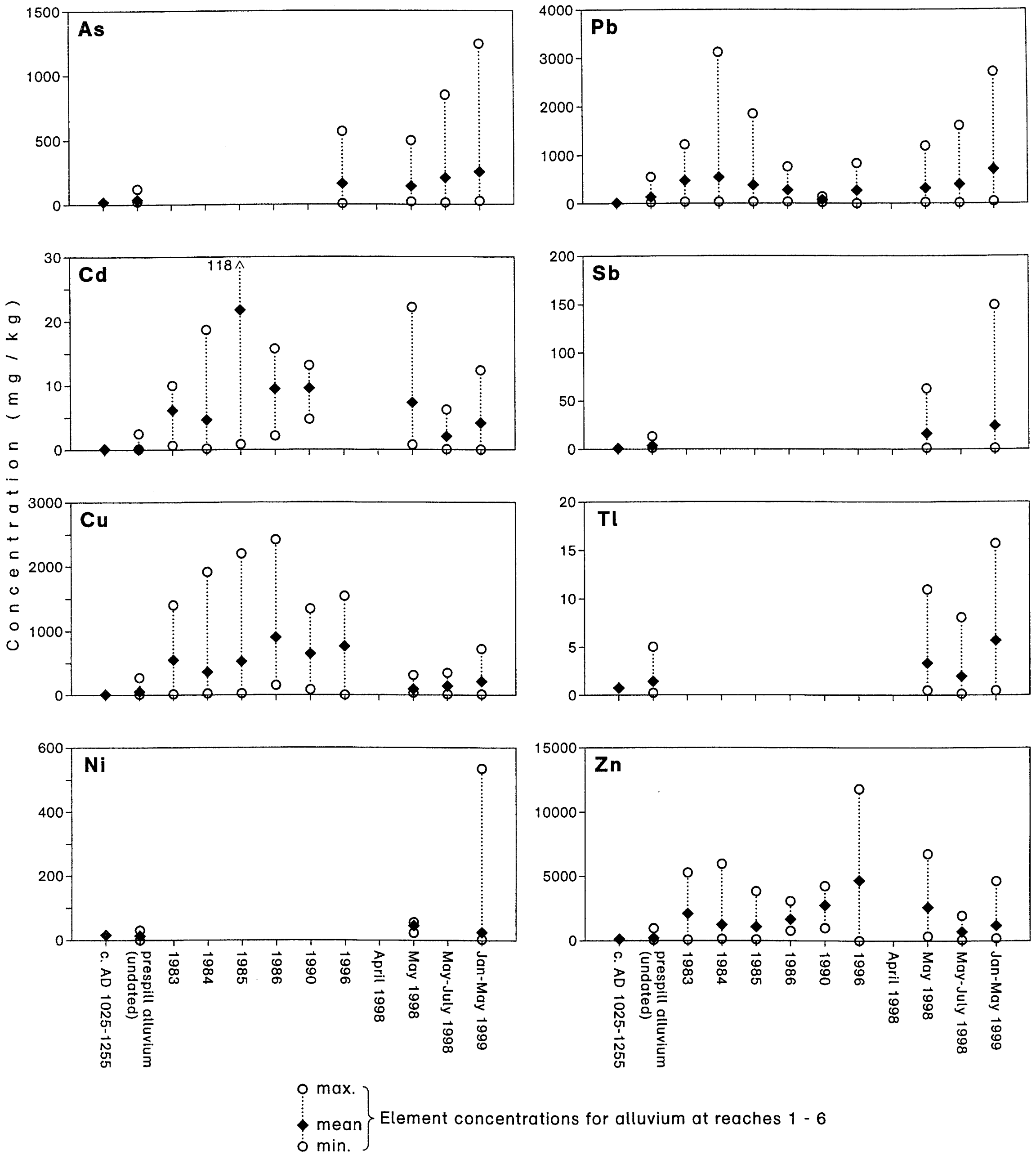

Fig. 5. Averages and ranges of metal and As concentrations for Río Guadiamar alluvium and soils sampled downstream of the Aznalcóllar tailings dam to reach 6, from ca. AD 1025–1255 (BP 925–695) (this study), undated pre-spill alluvium ($n=17$, this study), 1983–1986 ($n=6$; González et al., 1990), 1990 ($n=3$, Ramos et al., 1994), 1996 ($n=13$; Martín et al., 2000), May 1998 ($n=4$; Alastuey et al., 1999), May–July 1998 ($n=24$; Vidal et al., 1999) and January–May 1999 (this study).

Pb concentrations in 1996 Guadiamar channel sediment (Martín et al., 2000) are similar to those in the 1983–1986 and 1990 samples, but are higher for Zn. The pre-spill data all suggest that considerable contamination of the Guadiamar alluvium had already occurred in the catchment prior to the spill, and agree with other pre-spill studies (González et al., 1990; Ramos et al., 1994). Ramos et al. (1994), for example, reported that increased mining activity since the early 1980s had resulted in considerable metal enrichment of the Doñana soils, and that the pollution had increased from 1983 (as reported by González et al., 1990) to 1990, with a 'front' of metal contamination advancing steadily towards Doñana Park.

The May 1998 (Alastuey et al., 1999), May-July 1998 (Vidal et al., 1999) and January and May 1999 (this study) alluvial sediments and soils all exhibit As, Cd, Cu, Pb, Sb, Tl and Zn concentrations which are significantly lower than those in the deposited tailings. Ni concentrations in the samples collected after April 1998, however, are not significantly different than those in the tailings. Concentrations of Cd, Cu and Zn, in the January and May 1999 samples are significantly lower than those in the 1983, 1986 and 1990 pre-spill alluvium (Fig. 5), suggesting that the remedial operations have removed enough material to achieve levels prior to the increased mining phase in the early 1980s (cf., Ramos et al., 1994), or that Cd, Cu and Zn were mobilised from the sediment into soil, river or ground water. January and May 1999 alluvial Pb concentrations, however, are significantly higher than those from 1985, 1986 and 1990 (as reported by Macklin et al., 1999), but are not significantly different from those from 1983, 1996, May 1998 (Alastuey et al., 1999) or May–July 1998 (Vidal et al., 1999). As concentrations in January and May 1999 channel and floodplain alluvium are not significantly different than those in the 1996 Guadiamar channel sediment (Martín et al., 2000). The relative higher levels of post-April 1998 sample As and Pb compared with Cd, Cu and Zn may be due to additional inputs of As and Pb to the system. This is supported by the water data (Fig. 2, Table 2) which show increases of As in the lower parts of the catchment. Other contaminant sources such as olive oil effluent run-off, fertilisers, pesticides and sewage discharges (cf, Ramos et al., 1994) may also have contributed to the total metal and As load in the Guadiamar.

4.4.3. *Downstream and within-reach patterns in metal and As concentrations*

Although overall downstream decreases in average concentrations of Guadiamar channel and floodplain alluvium collected in January and May 1999 are recorded at the six study reaches (e.g., As, Cu, Pb, Sb, Tl), these are not steady declines; rather, increases in average concentrations occur at from reach 1 to 2 (Cd, Zn), 2 to 3 (Cu), 3 to 4 (As, Pb), and 5 to 6 (Ni, Zn) (Table 3). This scatter undoubtedly reflects the patchy distribution of the tailings remaining on, or reworked and incorporated into, floodplain and channel alluvium following or during the clean-up operations which finished in December 1998. The scatter may also point to (1) other, non-mining or -spill metal sources (as previously noted for Ni), or, for elements like Zn, (2) transport downstream in the dissolved (aqueous) phase (cf., van Geen and Chase, 1998). Within all of the reaches, concentrations in channel sediment are lower than those of terrace material, probably reflecting the more intensive cleanup operations within the channel areas, particularly at reach 1 (Macklin et al., 1999). These differences, however, may be due to other factors such as grain size variations. Floodplains and terraces typically have higher bulk metal concentrations than channels because they are composed of finer-grained sediments (Wolfenden and Lewin, 1977; Bradley and Cox, 1990). Sediments on isolated islands and those at some distance from the channel often exhibit high metal and As concentrations, but high concentrations are also found in near-channel sediments, again reflecting the irregular remaining tailings distribution, or grain-size variations. This near-channel sediment is likely to be easily remobilised during future flood events, but the floodplain material will only be remobilised by channel wandering and erosion (cf. Gallart et al., 1999).

4.4.4. *Comparisons with other mining-affected river catchments*

The ranges of January and May 1999 Guadiamar channel and floodplain alluvium metal and As concentrations are similar to, or lower than, those in other alluvial river systems elsewhere in the world affected by mining activity (Table 3), many of which, unlike the Guadiamar, have not undergone any remediation. Of particular interest is the nearby Río Tinto catchment, c. 30 km to the west of the Río Guadiamar, which also drains massive sulphide mines of the Iberian Pyrite Belt, and which has been contaminated by intense mining activity since the mid-19th century (van Geen et al., 1997; Hudson-Edwards et al., 1999; Leblanc et al., 2000). Fine-grained alluvium in the Tinto catchment exhibits similar average As and Cu concentrations to those in January and May 1999 channel and floodplain alluvium in the upper Guadiamar reaches, but higher average Pb and lower average Zn than most of the Guadiamar channel and floodplain alluvium (Table 3). Unlike the Guadimar, the Río Tinto is very acid (pH 1.5–2.0) for most of its length down to the Tinto estuary, and carries a considerable proportion of its metal load (particularly Cu and Zn) in the dissolved (aqueous) phase (Hudson-Edwards et al., 1999). Undoubtedly remobilisation of both Guadiamar and Tinto alluvium will continue to contribute to sediment-borne contamination of the Atlantic Ocean in south-west Spain (Leblanc et al., 2000), but the aqueous contribution from the Guadiamar may be considerably less than that of the Tinto.

The Río Pilaya, a tributary of the Río Pilcomayo in Bolivia (Table 3) was also affected by a tailings dam spill from the Porco mine in 1996 (Macklin et al., 1996). Geomorphological-geochemical investigations have shown that, while the 1996 Porco tailings spill may have had a significant short-term effect on water and sediment quality along downstream reaches of the Río Pilcomayo, the long-term effects of the Porco spill have been minimal due to cleanup operations which removed most of the tailings about 8 weeks after the spill, storage of sediment-borne metals within the channel bed and, especially, the influx of 'clean' sediment from several large tributaries (Macklin et al., 1996; Hudson-Edwards et al., 2001). Metal and As concentrations in the lower Río Pilcomayo (downstream of the Pilaya confluence) are considerably lower than those in upper Pilcomayo and the Guadiamar. This has implications for the Guadiamar in that similar dilution and minimisation of the spill impact may also occur in the downstream reaches of the catchment.

4.5. Sediment-borne metal concentrations in overbank sediment deposited during floods between January and May 1999

Sediment-borne metal and As concentrations in fresh splays and overbank sediment deposited during floods between January and May 1999 (herein described as 1999 flood-deposited sediment), are compiled in Table 3. This material represents channel and floodplain sediment *remobilised* by floods between January and May 1999, whereas the channel and floodplain alluvium sampled in January and May 1999 (Table 3) represents material that was deposited prior to January 1999 and was directly affected by the spill and subsequent clean-up operations. Sediment-borne As, Cd, Cu, Pb, Sb, Tl and Zn concentrations in the 1999 flood-deposited sediment show an overall downstream decrease from reach 1 (Table 3). Concentrations of As, Cu, Pb and Tl, however, increase in reach 2, and thereafter decline. Downstream decreases in metal concentrations in other river systems have been attributed to many factors including (1) dilution of contaminated sediment by uncontaminated sediment from tributaries, channels and erosion of channel banks, (2) hydraulic sorting of channel bed sediment on the basis of density, size or shape, (3) losses due to chemical and/or biological processes, and (4) storage of contaminated sediment in channel and floodplain deposits (Lewin and Macklin, 1987; Rang and Schouten, 1989; Macklin, 1996; Hudson-Edwards et al., 1996; Miller, 1997). The observed patterns in the Río Guadiamar 1999 flood-deposited sediment are probably due to a combination of these. Dilution by uncontaminated sediment may have occurred largely as a result of input from tributaries, because much of the channel and channel bank material from the Guadiamar was removed during the clean-up. The Barbacena tributary, for example, enters the Río Guadiamar between reaches 3 and 4 (Fig. 1) and may have significantly influenced the decline in element concentrations between these reaches.

At reach 5, concentrations of Cd, Cu, Pb and Zn in the 1999 flood-deposited sediment show an increase relative to reach 4, but decline at reach 6. The increase in between reaches 4 and 5 suggests that another contaminant source exists between these reaches. It is possible that tailings deposited between these reaches were remobilised during the January–May 1999 floods, and contributed to higher values at reach 5. At reach 4, however, the channel gradient is low and the river banks cohesive, meaning that little contaminated material could have been eroded from the floodplain, or from the bank or bed of the river. This suggests that the tailings source was further upstream, or that other contaminant metal sources may have contributed to these patterns. Reach 4 is located just upstream of the village of Aznalcazar, and sewage, a potential source of these metals, is discharged from this village into the Guadiamar. Alternatively, precipitation of metal-bearing Fe oxides from the river water downstream of the tailings dam (see above) may also account for the rise in sediment-borne metals.

At reach 2, amounts of 1999 flood-deposited metal and As are equal to, or higher, than the average and maximum January and May channel and floodplain alluvial values (Table 3). These very high values probably reflect the physical remobilisation of tailings-rich sediment upstream of these reaches. Given the relatively lower metal concentrations of the channel sediment relative to floodplain sediment at reach 1 (Macklin et al., 1999), floodplain sediment was more likely to contribute to the highly contaminated flood-deposited overbank sediment at reach 2. However, the higher reach 2 concentrations suggest that another source of tailings-contaminated sediment probably existed between reaches 1 and 2.

1999 flood-deposited sediment concentrations of all elements except Cd and Zn are close to average channel and floodplain alluvial values at reach 1 and 3, and at reaches 4, 5, and 6 the elemental concentrations are generally similar to, or lower, than the average channel and floodplain alluvial values (Table 3). Nickel shows a decrease from reaches 1 to 4, but rises steadily in reaches 5 and 6, where high average and maximum values are recorded in the floodplain and channel alluvium (Table 3). As previously mentioned, the rise in Ni may be a result of inputs of Ni-rich sediment from a presently unknown source.

4.6. Selective chemical extractions for sediment samples from reaches 1 and 6, tailings, pre-spill alluvium and marl

Although many of the January and May 1999 Guadiamar channel and floodplain sediments exhibit elevated total metal and As concentrations, these concentrations give little information about their speciation and mobility. Both single batch extractions and mineralogical analyses have been employed successfully to estimate the solubility of metal and As in soils and

Table 4
Mean values and ranges of pH, %C, %S and grain size for reach 1,6 and pre-spill alluvium, tailing and marl samples

	pH	%C	%S	Mean Grain Size (μm)	Median Grain Size (μm)
Reach 1 (n = 33)	4.17	0.78	4.94	563	468
	(2.53–6.88)	(0.05.2.32)	(0.01–13.30)	(43–1330)	(23–1340)
Reach 6 (n = 9)	7.89	3.55	0.26	24.81	6.81
	(7.72–8.29)	(3.23–4.89)	(0.03–1.29)	(12.1–83.8)	(4.95–11.21)
Pre-spill alluvium (n = 4)	6.35	0.14	19.28	130	42.99
	(5.87–6.86)	(0.08–0.21)	(5.53–33.6)	(46.4–244)	(21.2–60.4)
Tailings (n = 3)	2.74	1.16	0.97	182	123
	(2.59–2.87)	(0.21–2.08)	(0.02–2.51)	(85.6–413)	(23.2–367)
Marl (n = 2)	7.35	2.61	0.10	62	62
	(7.06–7.63)	(2.37–2.85)	(0.01–0.19)	(62)	(62)

Values in brackets are ranges (minimum to maximum values); n–number of samples analysed.

sediments (Novozamsky et al., 1993; Rauret, 1998), in terms of their uptake by plants and environmental impacts under varying scenarios (Karstensen, 1997; Vidal et al., 1999). With this view, selected samples from alluvium from reaches 1 and 6, tailings, pre-spill alluvium and marl were subject to five single leaching extractions of varying strength, and some mineralogical analysis. The leachates were analysed for five of the elements of concern (As, Cd, Cu, Pb, Zn), and these data were compared to pH, % C, % S, mean grain size (Table 4) and total metal and As concentrations (Table 3) to arrive at an understanding of the controlling factors on metal and As mobility.

The most soluble metal and As concentrations were determined using both DIW and a weak salt (0.01 M $CaCl_2$). As suggested by Vidal et al. (1999), use of these weak extractants, a low extractant/sediment ratio and a short shaking time allowed these concentrations to represent the amount of metal and As easily remobilised after rainfall. The 0.01 M $CaCl_2$ extraction also estimates metal availability to soil organisms (Pickering, 1986). Results for these and the other extractions are portrayed in Fig. 6, as both the absolute amounts of metal and As, and as desorption yield percentages. The average DIW and 0.01 M $CaCl_2$ results are, unsurprisingly, very similar (Fig. 6), except that 0.01 M $CaCl_2$ extracts higher amounts of metal and As than DIW. Both the average DIW and 0.01 M $CaCl_2$ results show that, in terms of absolute amounts leached, the decreasing order of abundance is generally Zn, Cu, Pb, Cd and As (Fig. 6). In terms of desorption yield, significant fractions of Zn, Cd and Cu were extracted, particularly in the tailings and reach 1 alluvium. The tailings released the most metal and As, followed by reach 1 alluvium, pre-spill alluvium, reach 6 alluvium and the marl. Vidal et al. (1999) also found that significant proportions of Cd and Zn (c. 40 and 20%, respectively) were extracted from post-spill hydromorphous soils from the Guadiamar.

The CH_3COONH_4 extraction is considered adequate to extract the ‘exchangeable’ metal and As, or that which could be potentially remobilised by ionic exchange (Tessier et al., 1979), but the fraction desorbed is highly dependent on the reagent concentration and soil/liquid ratio. In the Guadiamar samples, this extraction desorbs, on average, greater amounts of metal and As than either the DIW or the CH_3COONa extractions (Fig. 6), suggesting that ionic exchange may be a significant process in terms of contaminant element remobilisation. In contrast to the DIW extraction, absolute amounts of Zn are most easily desorbed in the CH_3COONH_4 extraction, followed by Pb, Cu, Cd and As. The tailings and reach 1 samples are most affected, with Cd at reach 6 and in the pre-spill alluvium showing significant yields (up to 30% of total Cd). Like the DIW and 0.01 M $CaCl_2$ extractions, samples from reach 1 and the tailings exhibiting low sediment pH (2.5–3.5) desorb the most metal and As, but unlike the DIW and 0.01 M $CaCl_2$ extractions, small amounts of As, Cd, Cu, Pb and Zn are extracted from samples with moderate pH (5–6) using CH_3COONH_4.

The Guadiamar sediments were also extracted with 1 M CH_3COONa. This can be considered to represent the fraction remobilised from carbonate minerals and exchangeable sites together (cf. Tessier et al., 1979), or that released after acidification of the soil to pH 5. The results are similar in terms of absolute concentration and desorption yield to those of the DIW, 0.01 M $CaCl_2$ and CH_3COONH_4 extractions, suggesting that acidification does not cause any further contaminant remobilisation above that due to the ambient sediment pH. These results are slightly different to those of Vidal et al. (1999), who carried out a similar extraction using 0.43 mol l^{-1} CH_3COOH and found that concentrations of desorbed metal from this extraction were higher than their $CaCl_2$ 0.01 mol l^{-1} extraction. The discrepancy is possibly due to the slightly different type of extractant and longer shaking time of 16 h used by Vidal et al. (1999).

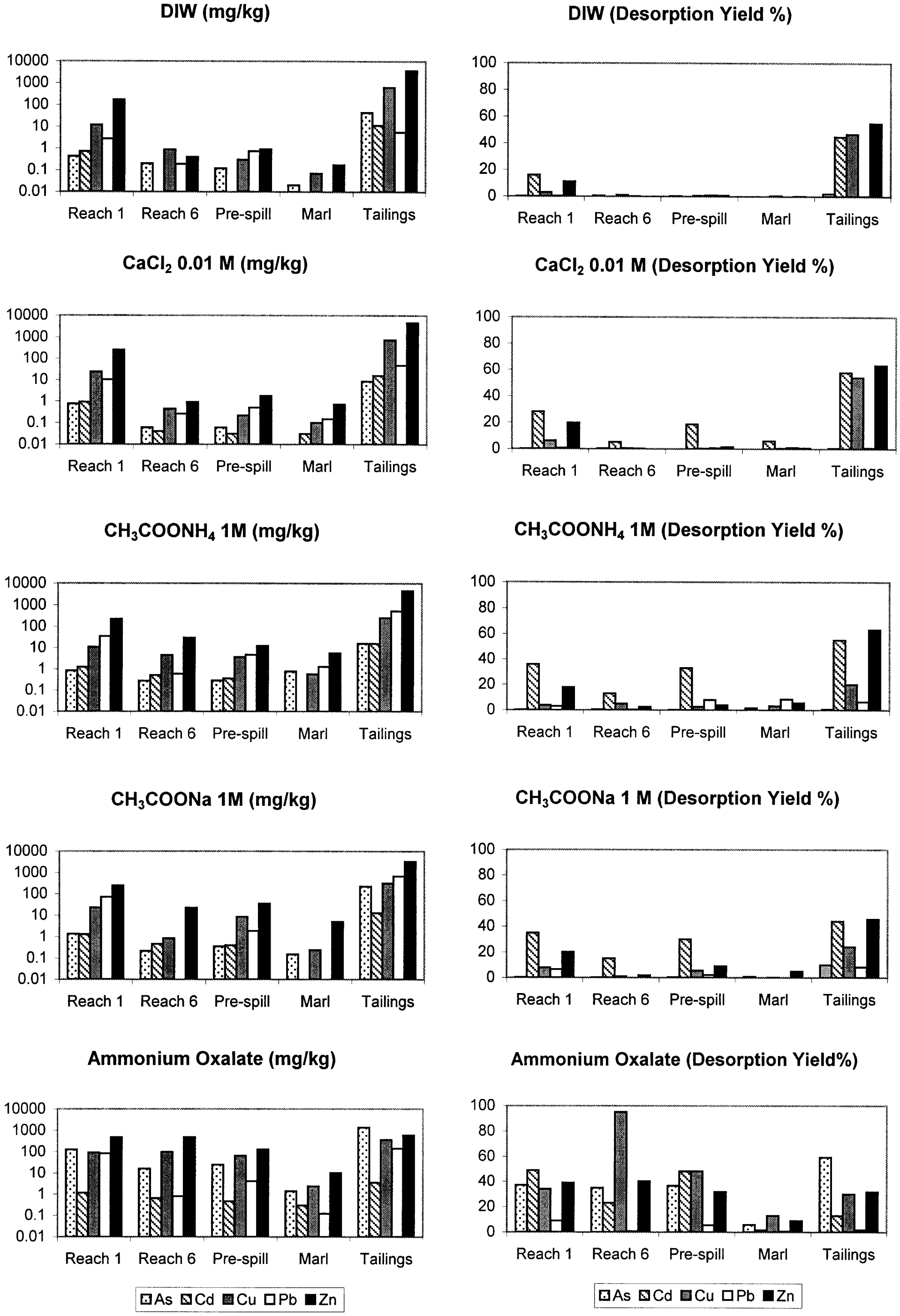

Fig. 6. Average chemical extraction As, Cd, Cu, Pb and Zn data for reach 1 and 6, tailings, pre-spill alluvium and marl samples. Results are shown as mg/kg extracted metal and As, and as desorption yield percentages of total metal and As.

The ammonium oxalate–oxalic acid extraction provides an indication of the metal and As desorbed from poorly crystalline Fe hydroxides such as ferrihydrite, and possibly from crystalline Fe hydroxides and oxides such as goethite and hematite (Schwertmann, 1959, 1964; Schwertmann and Cornell, 1991). This extraction thus estimates the fraction that may be sorbed to these Fe oxides and hydroxides formed as a result of the oxidation of the tailings, and also may partially estimate that which may be mobilised in the longer-term due to reduction after burial and early diagenesis. The average results for this extraction are notably different, and generally higher, than those of the DIW, CH_3COONH_4 and CH_3COONa extractions (Fig. 6), suggesting that the proportions of metal and As which may be released as a result of future sediment reduction may be relatively large. These extraction data also support the suggestion that metals are adsorbed by Fe oxides precipitating from the Rı́o Agrio–Guadiamar waters, which was made on the basis of mixing curves for the water data (Fig. 3) and MINTEQA2 speciation modelling (Section 4.2.2). The water data suggest that this is an active process going on in 1999 but the sediment data indicates it may have a long history. In terms of average absolute amounts, Zn generally shows the greatest amount of desorption in the ammonium oxalate-oxalic acid extraction, followed by Cu, Pb and Cd (except for the pre-spill alluvium in which more Cd is extracted than Pb and the tailings in which more As is extracted than Zn).

Reach 1 alluvium and tailings show very similar average patterns (albeit with different absolute concentrations) in all of the extractions except for the desorption yield ammonium oxalate extraction (Fig. 6), suggesting that the presence of tailings has a significant effect on metal and As desorption in reach 1 alluvium. By contrast, reach 6 and pre-spill alluvium also show very similar patterns in all of the extractions (Fig. 6), and have similar S contents, pH (Table 4) and total metal and As contents (except for Cd and Zn), suggesting that the clean-up at reach 6 was relatively effective, achieving pre-spill levels. In both reach 6 and pre-spill alluvium, however, a considerable proportion of Cd, and a limited fraction of Zn, is desorbed in the weak CH_3COONH_4 and CH_3COONa extractions. Finally, the patterns for reach 6 and pre-spill alluvium extraction data are similar, but an order of magnitude higher than, those of marl. This can be explained by the fact that marl underlies the Guadiamar catchment and is probably the major source of alluvial material.

There are no statistically significant correlations between the extraction data and either% C or grain size in the alluvium from reach 1 and 6, suggesting that these two parameters do not influence metal and As desorption in the Guadiamar sediments. By contrast, % S correlates well ($r^2 > 0.60$) with many of the metals and As in all but the DIW extraction. The% S likely reflects the presence of sulphide or sulphate minerals in the sediments. Mineralogical analysis does confirm the presence of both of these, although sulphides generally are more common that sulphates. Thus, the% S-extraction correlations observed probably reflect metal and As desorption from those sediments which still contain moderate amounts of tailings. Many of the extracted metal and As concentrations also show significant correlations ($r^2 > 0.60$) with their respective total metal and As concentration, suggesting that efforts should continue to be made to reduce total metal and As loads in the Guadiamar sediments.

5. Conclusions

The calamitous nature of mine tailings dam failures generally prompts mining companies and governmental agencies to immediately implement large-scale clean-up schemes. In the case of the Spanish Aznalcóllar spill, clean-up efforts by Boliden Apirsa, the Confederacion Hidrografica de Guadalquivir and the Consejerı́a de Medio Ambiente up to January 1999 were effective in that concentrations of metal and As in sediments collected in January and May 1999 were, on average, no higher than pre-spill concentrations. The pre-spill concentrations, however, were elevated above pre-intensive mining, 11th–13th century concentrations, and significant areas of the upstream part of the Guadiamar valley still have levels of As, Cd, Pb and Zn which are much higher than the respective pre-spill concentrations. In addition, much of the highly contaminated sediment remaining in the channel and floodplain up to May 1999 contains a large proportion of sulphide minerals which are potentially reactive. Chemical extractions have shown that Zn, Cd and Cu are potentially the most mobile elements, and that Pb and As are relatively immobile except possibly under reducing conditions. The greatest amounts of sediment metal and As desorption in DIW and $CaCl_2$ (soluble), CH_3COONH_4 (exchangeable) and CH_3COONa (acid-soluble) extractions occur in sediments exhibiting low (2–3) and moderate (5–6) pH. Total metal and As, and% S also appear to influence the amount of metal and As desorbed. By contrast, grain size and% C show no significant relationships with any of the extraction data and thus probably play no role in desorption. Even minor floods, like those occurring between January and May 1999, cause remobilisation of highly contaminated sediment in the upstream part of the catchment, and this sediment will eventually move downstream and threaten the Doñana National and Natural Parks. Dilution by relatively uncontaminated sediment appears to reduce metal concentrations downstream but small increases in metal and As concentration downstream may be due to other factors such as sewage and agricultural practices. Finally, more than a year after the spill and five months after the clean-up operation was completed, the Agrio–Guadiamar river waters continue to exhibit relatively low pH and high dissolved sulphate and metal concentrations in the upper reaches. Our sampling also showed that the composition of the river water varies significantly over very short time periods, probably due to the complexities of the hydrologic system. This strongly suggests that long-term monitoring needed to fully evaluate water quality.

Our geomorphological-geochemical research seeks to develop an understanding of the recovery of the Agrio–Guadiamar river system from the tailings dam spill *and* subsequent clean-up operations. This work strongly suggests that the following should be carried out prior to the start of mining activities: (i) background, pre-mining geomorphological survey and sediment and water geochemical data should be collected in order to be able to properly characterise and manage potential tailings dam spills and their clean-up, (ii) the relative (potential) contribution of contaminants to the river system from other sources such as sewage and agricultural activities should be quantified and (iii) mining companies and/or governmental agencies should put aside funds to draw an immediate response to tailings dam accidents.

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References

Alastuey, A., García-Sánchez, A., López, F., Querol, X., 1999. Evolution of pyrite mud weathering and mobility of heavy metals in the Guadiamar valley after the Aznalcóllar spill, south-west Spain. Sci. Total Environ. 242, 41–55.

Allison, J.D., Brown, D.S., Novo-Gradec, K.J., 1990. MINTEQA2/PRODEFA2, A Geochemical Assessment Model for Environmental Systems: User's manual, Environmental Research Laboratory, Office of Research and Development, US EPA, Athens, GA.

Almodóvar, G.R., Sáez, R., Pons, J.M., Maestre, A., Toscano, M., Pascual, E., 1998. Geology and genesis of the Aznalcóllar massive sulphide deposits, Iberian Pyrite Belt, Spain. Mineral. Deposita 33, 111–136.

Anonymous, 2000. Rain, design flaws contribute to Romanian tailings dam failure. Mining Engineering 52, 6.

Berger, A.C., Bethke, C.G., Krumhansl, J.L., 2000. A process model of natural attenuation in drainage from a historic mining district. Appl. Geochem. 15, 655–666.

Bradley, S.B., Cox, J.J., 1990. The significance of the floodplain to the cycling of metals in the river Derwent catchment, UK. Sci. Total Environ. 97/98, 441–454.

Cabrera, F., Soldevila, M., Cordón, R., Arambarri, P., 1987. Heavy metal pollution in the Guadiamar river and the Guadalquivir estuary (south west Spain). Chemosphere 16, 463–468.

Cabrera, F., Clemente, L., Díaz Barrientos, E., López, R., Murillo, J.M., 1999. Heavy metal pollution of soils affected by the Guadiamar toxic flood. Sci. Total Environ. 242, 117–129.

Díaz-Barrientos, E., Madrid, L., Cardo, I., 1999. Effect of flood with mine wastes on metal extractability of some soils of the Guadiamar river basin (SW Spain). Sci. Total Environ. 242, 149–165.

Draves, J.F., Fox, M.G., 1998. Effects of a mine tailings spill on feeding and metal concentrations in yellow perch (Perca flavescens). Environ. Toxicol. Chem. 17, 1626–1632.

Gallart, F., Benito, G., Martín-Vide, J.P., Benito, A., Prió, J.M., Regüés, D., 1999. Fluvial geomorphology and hydrology in the dispersal and fate of pyrite mud particles released by the Aznalcóllar mine tailings spill. Sci. Total Environ. 242, 13–26.

González, M.J., Fernandez, M., Hernandez, L.M., 1990. Influence of acid mine water in the distribution of heavy metal in soils of Donana National Park. Application of multivariate analysis. Environ. Technol. 11, 1027–1038.

Graf, W.L., 1994. Plutonium and the Rio Grande: Environmental Change and Contamination in the Nuclear Age. Oxford University Press, New York.

Grimalt, J.O., Ferrer, M., Macpherson, E., 1999. The mine tailing accident in Aznalcollar. Sci. Total Environ. 242, 3–11.

Hudson-Edwards, K.A., Macklin, M.G., Curtis, C.D., Vaughan, D.J., 1996. Processes of formation and distribution of Pb-, Zn-, Cd- and Cu-bearing minerals in the Tyne basin, NE England: implications for metal-contaminated river systems. Environ. Sci. Technol. 30, 72–80.

Hudson-Edwards, K.A., Macklin, M.G., Curtis, C.D., Vaughan, D.J., 1998. Chemical remobilisation of contaminant metals within floodplain sediments in an incising river system: implications for dating and chemostratigraphy. Earth Surf. Proc. Landforms 23, 671–684.

Hudson-Edwards, K.A., Schell, C., Macklin, M.G., 1999. Mineralogy and geochemistry of alluvium contaminated by metal mining in the Rio Tinto area, southwest Spain. Appl. Geochem. 14, 55–70.

Hudson-Edwards, K.A., Macklin, M.G., Miller, J.R., Lechler, P.J., 2001. Sources, distribution and storage of heavy metals in the Río Pilcomayo, Bolivia. J. Geochem. Explor. 72, 229–250.

James, L.A., 1989. Sustained storage and transport of hydraulic gold mining sediment in the Bear River, California. Ann. Assoc. Am. Geogr. 79, 570–592.

James, L.A., 1991. Incision and morphological evolution of an alluvial channel recovering from hydraulic mining sediment. Geol. Soc. Am. Bull. 103, 723–736.

Karstenesen, K.H., 1997. Contaminated soil. In: Van der Sloot, H.A., Heasman, L., Quevauviller, P.H. (Eds.), Harmonization of Leaching/Extraction Tests. Elsevier, Amsterdam, The Netherlands, pp. 57–74.

Knighton, A.D., 1991. Channel bed adjustment along mine-affected rivers of northeast Tasmania. Geomorph. 4, 205–219.

Leblanc, M., Morales, J.A., Borrego, J., Elbaz-Poulichet, F., 2000. 4,500-year-old mining pollution in southwestern Spain: long-term implications for modern mining pollution. Econ. Geol. 95, 655–662.

Lewin, J., Macklin, M.G., 1987. Metal mining and floodplain sedimentation in Britain. In: Gardiner, V. (Ed.), International Geomorphology 1986, Part 1. Wiley, Chichester, pp. 1009–1027.

López-Pamo, E., Barettino, D., Antón-Pacheco, C., Ortiz, G., Arránz, J.C., Gumiel, J.C., Martínez-Pledel, B., Aparicio, M., Montouto, O., 1999. The extent of the Aznalcóllar pyritic sludge spill and its effects on soils. Sci. Total Environ. 242, 57–88.

Macklin, M.G., 1996. Fluxes and storage of sediment-associated heavy metals in floodplain systems: assessment and river basin management issues at a time of rapid environmental change. In: Anderson, M.G., Walling, D.E., Bates, P.D. (Eds.), Floodplain Processes. John Wiley and Sons, Chichester, pp. 441–460.

Macklin, M.G., Lewin, J., 1989. Sediment transfer and transformation of an alluvial valley floor: the River South Tyne, Northumbria, UK. Earth Surf. Proc. Landforms 14, 232–246.

Macklin, M.G., Payne, I., Preston, D., Sedgwick, C., 1996. Review of the Porco Mine Tailings Dam Burst and Associated Mining Waste Problems, Pilcomayo basin, Bolivia. Report to the UK Overseas Development Agency.

Macklin, M.G., Hudson-Edwards, K.A., Jamieson, H.E., Brewer, P., Coulthard, T.J., Howard, A.J., Remenda, V.H., 1999. Physical stability and rehabilitation of sustainable aquatic and riparian ecosystems in the Rio Guadiamar, Spain, following the Aznalcóllar mine tailings dam failure. In: Mine Water and Environment, International Congress, International Mine Water Association, 13–17 September, 1999, Sevilla, Spain, pp. 271–278.

Martín, J.E., García-Tenorio, R., Ontalba-Salamanca, M.Á., Respaldiza, M.Á., da Silva, M.F., 2000. TTPIXE analysis of Guadiamar river sediments collected before the environmental disaster of 1998. Nucl. Instrum. Methods Phys. Res. B 161–163, 825–829.

Miller, J.R., 1997. The role of fluvial geomorphic processes in the dispersal of heavy metals from mine sites. J. Geochem. Explor. 58, 101–118.

Miller, J.R., Lechler, P.J., Desilets, M., 1998. The role of geomorphic processes in the transport and fate of mercury within the Carson River Basin, west-central Nevada. Environ. Geol. 33, 249–262.

Novozamsky, I., Lexmond, T.H., Houba, V.J., 1993. A single extraction procedure of soil for evaluation of uptake of some heavy metals by plants. Int. J. Environ. Anal. Chem. 51, 47–58.

Pickering, W.F., 1986. Metal ion speciation - soils and sediments (A review). Ore Geol. Revs. 1, 83–146.

Pirrie, D., Camm, G.S., Sear, L.G., Hughes, S.H., 1997. Mineralogical and geochemical signature of mine waste contamination. Tresillian River, Fal Estuary, Cornwall, UK. Environ. Geol. 29, 58–65.

Ramos, L., Hernandez, L.M., González, M.J., 1994. Sequential fractionation of copper, lead, cadmium and zinc in soils from or near the Doñana National Park. J. Environ. Qual. 23, 50–57.

Rang, M.C., Schouten, C.J., 1989. Evidence for historical heavy metal pollution in floodplain soils: the Meuse. In: Petts, G.E. (Ed.), Historical Change of Large Alluvial Rivers: Western Europe. Wiley, Chichester, pp. 127–142.

Rauret, G., 1998. Extraction procedures for the determination of heavy metals in contaminated soil and sediment. Talanta 46, 445–449.

Sassoon, M., 1988. Los Frailes aftermath. Min. Environ. Manage. 1, 8–12.

Schwertmann, U., 1959. Über die Synthese definierter Eisenoxyde unter verschiedenen Bedingungen. Z. Anorg. Allg. Chem. 298, 337–348.

Schwertmann, U., 1964. Differenzierung der Eisenoxide des Bodens durch Extraktion mit Ammoniumoxalat-Lösung. Z. Pflanzenern. Düng. Bodenkd. 105, 194–202.

Schwertmann, U., Cornell, R.M., 1991. Iron Oxides in the Laboratory. VCH Verlagsgesellschaft mbH. Weinheim, Germany.

Simón, M., Ortiz, I., García, I., Fernández, E., Fernández, J., Dorronsoro, C., Aguilar, J., 1999. Pollution of soils by the toxic spill of a pyrite mine (Aznalcollar, Spain). Sci. Total Environ. 242, 105–115.

Swan, A.R.H., Sandilands, M., 1995. Introduction to Geological Data Analysis. Blackwell, Oxford.

Tessier, A., Campbell, P.G.C., Bisson, M., 1979. Sequential extraction procedure for the speciation of particulate trace metals. Anal. Chem. 51, 844–851.

Turner, J.N., in prep. Physical Stability and Ecosystem Rehabilitation of the Agrio and Guadiamar Rivers, SW Spain. PhD thesis, University of Wales, Aberystwyth.

van Geen, A., Chase, Z., 1998. Recent mine spill adds to contamination of southern Spain. EOS 79, 449– 455.

van Geen, A., Adkins, J.F., Boyle, E.A., Nelson, C.H., Palanques, A., 1997. A 120 yr record of widespread contamination from mining of the Iberian pyrite belt. Geology 25, 291–294.

Vidal, M., López-Sánchez, J.F., Sastre, J., Jiménez, G., Dagnac, T., Rubio, R., Rauret, G., 1999. Prediction of the impact of the Aznalcóllar toxic spill on the trace element contamination of agricultural soils. Sci. Total Environ. 242, 131–148.

Wolfenden, P.J., Lewin, J., 1977. Distribution of metal pollutants in floodplain sediments. Catena 4, 309–317.