Acid mine tailings in southern Spain

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Abstract

Sediment and water samples were collected along the Guadiamar river in southern Spain on 1−3 May and on 24−25 May 1998, following the release of acid sludge from the Los Frailes zinc mine near Aznalcollar on 25 April 1998. A maximum Zn concentration of 12 mg/g in the sediment was measured approximately 10 km south of the mine. The low pH of 3.8 in Guadiamar river water approximately 20 km downstream of the mine contrasts with prevailing alkaline conditions (pH $\sim$ 8) upstream and in the adjacent Guadalquivir river. The concentration of dissolved sulfate increased from 1 mM upstream from the mine and in a nearby uncontaminated tributary to a maximum of 40 mM approximately 40 km downstream. Dissolved Zn concentrations were particularly sensitive to contamination by the tailings and ranged from as low as 3.6×10^{-8} M in a uncontaminated tributary to as high as 6.6×10^{-3} M 20 km downstream of the mine. By 25 May 1998, dissolved Zn concentrations in the most contaminated area had declined by more than an order of magnitude at all but one location. On the basis of a simple mixing model for the tailings, we estimate that 40 000−120 000 tons of Zn were released to the watershed by the accident. This is equivalent to the dissolved Zn flux reaching the adjacent, chronically contaminated, Tinto-Odiel estuary every 0.8−2.4 years. © 1999 Elsevier Science B.V. All rights reserved.

1. Introduction

The massive sulfide deposits of southern Spain and Portugal known as the Iberian pyrite belt typically contain 50% sulfur, 42% iron, 2−8% copper + lead + zinc by weight and significant quantities of gold and silver. Early indications of mining in the region date to the 3rd millennium BC. Still visible slag deposits indicate that approximately 25 M Tons of sulfide ore were mined from the region by the Romans through the 4th century AD (Strauss et al., 1977). Approximately 250 M Tons of sulfide ore were extracted from the Iberian pyrite belt from the mid-19th century through the late 1970s, approximately half of the total from a single deposit, the Rio Tinto, and another third from the nearby La Zarza and

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Tharsis mines (Strauss et al., 1977). Thus, until the 1970s, when a number of new sites came under production, most of the mining activity in the Iberian pyrite belt was restricted to the relatively small watershed of the Tinto and Odiel rivers. Mining of the Tinto and Odiel watershed has left a strong imprint on the environment. Widespread Cu and Zn contamination of sediment and organisms from the Tinto-Odiel has been reported (Stenner and Nickless, 1975; Nelson and Lamothe, 1993; Palanques et al., 1995). Contemporary Rio Tinto waters draining the region are highly acidic (pH 2.5) with dissolved Cd, Zn and Cu concentrations 10^5-10^6 times higher than in uncontaminated surface water of the Gulf of Cadiz (Garcia-Vargas et al., 1980; van Geen et al., 1997). A metal-enriched plume originating in the Tinto-Odiel has been detected 300 km downstream as it enters the western Mediterranean Sea through the Strait of Gibraltar (van Geen et al., 1988, 1991; van Geen and Boyle, 1990). Two dated sediment cores from the Spanish continental shelf show that metal inputs to the region increased significantly with the onset of intensive mining activities in the Tinto-Odiel watershed during the second-half of the 19th century (van Geen et al., 1997). This contribution focuses on a more recent and well-documented massive spill of acid-mine tailings into the adjacent Guadiamar watershed, upstream from Doñana Park, one of Europe's largest nature preserves (Fig. 1).

On 25 April 1998, the retaining wall of a tailings reservoir collapsed at the Los Frailes zinc mine near Aznalcollar releasing approximately 5×10^6 m^3 of acid sludge into the Guadiamar river. Emergency dikes were built shortly after the accident to prevent contamination of Doñana National Park located 40 km to the south of the mine. Samples of river sediment and water from the Guadiamar and the nearby Guadalquivir and Tinto rivers were collected on 1−3 May 1998 to document the scale of the accident in relation to local background levels and to the chronically contaminated Tinto system. The sites along the Guadalquivir were revisited to collect river water 1 month after the spill, on 24−25 May 1998. We provide here an expanded discussion of initial results presented by van Geen and Chase (1998),

including new dissolved Zn data for samples collected on 24−25 May 1998.

2. Methods

Small cores of river bank sediment were collected on 1−3 May 1998, along the Guadiamar, Guadalquivir, and Tinto rivers just above the water level using disposable plastic syringes (10 cm^3) with the ends cut off. After a dramatic rise in areas directly affected by the Los Frailes spill, the water had already returned to a more normal level by the time of the first sampling. In areas not impacted by the Los Frailes tailings, sampled sediment was probably deposited during the previous rainy season. After freeze-drying, ~ 3 g of sediment from 0 to 1 cm and from 4 to 5 cm depth was homogenized by shaking in a vial. An approximately 10 mg subsample was digested in HNO$_3$/HF/HClO$_4$ Seastar acids and taken up in at least 10 ml 1% HNO$_3$ (Seastar) solution according to the method of Fleisher and Anderson (1991). The Zn content of the sediment solutions was determined by graphite-furnace atomic absorption spectrophotometry (GFAAS) on a Hitachi Z8200 instrument with calibration by standard additions. A procedural blank containing all acids was treated like a sample. The detection limit for Zn in the sediment, estimated as three times the standard deviation of the blank, was 3 µg/g. Analyses of replicate digests agreed to approximately 15%. The sand fraction of each sediment sample was determined on a separate fraction by wet sieving through a 0.63-µm mesh.

Water samples were collected in 125 ml acid-cleaned polyethylene bottles from the river banks at the end of a 3 m pole. These samples were filtered within 12 h through acid-cleaned 0.4-µm polycarbonate membrane filters (Nuclepore) in a low-dust environment (hotel bathroom) following established clean procedures (van Geen and Husby, 1996). The main difficulty in sampling this type of environment is potential cross-contamination due to the extremely wide range in concentrations. The entire filter rig was, therefore, carefully cleaned between samples by rinsing and pre-filtering with water brought from the labora-
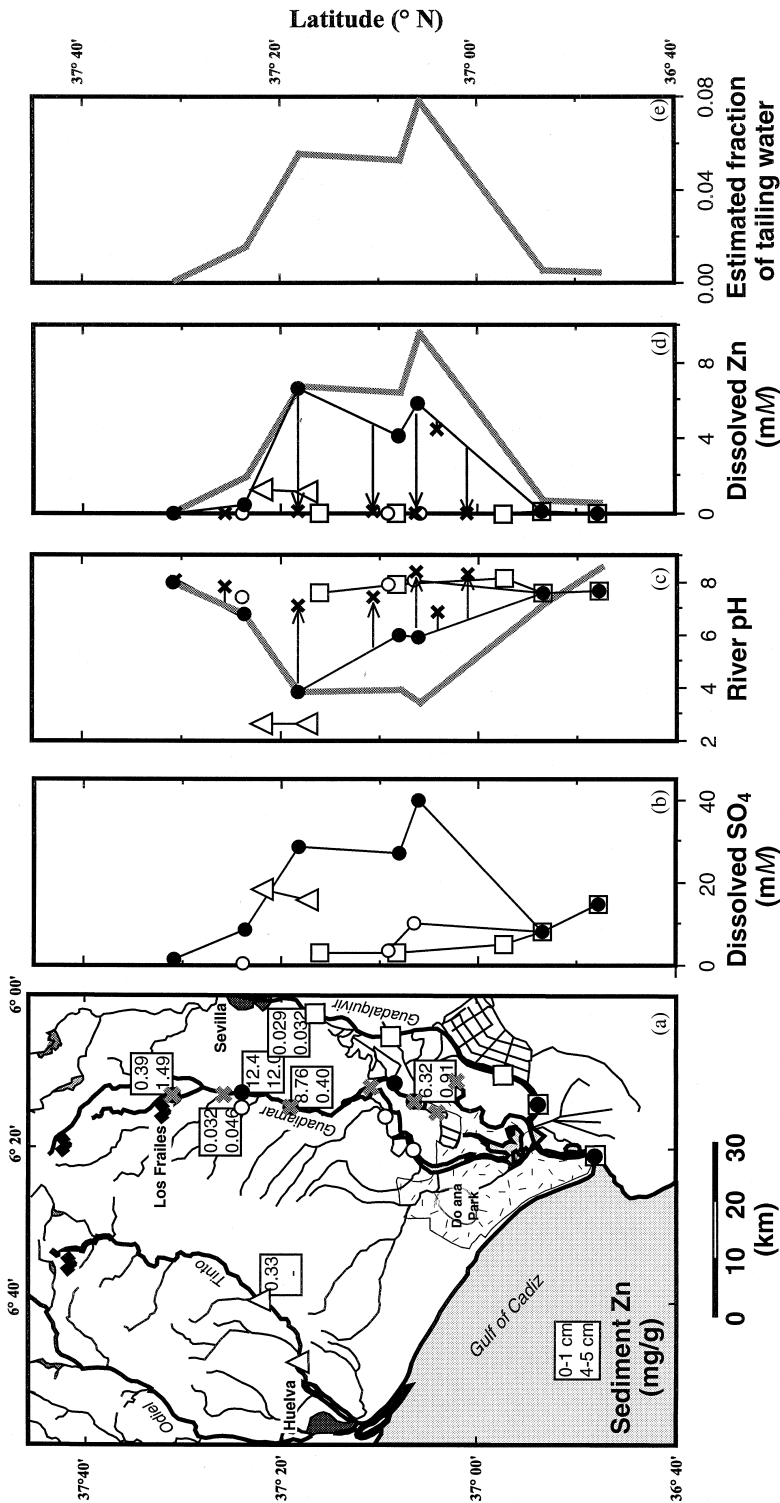
Fig. 1. (a) Map of south-western Spain showing the locations of samples collected from the banks of the Guadiamar (open and filled circles), Guadalquivir (open squares), and Tinto (open triangles) rivers on 1–3 May and 24–25 May 1998 (diagonal crosses). The open circles indicate uncontaminated sites within the watershed of the Guadiamar. Square insets in: (a) list sediment Zn concentrations at two depths below the surface; (b) dissolved sulfate concentrations, shown as a function of latitude; (c) river pH; (d) dissolved Zn concentrations; and panel (e) shows variation in our estimate of the fraction of mine tailings along the main path of the Guadiamar and into the lower Guadalquivir based on a conservative mixing model constrained by sulfate (Fig. 3a). The thick grey lines in panels (c) and (d) indicate pH and Zn concentrations along Guadiamar predicted by the model assuming conservative mixing of mine tailing, river water, and seawater. Arrows pointing to crosses (c,d) show the change in properties from 1–3 May to 24–25 May 1998.

tory that contained $< 10^{-9}$ mol/l Zn (MilliQ, Millipore). Filtered samples were acidified with 2 μl/ml of 12 N HCl (Seastar) upon return to the laboratory, approximately 1 week after collection and filtration. Dissolved Zn concentrations were measured by GFAAS with standard additions by diluting the samples to within the linear range of the instrument with a 1% HNO_3 solution (Seastar). The estimated precision of dissolved Zn measurements was ~ 10%, with a detection limit of ~ 5×10^{-9} M reflecting the variability of the blank. Dissolved Fe concentrations were measured in a similar fashion for a subset of samples by GFAAS and standard additions.

River pH was measured in the field with a calibrated Orion electrode. Conductivity measured in the field with a portable meter calibrated with NaCl and H_2SO_4 solutions proved to be a more sensitive indicator of the distribution of the tailings than pH. Samples were diluted in low conductivity MilliQ water to the 0–200 μΩ/cm conductivity range of the instrument. The conductivities reported here were measured later in the laboratory, with samples and standards at the same temperature. Sulfate concentrations in filtered and acidified samples were measured by turbidimetry after addition of barium chloride (Tabatabai, 1974). Na and Ca concentrations in the water samples were measured by flame atomic absorption spectrophotometry (Hitachi Z8200) following dilution in a $HNO_3/HCl/La_2O_3$ matrix to within the linear absorbance range of the instrument.

3. Results

Sediment concentrations of Zn in river bank sediments of the Guadiamar were extremely elevated over a distance of 40 km, with a maximum of 12 mg/g in the upper 5 cm of the sediment ~ 10 km from the mine (Table 1 and Fig. 1a). Further downstream, concentrations at 4–5 cm depth were approximately an order of magnitude lower than at the surface. Zn concentrations in the sediment were also relatively low in a single sample collected from the Tinto river (0.3 mg/g) and much lower in sediment from the

Guadalquivir downstream of Seville (0.03 mg/g). At a site very close to the mine but upstream from the tailings pond (37.5°N/6.2°W), the Zn content of the sediment at 4–5 cm was almost four times greater than at the surface. Comparison of the Zn concentration and sand fraction of contaminated sediment from the Guadiamar shows that the signature of the Los Frailes tailings was concentrated in a relatively fine particulate fraction (Fig. 2).

On 1–3 May 1998, dissolved Zn concentrations varied over five orders of magnitude from as low as 3.6×10^{-8} M in an uncontaminated tributary of the Guadiamar, the Agrio river, to 6.6×10^{-3} M ~ 20 km downstream of the mine (Table 1 and Fig. 1d). Sulfate concentrations increased from 1 mM upstream of the mine and in the uncontaminated Agrio river to a maximum of 40 mM approximately 40 km downstream, i.e. 20 km downstream of the sample containing the highest dissolved Zn concentration (Fig. 1b). As in the case of Zn, the highest dissolved Fe concentration of 1.3×10^{-3} M was measured upstream of the sulfate maximum (Table 1). The low pH of 3.8 of Guadiamar water containing the highest Zn and Fe concentrations 20 km downstream of the mine contrasts with prevailing alkaline conditions (pH ~ 8) upstream and in the adjacent Guadalquivir (Fig. 1c). Nowhere along the Guadiamar, however, did the pH drop to the extremely low value of 2.6 measured in the Tinto river.

The linear relation between conductivity and sulfate concentration in the Guadiamar river water indicates the dominant role of the proportion of sulfate-rich tailings in determining the conductivity of contaminated samples (Fig. 3a). The suite of samples from the Guadalquivir river and two samples from Doñana Park that were apparently not contaminated also show a linear relation between conductivity and sulfate, but the slope of this relation is different from that for contaminated samples. Dissolved Na^+ measurements indicate that the conductivity and sulfate concentration in the uncontaminated samples were controlled by the proportion of seawater in these samples (Fig. 3b). The distinction can be made because Na^+ is not significantly enriched in the tailings but is very much so in seawater (Table 1).

Table 1
Sediment and water chemistry of the Guadiamar, Guadalquivir, and Tinto rivers in May 1998

| Station Latitude (°N)	Longitude (°W)	Sediment Sand (%) 0–1 cm/4–5 cm	Zn (mg/g) 2/5/1998	Water Conductivity (μΩ/cm) 2/5/1998	Conductivity 25/5/1998	pH 2/5/1998	pH 25/5/1998	SO_4^{2-} (mM) 2/5/1998	Na^+ (mM) 2/5/1998	Ca^{2+} (mM) 2/5/1998	Zn (M) 2/5/1998	Zn (M) 25/5/1998	Fe (M) 2/5/1998	Fe (M) 25/5/1998
Guadiamar River and Doñana Park (uncontaminated)														
37.397	6.253	70/73	0.03/0.05	1080		7.45		0.70	2.62	2.22	3.61E-08			
37.153	6.293			5600	13400	7.88	7.54	3.64	27.5	3.57	1.68E-07	4.67E-08		
37.108	6.315			16400		8.08		10.5	99.2	5.20	4.91E-07			
Guadiamar River (contaminated)														
37.513	6.223	93/77	0.39/1.49	705	543	7.98	8.05	1.50	1.38	1.79	7.34E-07	1.21E-07		
37.429	6.220				2540		7.81					2.57E-05		
37.396	6.231	18/35	12.40/12.00	4000	2340	6.76	7.10	8.92	2.29	6.08	4.97E-04	1.32E-04	1.24E-07	
37.305	6.261	43/54	8.76/0.40	10200		3.78		28.6	4.34	11.2	6.59E-03		1.28E-03	
37.177	6.204				4260		7.41					1.08E-04		
37.133	6.183			9400		6.04	8.39	27.3	4.26	12.7	4.13E-03	4.83E-07	2.60E-04	
37.100	6.250	67/84	6.32/0.91	15000	12600	5.90	6.85	40.1	4.53	19.7	5.83E-03	4.40E-03	2.35E-04	
37.067	6.267				11400		8.29					9.86E-07		
37.019	6.276				5310									
Guadalquivir River														
37.267	6.033	39/33	0.03/0.03	2520		7.58		2.85	8.00	3.05	4.87E-08			
37.139	6.124			3200		7.86		3.10	9.55	3.28	1.47E-07			
36.957	6.176			5820		8.13	7.68	4.93	30.0	3.87	1.53E-06	2.57E-06		
36.891	6.241			11600		7.62		7.98	63.6	4.86	7.94E-05		6.23E-08	
36.798	6.338			36200		7.68		15.0	215	7.20	1.84E-05			
Rio Tinto														
37.365	6.673	38	0.33	11400		2.60		18.2	1.95	1.57	1.26E-03		2.85E-03	
37.288	6.801			9000		2.62		15.7	10.3	2.86	1.09E-03			
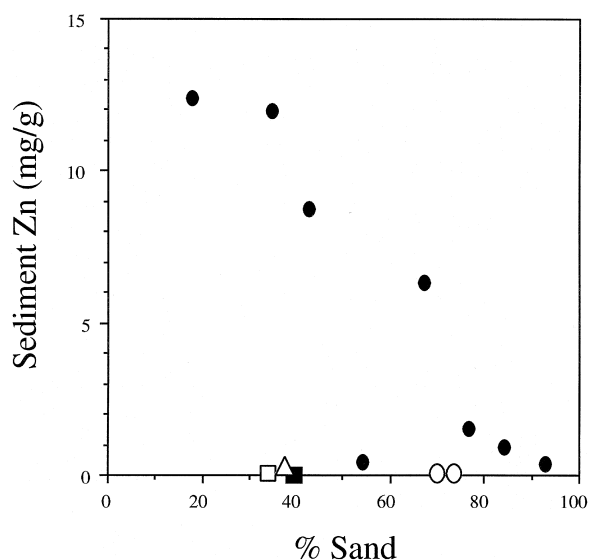
Fig. 2. Variations in sediment Zn concentrations in relation to grain size. As in Fig. 1, symbols are keyed to the Guadiamar (open and filled circles), Guadalquivir (open squares), and Tinto (open triangles) rivers.

Because the Guadalquivir and Doñana samples conform to the same Na^+-conductivity relationship, the elevated conductivity and sulfate levels of (uncontaminated) Doñana Park water were probably due to seawater intrusion, perhaps enhanced by evaporation. The relation between conductivity and Ca^{2+} suggests that both seawater and the tailings contained a significant amount of Ca (Fig. 3c). This is probably because CaO is added to the recycled tailings during normal operation of the extraction plant to optimize extraction of the sulfide ore (P. Adamek, Boliden, personal communication). The more acidic samples from the Tinto river contain relatively little Ca^{2+}.

By 24−25 May 1998, dissolved Zn concentrations had dropped by an order of magnitude in the most contaminated region of the Guadiamar with the exception of one location (Zn 4.4×10^{-3} M, pH 6.8) that still showed Zn levels comparable to the highest values measured on 1−3 May (Fig. 1d and Table 1). This location was not sampled on the previous occasion and appears to be a poorly flushed cul-de-sac that extends from the Guadiamar (Fig. 1a). At all other locations along

the Guadiamar sampled on 24−25 May the pH was > 7, which is barely distinguishable from local background levels upstream of the mine.

4. Discussion

Even though the data set presented here is limited in extent, we feel it can be used to infer the broad-scale impact of the spill for two reasons. First, the extremely wide dynamic range of Zn concentrations observed in both sediment and water suggests that factors other than the spill were secondary in regulating the distribution of this element. Second, in the case of dissolved Zn, river flow provides some measure of spatial averaging and reduces the chance of recording localized features.

There is no doubt that the low pH and extremely elevated sulfate and Zn levels measured downstream of the mine on May 1−3 were caused by the massive release of sulfide mine tailings 1 week earlier. Without a more extensive analysis of the samples, however, it is difficult to account quantitatively for the complex chemical reactions that occurred as the mine tailings were diluted with alkaline river water. Nevertheless, a simple model based on conservative mixing of sulfate can be used to show that the mine tailings were diluted 18-fold with alkaline river water in the pH 3.8 sample collected 10 km south of the mine (Fig. 1e). The mixing model accounts for acid−base reactions involving only water and carbon dioxide (Morel and Hering, 1993). Key assumptions are an initial pH of 2 for the mine tailings on the basis of a local newspaper article and alkaline river water PCO_2 initially in equilibrium with the atmosphere. At the two sites near the mouth of the Guadalquivir, the non-tailing sulfate contribution from seawater was determined from Na^+ concentrations. This simple model indicates that the downstream increase in pH, despite a higher proportion of tailings (Fig. 1b), could be accounted for by small increases in alkalinity due to dissolution of this carbonate-rich terrain or, perhaps, the reported neutralization of the river with lime soon after of the spill (P. Adamek, Boliden, personal communication).
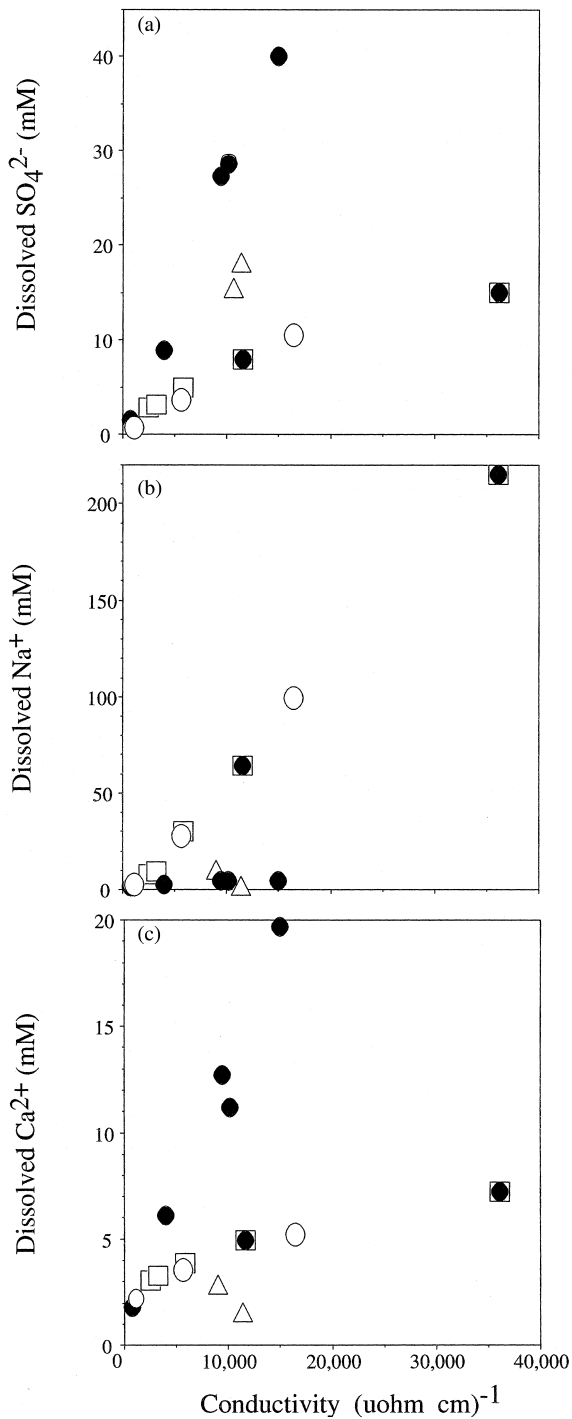
Fig. 3. Variation of dissolved sulfate (a), sodium (b), and calcium (c) in river water as a function of conductivity on 1–3 May 1998. As in Fig. 1, symbols are keyed to the Guadiamar (open and filled circles), Guadalquivir (open squares), and Tinto (open triangles) rivers.

Observed concentrations of dissolved Zn downstream of the maximum fall short of those predicted by conservative mixing (Fig. 1d). Dissolved Fe concentrations decrease from 1.3 mM in the sample with the highest dissolved Zn (pH 3.8) to 0.26 and 0.23 mM in the next two samples downstream (pH 6.0). Surface sediment at this site is enriched in Zn (6.32 mg/g; Fig. 1a) despite the absence of the characteristic black tailings that were visible further upstream. This suggests Zn may have been removed from river water as the pH increased with dilution, probably in conjunction with Fe oxidation and precipitation (Webster et al., 1998). Precipitation of $ZnCO_3$ is another possibility (Madrid and Diaz-Barrientos, 1992). Despite this apparent loss, dissolved Zn concentrations at the mouth of the Guadalquivir on 2 May 1999, were at least an order of magnitude higher than levels previously reported for the same region (van Geen et al., 1991, 1997). This suggests that a fraction of the tailings probably did reach the Guadalquivir, despite the construction of a dam across the Guadiamar north of Doñana Park soon after the spill (P. Adamek, Boliden, personal communication). The dramatic decrease in dissolved Zn observed 3 weeks after the initial sampling (Fig. 1c) most likely reflects both dilution by uncontaminated river water and loss to the sediment.

Tinto river waters were more acidic than any of the samples collected from the Guadiamar, although sulfate and Zn concentrations were lower (Fig. 1). The more acidic Tinto River water had a pH of 2.6 and a dissolved Fe of 2.8 mM, whereas, its sulfate and Zn concentrations were only approximately 50% of those in the most contaminated samples from the Guadiamar. To compare Zn fluxes in the two systems, the sediment sample 10 km south of the mine containing 12 mg/g (~ 24 mg/cm^3) Zn as solid sludge was assumed to approximate the composition of particulate material released at the mine. The mixing model suggests the tailings contained 18×6.6 mM = 118 mM, which is 8 mg/cm^3 Zn in dissolved form. Depending on the proportion of dissolved and particulate material released, which was not known at the time this paper was written, this yields a total Zn concentration in the acid sludge

of 8–24 mg/cm^3. The release of 5×10^6 m^3 of tailings therefore added 40000–120000 tons of Zn to the watershed. This is comparable to the annual production capacity of the Los Frailes mine of 125000 tons Zn. On the basis of the dissolved Zn content in the Tinto-Odiel watershed (1.3 mM) and a combined mean flow of 20 m^3/s (van Geen et al., 1997), the amount of Zn released from the spill is calculated to be equivalent to the dissolved Zn flux reaching the adjacent Tinto-Odiel estuary over a 0.8–2.4-year period. Since the Tinto-Odiel system has been contaminated for at least the past 100 years (van Geen et al., 1997), this chronically contaminated watershed should be compared systematically to the Guadiamar as the latter system recovers in coming years following a massive remediation effort. In this context, it is worth noting that river pH and sediment metal data collected before the accident indicate that the Guadiamar watershed had been subjected to mine-related metal contamination before 25 April 1998 (Gonzalez et al., 1990; Ramos et al., 1994).

5. Conclusions and outlook

Samples collected along the Guadiamar river 1 week after the release of 5×10^6 m^3 of acid tailings from the Los Frailes mine show up to 10^2- and 10^5-fold increases in Zn concentrations in the particulate and dissolved phase, respectively, relative to uncontaminated background levels. Although the pH of the Guadiamar had already recovered by the time of a second sampling 3 weeks later, dissolved Zn concentrations in Guadiamar river water were still extremely high. The amount of Zn released by the accident (40000–120000 tons) appears to have been of the same order as the annual Zn production of the Los Frailes mine. Based on studies of the adjacent Tinto-Odiel watershed it is likely that the release of tailings dramatically raised concentrations of other potentially toxic elements such as As, Cd, Cu and Pb (Vatland, 1996; van Geen et al., 1997).

Were it not for the existence of Doñana Park downstream of Los Frailes, the impact of the recent tailings release would not have been of such unprecedented concern. Integrated over the past 100 years, the nearby Tinto-Odiel system has received a flux of metal-enriched tailings that is at least an order of magnitude higher (van Geen et al., 1997). By comparison, the tailings released until the turn-of-the-century to the Clark Fork river system in Montana are distributed over hundreds (as opposed to tens) of kilometers (Axtmann and Luoma, 1991; Nimick and Moore, 1994). Unrestrained discharges of metal-contaminated tailings on a massive scale continue even today on the island of Bougainville in Papua New Guinea (Moore and Luoma, 1990). What is unique about the Los Frailes accident is the scale of the remediation effort, which resulted in the removal of most of the visible tailings. Since conditions in the Guadiamar watershed soon after the accident were documented by a number of research groups, the next several years present a special opportunity to assess the effectiveness of this particular effort, and remediation in general, into restoring the biogeochemical health of a watershed heavily contaminated with acid-mine tailings.

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