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Recent Mine Spill Adds to Contamination of Southern Spain

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The retaining wall of a tailings reservoir collapsed at a zinc mine in Spain last spring, releasing into the watershed possibly nearly as much zinc as the mine produces annually. The accident happened April 25, 1998, at the Los Frailes mine near Aznalcollar in southern Spain, sending ~5 x $10^6 m^3$ of acid sludge into the Guadiamar River. Based on a suite of water and river bank sediment samples collected downstream of the spill on May 1-3, 1998, an estimated 40,000 to 120,000 tons of Zn was added to the watershed. This is comparable to the annual production capacity of the mine of 125,000 tons. While the scale of the accident was certainly very large, an equivalent amount of Zn has been reaching the adjacent Tinto-Odiel estuary every 1-2 years as a result of mining since the middle of the 19th century. Emergency dikes were built shortly after the accident to prevent contamination of Doñana National Park, an important wildlife reserve 40 km to the south of the mine. The composition of samples collected north of the park suggest this diversion was effective.

One week after the spill, samples of river sediment and water were collected from the Guadiamar and the nearby Guadalquivir and Tinto Rivers to document the scale of the accident in relation to local background levels and to the chronically contaminated Tinto River system. Extremely elevated levels of particulate Zn were found in rivers downstream from the mine over a distance of 40 km, as well as a 10^5-fold increase in dissolved Zn concentrations. A maximum Zn content of 12 mg/g in the sediment collected about 10 km south of the mine was comparable to that reported for sulfide ore in the Iberian pyrite belt [*Strauss et al.*, 1981] and 100 times that in sediment collected from uncontaminated river banks (Figure 1a). This area was already contaminated to some extent before the recent accident, however. Increased mining activity since the early 1980s has resulted in substantial trace metal enrichment of downstream sediments, with Zn values as high as 4.2 mg/g reported in 1990 about 15 km south of the mine [*Ramos et al.*, 1994]. Dissolved Zn concentrations span an even wider dynamic range, from as low as 0.000036 mM in an uncontaminated tributary to 6.6 mM 20 km downstream of the mine (Figure 1d). The concentration of dissolved sulfate increases from 1 mM upstream from the mine and in a nearby uncontaminated tributary to a maximum of 40 mM about 40 km downstream (Figure 1b). A low pH of 3.8 measured in the Guadiamar about 20 km downstream of the mine contrasts with prevailing alkaline conditions (pH ~8) upstream and in the adjacent Guadalquivir (Figure 1c).

The low pH and extremely elevated sulfate and Zn levels measured downstream of the mine were no doubt caused by the massive release of sulfide mine tailings one week earlier. Without a more extensive analysis of the samples, however, it is difficult to account quantitatively for the complex chemical reactions which occurred as the mine tailings were diluted with alkaline river water. Nevertheless, a simple model based on conservative mixing of sulfate suggests 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 (Figure 1e). The mixing model accounts for acid-base reactions involving only water and carbon dioxide [e.g., *Morel*, 1983]. Key assumptions are an initial pH of 2 for the mine tailings on the basis of a local newspaper article and alkaline river water P_{CO2} initially in equilibrium with the atmosphere. The non-tailing sulfate contribution from seawater at two sites near the mouth of the Guadalquivir was determined from Na^+ concentrations. The model indicates that the downstream increase in pH despite a higher proportion of tailings (Figure 1b) can be accounted for by small increases in alkalinity owing to, for instance, dissolution of this carbonate-rich terrain. Observed downstream concentrations of dissolved Zn fall short of those predicted by conservative mixing (Figure 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). This suggests Zn is removed from river water as the pH increases with dilution, probably in conjunction with Fe oxidation and precipitation, particularly in the presence of elevated sulfate [*Webster et. al*, 1998].

Dissolved Zn is a sensitive indicator of the path followed by the contaminated plume. Zinc concentrations below 5 x 10^{-7}M in the Guadiamar at two locations just north of Doñana Park suggest efforts to divert the sludge were largely successful (Figure 1d). Relatively high sulfate concentrations at these locations (3.6 and 10.5 mM) can be attributed to evaporation or seawater intrusion, based on observed Na concentrations (27.6 and 95.1 mM). Zinc concentrations in the Guadalquivir increase from 4.9 x 10^{-8}M just south of Seville to a maximum of 7.9 x 10^{-5} M, about 15 km from the coast. This suggests the bulk of the metal plume entered the Guadalquivir south of about 37°N, despite the presence further north of many small connecting canals and tributaries.

Mining in the Iberian pyrite belt has historically been most active in the Tinto-Odiel watershed, which today is highly contaminated [*van Geen et al.*, 1997]. Tinto River water was more acidic than any of the samples collected from the Guadiamar, although sulfate and Zn concentrations were lower. 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 about 50% of those in the most contaminated samples from the Guadiamar. To compare Zn fluxes in the two systems, the sediment sample

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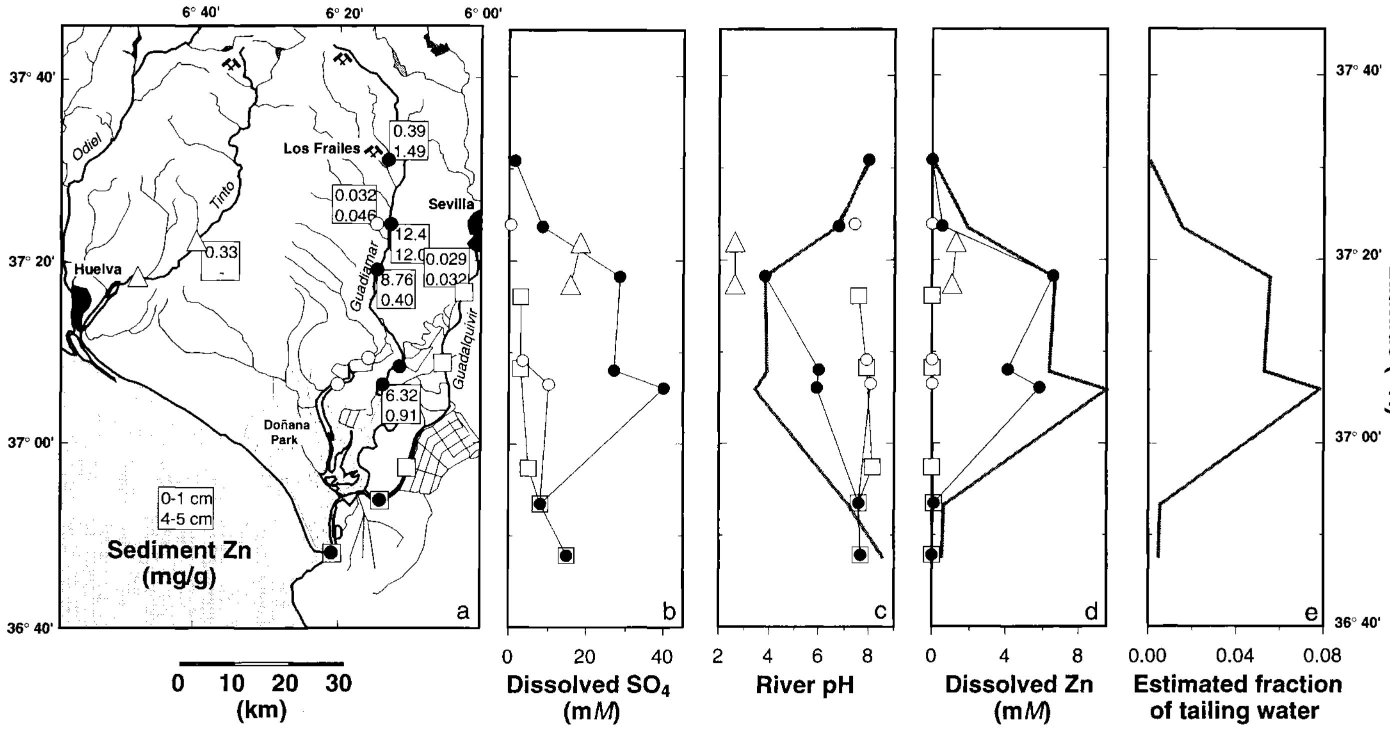

*Fig. 1. a) Map of southwestern Spain showing the location of samples collected from the banks of the Guadiamar (open and filled circles), Guadalquivir (open squares), and Tinto (open triangles) Rivers on May 1-3, 1998. Square insets list sediment Zn concentrations at two depths below the surface. The dried sediment was digested in $HNO_3/HF/HCLO_4$ and Zn content determined by Graphite-Furnace Atomic Adsorption (GFAA)/Zeeman background correction with calibration by standard additions. A reduction in the Zn content of contaminated samples as the proportion of sand increases from 20% to 90% suggests that the released particles are relatively fine. Water samples were collected from a 3-m pole and filtered through 0.4 µm filters within 12 hours following established clean procedures [*van Geen and Husby, *1996]; b) Sulfate concentrations in filtered samples acidified with 2 µL/mL of 12 N HCl were measured by $BaSO_4$ precipitation [*Tabatabai, *1974] and shown as a function of latitude; c) River pH measured in the field with a calibrated electrode; d) Dissolved Zn concentrations measured by GFAA and standard additions following dilution in 1% HNO_3; e) Variation in estimate of the fraction of mine tailings along the main path of the Guadiamar (eastern branch) and into the lower Guadalquivir based on a conservative mixing model constrained by sulfate (see b). The thick grey lines in c) and d) indicate model-predicted pH and Zn concentrations along the Guadiamar assuming conservative mixing of mine tailing, river water, and seawater.*

10 km south of the mine containing 12 mg/g, or ~24 mg/cm^3, Zn as solid sludge was assumed to approximate the composition of particulate material released at the mine. The mixing model suggested the tailings contained 18 x 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 is unknown, this yields a total Zn concentration in the acid sludge of 8-24 mg/cm^3. The release of 5 x 10^{6}m^3 of tailings therefore added 40,000-120,000 tons of Zn to the watershed. 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 was calculated to be equivalent to the dissolved Zn flux reaching the adjacent Tinto-Odiel estuary over a 0.8-2.4-year period. Much could therefore be learned about the long-term impact of the recent accident by studying the current situation in the Tinto watershed. As this initial study was completed, a dataset consistent with the observations presented here was discovered at Web site http://www.cma.caan.es/aznalcollar/ingles/i_idxaznacollar.htm. For more information about this topic, also see Web site http://headlines.yahoo.com/Full_Coverage/World/Toxic_Spill_in_Spain/.

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