A 120 yr record of widespread contamination from mining of the Iberian pyrite belt

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ABSTRACT

A metal-enriched seawater plume entering the western Mediterranean Sea through the Strait of Gibraltar originates 300 km to the west in the Rio Tinto estuary of southwestern Spain. Mining of Rio Tinto ore, one of the largest metal-rich sulfide deposits in the world, started well before Roman times. Contemporary Rio Tinto waters draining the region are highly acidic (pH 2.5) with dissolved cadmium, zinc, and copper concentrations 10^5–10^6 times higher than in uncontaminated surface water of the Gulf of Cadiz. Two dated sediment cores from the Spanish continental shelf show that metal inputs to the region increased with the onset of intensive mining activities during the second half of the 19th century. Although the impact of mining may have decreased over the past few decades, the Tinto river and estuary remain highly contaminated.

INTRODUCTION

The massive sulfide deposits of southern Spain and Portugal were formed about 300 Ma by precipitation from hydrothermal fluids during a period of intense submarine volcanism (Boulter, 1993). Subsequent uplift and compression resulted in the distribution of >1000 Mt (million metric tons) of massive sulfide ore bodies over a region 250 km long and 30 km wide, known today as the Iberian pyrite belt (Munha et al., 1986; Fig. 1). The deposits typically contain 50% sulfur, 42% iron, 2%–8% copper + lead + zinc by weight and significant quantities of gold and silver (Strauss et al., 1977). Early indications of mining in the region date to the third millennium B.C. Silver deposits later became an important source of wealth for the Phoenicians (Morral, 1990). About 5 Mt of pyrite had been mined from the Rio Tinto by the time Carthage fell at the end of the Third Punic War in 146 B.C. (Pinedo, 1963). Spain became a Roman province, and mining of the rich deposits of the Iberian pyrite belt for copper and silver started on a larger scale. Still-visible slag deposits indicate that about 25 Mt of sulfide ore was mined from the region by the Romans through the 4th century A.D. (Strauss et al., 1977). The sites then remained virtually untouched until the mid-19th century when mining started again, initially driven by the demand for copper and later also for sulfuric acid.

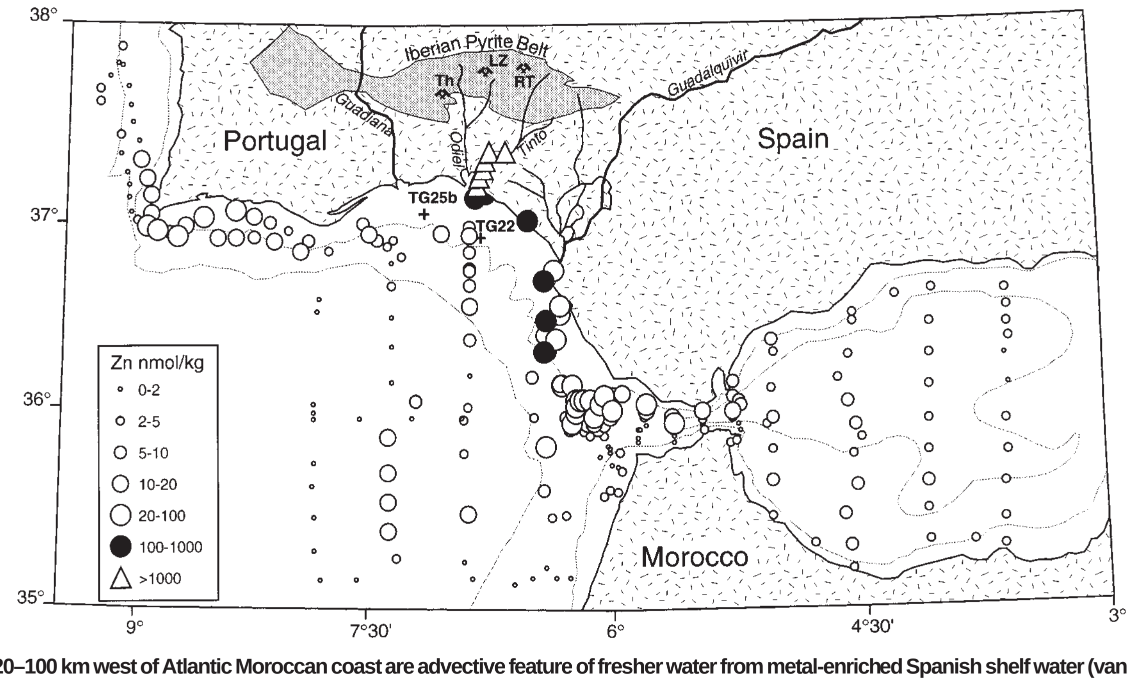

Figure 1. Map of Gulf of Cadiz, Strait of Gibraltar, and Alboran Sea, showing distribution of dissolved Zn in surface waters. Symbols correspond to Zn concentration ranges shown in inset. Most samples from Gulf of Cadiz east of mouth of Guadiana River and all samples from Strait of Gibraltar and Alboran Sea were collected on board USNS Lynch in March–April 1986 (van Geen and Boyle, 1990; van Geen et al., 1991). Samples off coast of Portugal were collected on board RV *Noruega* in October 1988 (van Geen et al., 1990). Samples from Rio Tinto and its estuary were collected from a small boat and from shore in December 1992. Spanish shelf waters are entrained into Mediterranean inflow and also into northward-flowing coastal current (Frouin et al., 1990). Elevated concentrations of Zn 20–100 km west of Atlantic Moroccan coast are advective feature of fresher water from metal-enriched Spanish shelf water (van Geen et al., 1991). Crosses on Gulf of Cadiz shelf show locations of sediment cores TG25b and TG22. Isobaths are plotted at 100 and 500 m depth. Three historically most important mining sites within Iberian pyrite belt: RT—Rio Tinto, Th—Tharsis, LZ—La Zarza.

About 250 Mt of sulfide ore were extracted from the Iberian pyrite belt from the mid-19th century through the late 1970s, about one-half of the total from a single deposit, the Rio Tinto, and another third from the nearby La Zarza and Tharsis mines (Strauss et al., 1977; Fig. 1). 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.

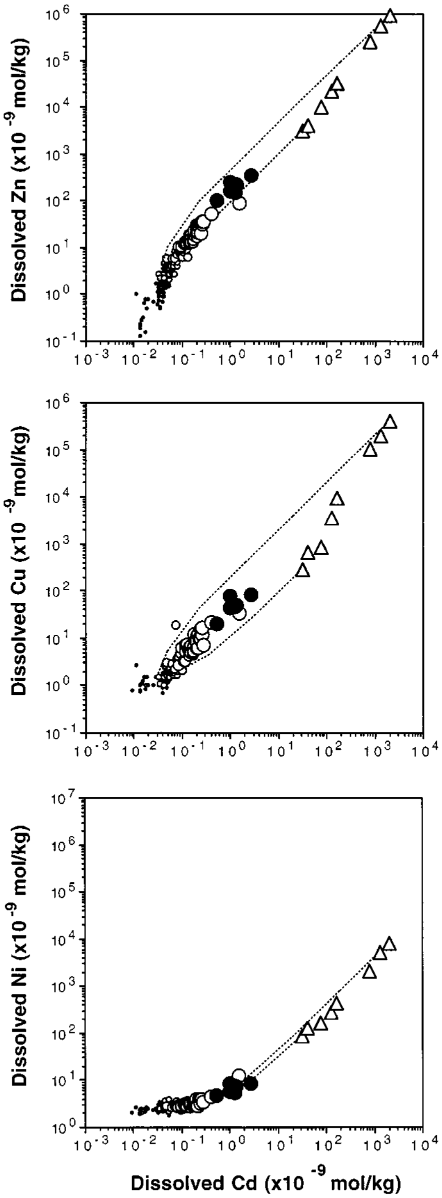

Figure 2. Variations in dissolved Zn, Cu, and Ni as function of Cd for all samples shown in Figure 1. Symbols refer to same Zn concentration ranges as in Figure 1. Log scales are used to cover the six orders of magnitude in metal concentrations. Dotted lines show conservative mixing relationships between offshore water (Cd, 0.030; Cu, 1.3; Ni, 2.6, and Zn 1.0; all $\times 10^{-9}$ mol/kg) and two different metal-enriched endmembers: (1) river water near Lucena del Puerto (see Table 1 for composition) or (2) coastal water collected 3 km south of Tinto-Odiel estuary mouth (Cd, 32; Cu, 290; Ni, 90; and Zn, 3060; all $\times 10^{-9}$ mol/kg). Difference between conservative mixing lines is measure of removal within estuary in December 1992, assuming Cd behaves conservatively.

METAL ENRICHMENTS IN RIVER AND SEAWATER

It has been known for some time that Spanish coastal waters of the Gulf of Cadiz are highly enriched in a number of metals including Cd, Cu, and Zn and that these enrichments are advected to the western Mediterranean through the Strait of Gibraltar (Boyle et al., 1985; Sherrell and Boyle, 1988; van Geen et al., 1988; 1990; 1991; van Geen and Boyle, 1990). Some of these observations are summarized in Figure 1 which shows the distribution of dissolved Zn in surface waters of the region. The range of Zn concentrations observed in 1986 and 1988 extends from <1 $\times 10^{-9}$ mol/kg in surface Atlantic waters unaffected by Spanish shelf water to as high as 200 $\times 10^{-9}$ mol/kg south of the mouth of the Guadalquivir River. Patterns of Cd and Cu enrichments throughout the region closely parallel the Zn pattern (Fig. 2). Metal concentrations in the two main rivers of the region, the Guadiana (watershed of 68 000 km^2, mean discharge 80 m^3/s) and the Guadalquivir (57 000 km^2, 160 m^3/s), however, are comparable to rivers draining other industrialized regions and cannot explain the observed levels of enrichment. Prompted by reports of metal contamination in the Tinto-Odiel rivers and estuary (Garcia-Vargas et al., 1980; Nelson and Lamothe, 1993), we sampled the waters of this relatively small system (combined watershed 3400 km^2, mean discharge 20 m^3/s, J. Borrego, 1996, personal commun.). Concentrations of Cd, Cu, and Zn in filtered samples collected from the Tinto river in December 1992 were >1000-fold higher than in either the Guadiana or the Guadalquivir rivers (Table 1).

Not all dissolved metals pass through the Tinto estuary with equal efficiency, however. Seawater proportions in samples collected within the estuary were determined from their Mg content. Relationships between the concentrations of Mg and other metals in December 1992 (not shown) indicate that although dissolved Cd mixes conservatively across the salinity gradient, there is significant removal of Cu and Zn from the water column onto suspended particles and/or bottom sediment. Since dissolved Cd passes the estuary without significant removal, it can be used as a reference to determine the relative proportion of different metals over the several orders of magnitude in concentration spanned by waters in the Gulf of Cadiz, the Strait of Gilbraltar, and the western Mediterranean. Despite the different sampling years and run-off conditions, extrapolation of the shelf water data shows that the relationships between concentrations of Cd and other metals in surface waters throughout this region are dominated by input from a single source, the Tinto-Odiel estuary (Fig. 2). The data confirm that Ni is insufficiently enriched in the estuary to significantly affect the composition of surface waters of the Gulf of Cadiz. Leblanc et al. (1995) and Elbaz-Poulichet and Leblanc (1996) recently reached similar conclusions on the basis of dissolved metal concentrations measured in water from the Rio Tinto collected in July 1994.

The unusual features of Tinto River water can be attributed to mining of the sulfide ore in the watershed. Upstream from the Rio Tinto mine, the pH of the river is 7.2 (Garcia-Vargas et al., 1980). The pH of the sample collected at Lucena del Puerto, 40 km upstream from the mouth, is 2.6; the

TABLE 1. COMPARISON OF SOURCE ORE AND RUN-OFF COMPOSITION IN TINTO-ODIEL WATERSHED

Element	Sulfide ore (µg/g)	Continental crust (µg/g)	Enrichment factor	Rio Tinto water ($\times 10^{-6}$ mol/kg)	Mobilization relative to S
S	500000	260	1900	30000	1
Ag	18	0.07	240	<0.0006	<0.002
Al	(30000)*	160000	(0.2)	3200	(1.5)
As	4000	1.8	2200	2.2	0.46
Cd	(6.9)†	0.2	(34)	2.0	(17)
Co	100	25	4	19	4.6
Cu	6900	55	120	390	3.6
Fe	420000	72000	5.8	8800	0.61
Mn	400	1000	0.4	240	17
Ni	13	75	0.2	7.8	18
Pb	7600	12	630	0.43	0.006
Zn	13000	70	190	920	2.4

Note: Co, Cu, Mn, Ni, Pb, and Zn data are mean for La Zarza ore (Strauss et al., 1981). Ag and As data show mean for Iberian pyrite belt (Strauss et al., 1977). Abundances in average continental crust from Taylor (1964). Rio Tinto dissolved-metal concentrations were determined by graphite furnace atomic absorption spectroscopy for Ag, Al, As, Cd, Co, Cu, Fe, Mn, Ni, Pb, and Zn. The sulfate concentration was determined by the method of Tabatabai (1974). As and Co data for Rio Tinto water are from Vatland (1996).

*Al from Strauss et al., (1981) for rock sample #23 with high sulfide content.

†Cd from Murray Brook deposit of northeastern Canada similar in composition to Rio Tinto ore (Boyle, 1994).

decrease is due to sulfide oxidation. The riverine sulfate flux, calculated from a 30×10^{-3} mol/kg concentration (Table 1) and the Tinto-Odiel River flow, corresponds to about 60% of the 1 Mt/yr mining rate of S in the Tinto-Odiel watershed over the past 100 yr (Strauss et al., 1977; Pinedo, 1963). Both Cu and Zn are enriched more than 100-fold in the ore relative to the mean composition of the Earth's crust (Table 1). Because S is particularly enriched in the ore and very mobile once oxidized, we can use it to index the relative mobility of other constituents in the ore. On the basis of a comparison of ore and river water composition normalized to sulfur, metals listed in Table 1 can be grouped into four categories: (1) Cd, Co, Cu, and Zn are enriched in the ore and possibly more mobile than S; (2) As, Fe, and S are enriched in the ore and of comparable mobility; (3) Ag and Pb are enriched in the ore but highly immobile; (4) Mn and Ni are somewhat depleted in the ore but enriched in the river. The last group suggests mobilization from other associated ores in the Iberian pyrite belt enriched in these elements (documented for Mn) or from surrounding soils.

HISTORY OF CONTAMINATION

Mining activities in the Tinto-Odiel watershed have also affected the composition of estuarine and shelf sediments. Sediment enrichments attributable to mining do not span the same range as dissolved metal levels in the water column, but a plume of elevated Cu and Zn concentrations in surface sediments of the Gulf of Cadiz has been traced to its origin in the Tinto-Odiel estuary (Nelson and Lamothe, 1993; Palanques et al., 1995). Available data for metal enrichments in estuarine sediments as well as in acorn barnacles confirm that contamination of the nearby Guadiana river and estuary comes nowhere close to levels observed in the Tinto-Odiel system (Stenner and Nickless, 1975; Nelson and Lamothe, 1993). Two sediment cores within the mud blanket that covers the continental shelf about 25 km south of the estuary (TG25b and TG22 in Fig. 1; Nelson et al., 1997) were selected to determine when the impact of mining activities reached regional proportions. In both cores Zn profiles show concentrations as high as 300 µg/g in the upper part of the core relative to downcore background values of 50 µg/g (Fig. 3). Also significantly enriched in these cores is Cu (50 versus 11 µg/g in TG25b), but Cd is not (~0.1 µg/g), probably owing to its lower affinity for particles. In both cores, the earliest Cu and Zn enrichments relative to background are detected at 15.5 cm depth. Although natural processes can, under certain conditions, produce metal enrichments in surface sediments, the very consistent pattern seen in these two cores most likely reflects input of mining effluents via the Tinto-Odiel estuary.

The timing of the onset of contamination is determined independently from age models for cores TG25b and TG22 constrained by the naturally occurring radioisotope ^{210}Pb (half-life of 22.3 yr).

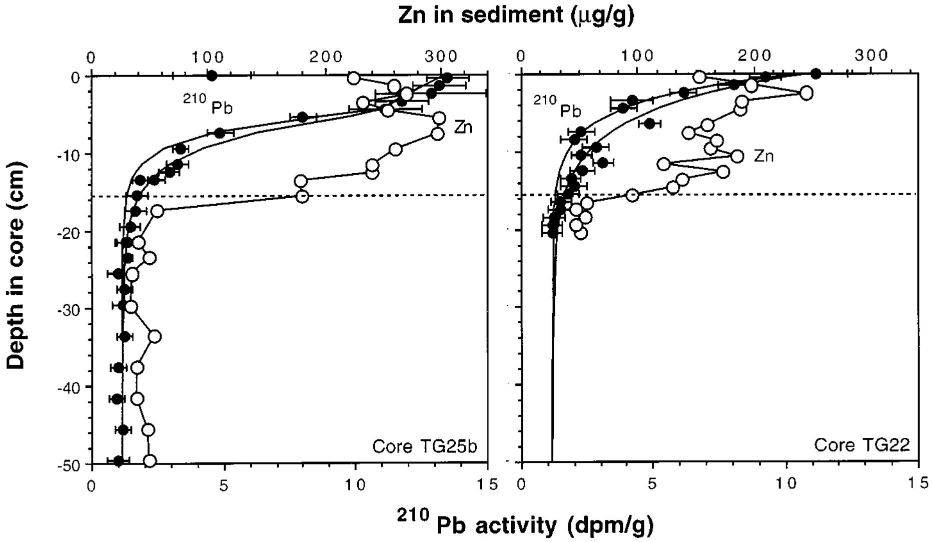

Figure 3. Downcore distributions of natural radionuclide ^{210}Pb in disintegrations per min/g (dpm/g) and metal Zn in sediment of cores TG25b (lat 37°00.8'N, long 7°11.7'W, 56 m depth) and TG22 (lat 36°53.0'N, long 6°54.1'W, 69 m depth) collected in 1986 from continental shelf south of Tinto-Odiel estuary. Horizontal dashed line indicates first departure of Zn concentration from background at 15.5 cm in both cores. In top 5 cm of core TG25b ^{210}Pb activities indicate mixing by benthic biota that can be modeled with a constant mixing-rate-coefficient of 11 cm^2/yr. No such mixed layer is visible in core TG22. Spatial variability in rate of coastal sediment mixing has been documented previously (Carpenter et al., 1984). Solid lines show model ^{210}Pb profiles for both cores corresponding to range in sedimentation rate of 0.08–0.12 cm/yr in core TG25 and 0.11–0.16 cm/yr in core TG22. Based on best fit model, ages of 15.5 cm horizon in cores TG25b and TG22 are 130 and 120 yr, respectively.

Fine-grained particles in the water column are initially enriched in ^{210}Pb relative to the radioactivity supported by their ^{238}U content. As these particles accumulate over the shelf, excess ^{210}Pb decays, and the resulting exponential activity profile with depth can be used to determine the sedimentation rate (Carpenter et al., 1984). In core TG25b, sediment mixing by benthic organisms down to 5 cm depth must also be taken into account. Figure 3 shows that the ^{210}Pb data are consistent with sedimentation rates ranging from 0.08–0.12 cm/yr in core TG25b and 0.11–0.16 cm/yr in core TG22. The sedimentation rate over the past century in core TG25b is consistent with a long-term sedimentation rate of 0.07 cm/yr calculated from the difference in the apparent radiocarbon age of organic matter at 2–20 cm (4780 ± 100 ^{14}C yr) and 206–223 cm (7980 ± 130 ^{14}C yr, Nelson et al., 1997). Therefore, the earliest interval with detectable Zn contamination was deposited sometime between 1840 and 1890. Figure 4 shows that this interval corresponds to the period of rapid increase in Cu production at the Rio Tinto mine (Harvey, 1981).

The sediment contamination record allows us to evaluate the relative importance of other metal inputs to the Gulf of Cadiz. From 1977 to 1990, metal-rich acid effluents were transported daily from a titanium oxide processing plant operating in the Tinto-Odiel estuary and dumped near the center of the Gulf of Cadiz (van Geen et al., 1991; Nelson and Lamothe, 1993; Palanques et al., 1995). Because shelf sediments were contaminated well before dumping started and Cu and Zn inputs due to offshore dumping are equivalent to a small fraction of the river input to the Tinto-Odiel estuary (from Table 1, the mean discharge, and van Geen et al., 1991), it seems unlikely that offshore dumping could have created the surface water metal enrichment pattern of Figure 1.

Although increased atmospheric Cu input during the peak of Roman activity in Spain has been detected as far away as Greenland (Hong et al., 1996), the impact on shelf sediments of the Gulf of Cadiz via the estuarine pathway during Roman times does not seem to have been comparable to that of mining over the past 120 yr. On the basis of a long-term mean sedimentation rate of ~0.07 cm/yr in the lower part of core TG25b, the

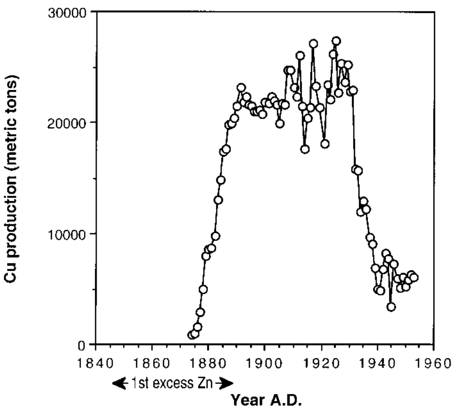

Figure 4. Annual Cu production at Rio Tinto mine (Harvey, 1981). Arrows show range in estimates of first occurence of detectable Zn contamination in Gulf of Cadiz shelf cores.

age of the horizon at 223 cm can be estimated at ~3000 yr B.P. Because no significant Zn enrichments were detected below 15.5 cm depth throughout this core, we see no evidence of shelf sediment contamination due to Roman mining.

CONCLUSIONS AND IMPLICATIONS

The effect of mining on the composition of the Tinto river water is typical for sulfide ores. The composition of a number of Welsh streams draining areas that have also been mined since Roman times (Fuge et al., 1994), for instance, closely resembles the river data in Table 1. To our knowledge, the present study is the first recognition of a metal signature originating mainly from one specific mining area that extends over several hundred kilometres into the sea. Because run-off in the region is highly variable seasonally and interannually, the extent of the Tinto-Odiel dissolved metal plume into the Gulf of Cadiz and the western Mediterranean is likely to vary as well (van Geen et al, 1991).

Two cores show that metal concentrations in shelf sediments increased during the second half of the 19th century at the time of a rapid increase in the scale of exploitation of the Rio Tinto mine. The sediment cores also indicate that metal inputs from the Tinto-Odiel may have decreased significantly over the past few decades, especially if the considerable lag expected from mixing of sediment in the watershed and on the continental shelf is taken into account (Fig. 3). The reduction may be due to the reduction in mining at Rio Tinto and improvement in ore extraction and treatment technology in other mines where activities are concentrated today. The present scale of contamination suggests that it will be difficult to restore the Tinto-Odiel estuary to its condition before mining on an industrial scale began.

It is not known to what extent metal contamination of river water and sediment in the Tinto-Odiel estuary over the past century has affected the health of the local population. Inhabitants of the area still consume shellfish from the estuary as well as domestic animal products from the watershed. The state of the Tinto-Odiel estuary presents an opportunity to determine the impact of metal contamination by comparing the incidence of various illnesses in the area with that in of one of the nearby uncontaminated estuaries (Nelson and Lamothe, 1993).

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