

Rio Tinto estuary (Spain): 5000 years of pollution

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Abstract Mining of massive sulfide deposits in southwestern Spain extending back to the Copper and Bronze Ages has resulted in the pollution of the Rio Tinto fluvial-estuarine complex, the site of Columbus' departure for the New World in 1492. Additional sources of potential pollution include the large industrial complex at Huelva near the lower portion of the estuary. Extensive analysis of surface sediment samples and cores has established that there are no geographic trends in the distribution of the pollutants, which include Cu, Fe, Pb, Zn, Ti, Ba, Cr, V and Co. These data have, however, demonstrated that tidal flux within the estuary carries phosphorus and perhaps other elements from the industrial complex at Huelva to the tidal limit of the system, several kilometers upstream from the discharge site. Radiometric analysis of short cores shows that sedimentation rates over at least the past couple of centuries have been about 0.3 cm/year. These data and that from a single deep core demonstrate that the estuary was polluted from mining activity long before the large-scale operations began in the late nineteenth century.

Key words Sediment pollution · Massive sulfides · Phosphate · Open-pit mining · Estuary

Introduction

The Rio Tinto system in the province of Huelva, southwestern Spain, has great historical significance as well as environmental interest. It is one of the most polluted fluvial-estuarine systems in the world and most likely has been so for thousands of years. It is in the headwaters of this river that mining supporting the Copper Age and Bronze Age took place. The estuary, at the town of Palos de la Frontera, was the origin of Columbus' expedition in 1492 and for subsequent trips. Most recently, the city of Huelva has become the site of one of the most polluted industrial areas of the world. It is possible, however, that the pollution of the system began thousands of years ago with the original mining of the massive sulfide deposits near the headwaters of the Rio Tinto.

This investigation was conducted in order to answer the following questions:

1. What is the level and distribution of metals and other important pollutants in the sediments of the system?
2. What is the influence, if any, of tidal transport of the pollutants being discharged in and near the industrial complex at Huelva?
3. What is the chronology associated with the pollutants and to what extent, if any, have they been incorporated into the sediments that have accumulated in the estuary?

Study area

The massive sulfide deposit called the Iberian Pyrite Belt is one of the largest and most famous of such deposits in the world. It extends in essentially an east to west orientation across about 250 km of southwestern Spain and southern Portugal (Fig. 1) with an average width of 30–40 km. The thickness of the complex ranges up to hundreds of meters. The rich ore body is limited to a length of 5 km and is 750 m wide and 40 m thick. These sulfides were formed in the early Carboniferous, about 300–350 Ma, over a sequence of Devonian shales and quartz arenites and are overlain by Lower Carboniferous turbidites (Moreno 1993). The mineralization was produced by tremendous hydrothermal activity on the sea floor during a period of intense volcanic activity. The

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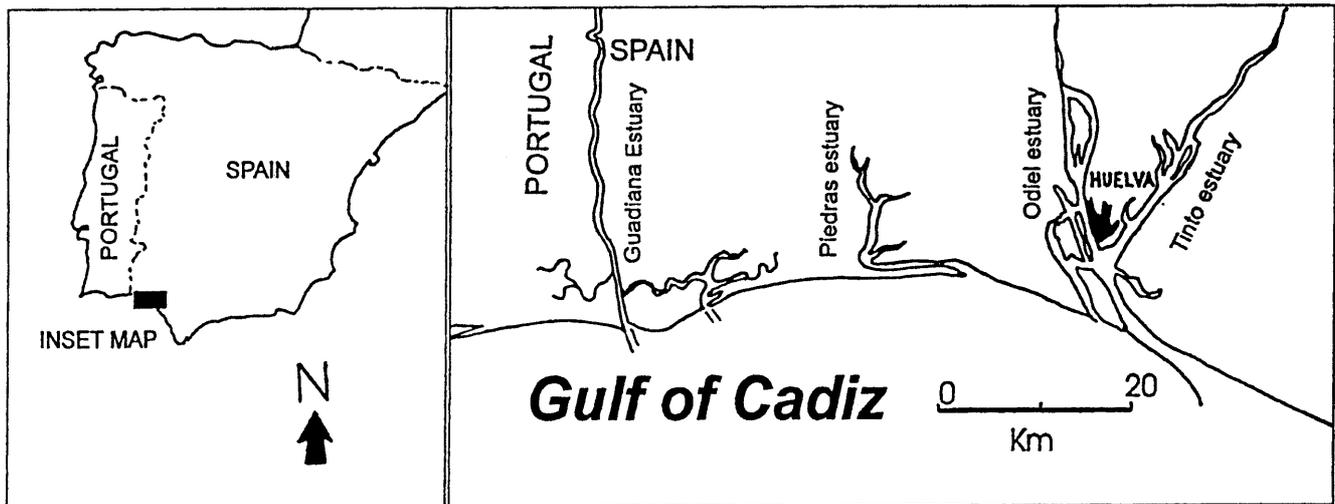


Fig. 1

Map showing the location of the Rio Tinto system in south-western Spain

massive deposit is very rich in Fe, Cu, Zn, As, Pb, Ag and Au. Deformation of this complex took place during the Hercenian Orogeny (Strauss and others 1977).

Historical perspective

Mining of these massive sulfide deposits has been going on for about 5000 years, beginning with the Iberians and Tartessians who developed the first mine about 3000 b.c. near the present community of Nerva (Fig. 2). This underground, small-scale operation was followed by that of the Phoenicians (2800–2600 b.p.) and the Romans (2000–1800 b.p.). The area is the site of the beginnings of the Copper Age and the Bronze Age (Coles and Harding 1979), and the Romans made some of their first coins from materials mined here, especially the silver and gold. Subsequent cultures, including the Visigoths (1600–1300 b.p.) and Moors (1300–500 b.p.), essentially abandoned the mining operations. Then in the nineteenth century the mining was taken over by the United Kingdom, and large-scale, open-pit operations prevailed until the deposits had been essentially depleted about a century later. Peak production for the large volume products such as pyrite was between 1875 and 1930 (Ferrero 1988). The copper production was stopped in 1986 and silver and gold production ended in 1996. A much smaller-scale copper production was initiated again in 1994 but proved uneconomic and was halted in 1998.

The amount of material excavated from these ancient operations has been estimated from the volume of waste produced. The Tartessians removed about 3 million tons using small galleries and shallow depths with typically only one or two people working the mine. The Romans

expanded the operations with larger galleries and greater depths. They dug below the water table and used clever water-wheel systems to pump the galleries dry. These operations accounted for about 24.5 million metric tons of material (Flores 1979). The expansion of the mining to open-pit methods led to the total production of about 1600 million metric tons of material.

The other and recent aspect of the potential pollution of this fluvial-estuarine system is the industrialization of the Huelva area beginning in 1967. Within only a few years, operations began of (1) a huge phosphate beneficiation plant which processes raw ore from nearby Morocco and other locations, (2) a plant for processing Australian heavy minerals such as magnetite and ilmenite (“black sand”) and (3) a large paper mill located at San Juan del Puerto (Fig. 2). Each of these industries is contributing huge volumes of pollutants to the local estuaries. The phosphate plant has produced millions of tons of phospho-gypsum which is piled along the west margin of the Rio Tinto estuary (Fig. 2). Tailings of the pyrite plant are similarly located and the paper plant discharges a large volume of contaminated wastewater.

Rio Tinto system

The Rio Tinto drainage system includes an area of 1670 km² and the river/estuary extends for 95 km to the mouth near Huelva. The headwaters of the river are in the area of intense mining from which the river descends from elevations near 400 m down to about 40 m at the town of Niebla (Fig. 2) below which meandering begins with a modest flood plain. The annual discharge of the Rio Tinto, as gauged at Niebla, has ranged from almost nothing to about 350 Hm³ over the period of record (Fig. 3a). There is great variation in discharge during the hydrological year with most taking place during the winter whereas during the summer it is almost nothing (Fig. 3b). Floods have played a major role in the Rio Tin-

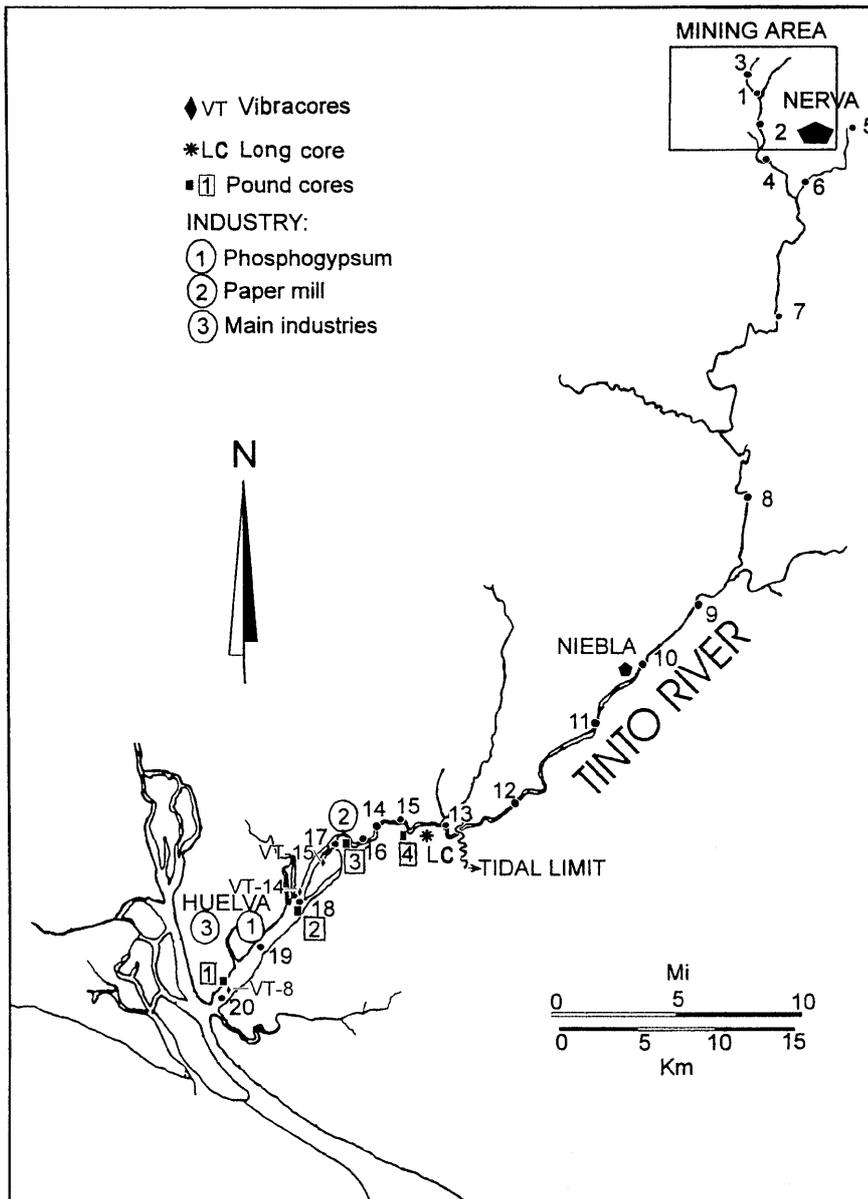


Fig. 2
Map of the Rio Tinto system showing the locations of mining and polluting industries, surface sediment samples, short pound cores and the long core

to with the most recent taking place in 1995 (Schell and others 1996).

Tidal influence begins a few kilometers upstream from the community of San Juan del Puerto (Fig. 2). The estuarine portion of this system consists of extensive intertidal and supratidal flats with marsh fringes typically just above neap high tide. Mean tidal range is 2.2 m at the mouth of the estuary with some decrease upstream (Fig. 4). Water quality of this estuary is extremely poor with low tide pH values typically at 2.0–2.5. Flood tides bring in Atlantic water and raise the pH to near neutral levels in the lower portion of the estuary. There is no macrobenthic community and only during flood tides are there nekton or plankton in the estuary. The only organisms in the river portion of the system are microalgae, bacteria and fungi (Moreira and others 1997).

The estuarine portion of the Rio Tinto system is characterized by braided channel systems of gravel, sand and mud with terrigenous gravel being limited to the uppermost portion. Tidal channels are typically floored by bedforms in sand with mud concentrated on the channel margins and in the lower intertidal zones. Shell material is conspicuously absent from the surface sediments of the estuary.

Previous work

The scientific literature on the Rio Tinto is quite sparse until about 1990. During the 1990s, there was an explosion of research effort invested into this region, much of

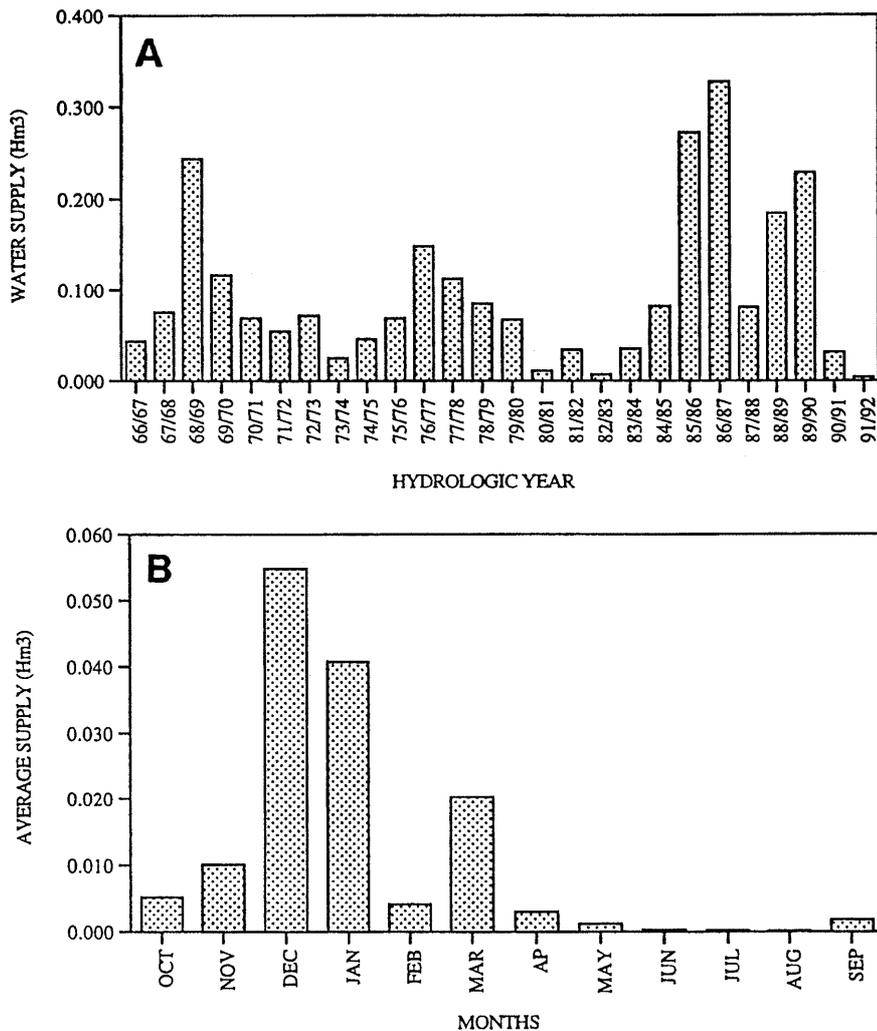


Fig. 3 Hydrologic data for a long-term discharge and b annual discharge patterns over the period of 1966–1992 for the Rio Tinto taken at the town of Niebla (see Fig. 2 for location)

it aimed at the pollution of the Rio Tinto and the adjacent Odiel River. Efforts have included analyses of both the water and the sediments of the estuary but none have been very comprehensive.

Although there had been considerable effort directed toward the ore body itself (e.g. Strauss and others 1977, 1981; Klau and Large 1980) and to the history of the mining in the region (e.g. Flores 1979; Harvey 1981; Morral 1990) there had been no significant attempt to assess the influence of the mining activities on the river and estuary of the Rio Tinto system until recently.

A group led by R. Amils from the University of Automa Madrid has been investigating the microbial community of the estuary with surprising results (e.g. Lopez-Arcilla and others 1994; Moreira and others 1997). They have found an abundant and diverse assemblage of bacteria, algae and fungi inhabiting these very acidic waters. Water chemistry of the Rio Tinto has been well documented and the database is growing rapidly. The local environmental authorities have been collecting water samples on a weekly basis from a single station in the middle of the estuary near the phospho-gypsum stacks

(Fig. 2) since 1977. They measure pH, dissolved oxygen and salinity, but their sampling is weekly, regardless of the tidal situation, thus giving a great range in these parameters depending on tidal stage.

Most of the data on water samples are from the river and estuary and few from the mining region. Published data of the analyses and the locations of the samples within the estuary are not shown in detail (Leblanc and others 1995; van Geen and others 1997). Both investigations conclude that the estuary system is discharging high concentrations of metal pollutants into the Gulf of Cadiz and beyond. High levels of radioactivity have also been documented in estuarine waters as a consequence of the beneficiation process being carried out at the phosphate plant where effluent is discharged into both the Odiel and Rio Tinto systems (Martinez-Aguirre and Garcia-Leon 1991). Borrego and others (1999) have analyzed samples from seven locations near the industrial complexes along the Odiel, the Rio Tinto and the combined estuaries (Huelva estuary) for numerous parameters and have found very elevated concentrations from industrial and domestic waste. Visual indications of the high levels of pollution

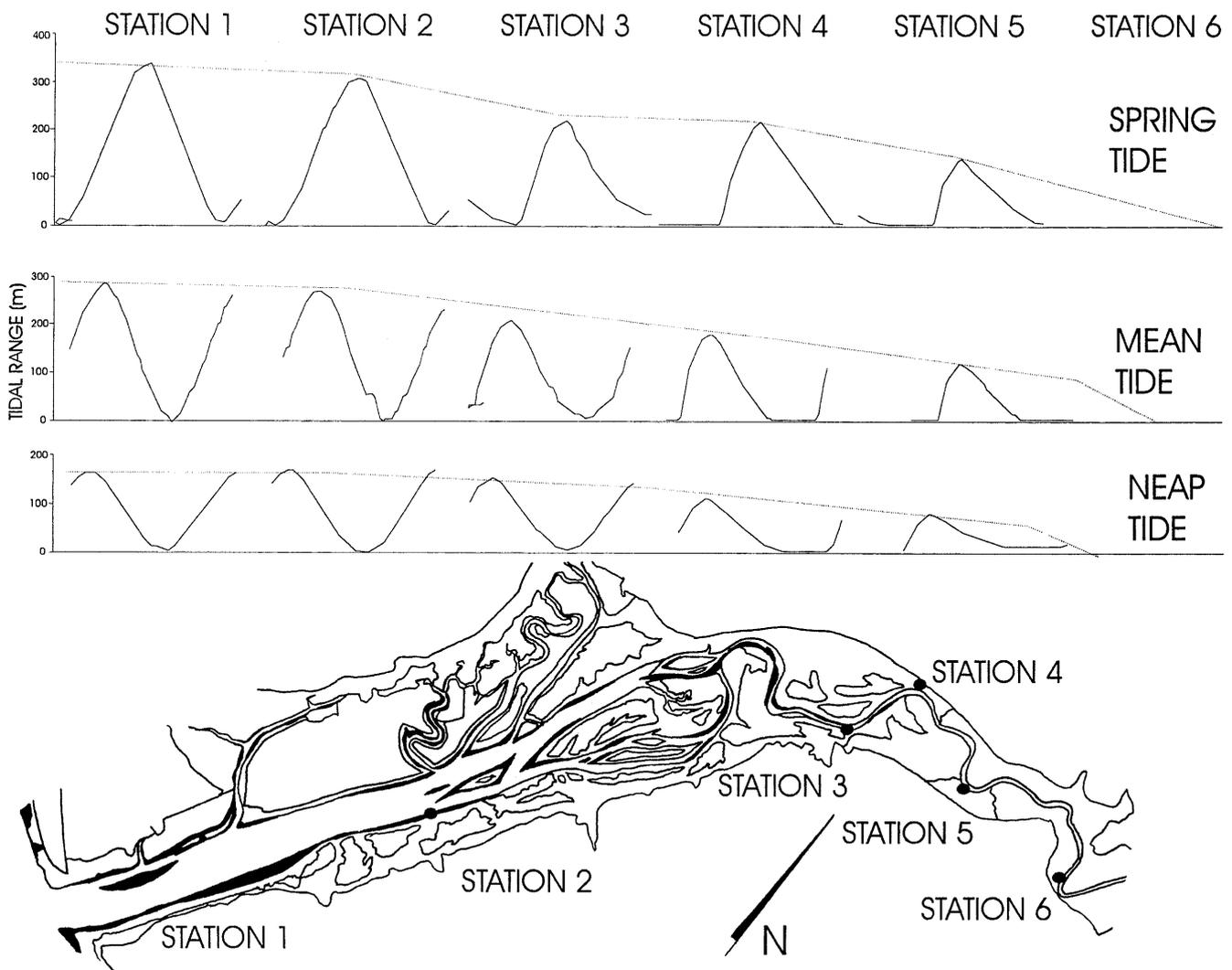


Fig. 4

Tidal curves showing the change in range up the estuary for spring, mean and neap conditions

are the red color of the water in the river and the presence of large amounts of sulfur in modern fluvial sediments (Fig. 5).

Sediment samples have been analyzed from several locations throughout both the Odiel and Rio Tinto systems. Probably the most geographically comprehensive study to date has considered both of these fluvial-estuarine complexes (Lissen 1991). The data set extends from the headwaters of both drainage systems to the open sea. More recently, Nelson and Lamothe (1993) looked at the anomalous heavy metal concentrations along both systems as well, but had a limited number of samples (11 samples from 6 locations). Another recent investigation of heavy metals was undertaken for 12 sites from the mine area to the mouth of the estuary (Schell and others 1996). These studies all concluded that there were quite elevated concentrations of many heavy metals (e.g. Pb, Cu, Ca, Mn,

As, Zn, Fe, Ag) in the estuaries as a consequence of the mining activities. They did not address the contributions of the phosphate plant at Huelva nor the influence, if any, of tidal flux in distributing these pollutants. All authors agree that the mining began about 5000 years ago but few have tried to unravel the chronology of the significant pollution in the fluvial-estuarine system. Two publications have considered the time framework of this pollution using limited data and reaching conflicting results. Detailed examination and analysis of a 50-m core taken from the marsh adjacent to the Odiel estuary at Huelva City go a long way toward interpreting the history of mining pollution (Ruiz and others 1998). Twenty samples were taken from the core and analyzed for 11 oxides and 16 elements, many of which might have had their origins in the mining operations or in the nearby industrial complex. The beginning of significant contributions of heavy metals from the mining activity is about 5 m below the top of the core. A ^{14}C date of 5390 ± 155 years b.p. was obtained at 10 m down the core. The authors interpret the first occurrence of the concentrations of pollutants to represent the beginnings of mining about 4800 years ago, although there is no radiomet-



Fig. 5

Photographs showing pollution in the Rio Tinto; **a** the red color from which the river gets its name shown here above the influence of tides and **b** abundant sulfur that has accumulated in the fine sediments near the landward limit of tidal influence

ric data to corroborate this interpretation. Recent pollution is assigned to the 0.3–0.4-m layer at the top of the natural portion of the core and therefore is assigned a date of about 1967, although no Pb or Cs series dating was done on the core.

A more distant pair of short cores was collected from the continental shelf in the Gulf of Cadiz off the mouth of the estuary at water depths of 56 and 69 m (van Geen and others 1997). The analyses for metal pollutants and Pb-210 series dating showed that the earliest level with detectable Zn contamination accumulated between 1840 and 1890, the period when large-scale mining operations began. This is in marked contrast to the data of Ruiz and others (1998) which show considerable contamination beginning at about the time of the start of mining practices thousands of years ago.

Database

Surface sediment samples for geochemical analysis were taken from throughout the fluvial-estuarine system

(Fig. 2). Effort was made to include sites within the mining area, from an apparently pristine stream near the headwaters of the Rio Tinto and from throughout the fluvial-dominated portion of the system. Samples were also taken of the country rock in the mining area. Some limitations were posed by access, especially in the area of high relief just below the mining areas. The estuarine portion of the system where current industry is located was sampled so as to include material from both sides of the estuary (Fig. 2).

Short pound cores were taken from the channel margins of the estuary and near its upper limits. Geochemical analyses and radiometric dating were done for three vibracores taken from various locations in the estuary (Fig. 2).

Initial geochemical analyses included the sand fraction of the samples but it was apparent that there were very low concentrations of pollutants in this portion of the sediment, a conclusion also reached by Nelson and Lamothé (1993). The mud fraction ($<63\ \mu\text{m}$) of the surface samples and of two of the pound cores was analyzed for nine oxides and eight trace elements by using an ARL DC plasma-emission spectrometer at the University of South Florida. The samples were dissolved in a 4:1 mixture of $\text{HF}:\text{HClO}_4$, evaporated to dryness and brought to final dilutions in 1 M HNO_3 . Solutions were diluted by a factor of 20 for analysis of major elements. Calibration curves were constructed using the US Geological Survey standards G-2, QLO, MAG-1 and SCO-1 which were prepared and analyzed with the samples. Precision for all major elements is within 1–2% except for phosphorus which is within 10%. Trace element precision is variable but is at least within 25%.

In addition to the geochemical analysis, Pb-210 series dating was conducted on the four pound cores in order to determine the recent chronology of pollution associated with the industrialization of Huelva in 1967 and the huge expansion of mining in the late nineteenth century. These analyses were conducted at Florida State University, Department of Oceanography by W. Burnett and associates.

Geochemical analysis of the vibracore samples included Cu, Zn, As and this was done at the University of Huelva by los Servicios Centrales using an ICP mass spectrometer.

Distribution of pollutant species in surface sediments

The obvious first step in trying to determine the source of pollutant species in the Rio Tinto system is to consider the distribution of the various elements downstream from the mining activities. A total of 43 sediment samples from 18 different distances from the mine area formed the database for determining if any downstream trends in concentration are present. There is no question

from these data that there are very elevated levels of most of the elements contained in the sulfide ore bodies throughout the Rio Tinto system. Some are orders of magnitude above normal background levels (Schell and others 1996). Important pollutants included in the analyses are Fe, Ti, Ba, Ni, Co, Cr, V, Zn and Cu. Other species concentrations that were determined, such as Al, Mg, Ca, K and Na, are either not important constituents of the ore body, or are not major pollutants, or they could come from sources such as the turbidites associated with the massive sulfide deposits.

As was stated by others (Nelson and Lamothe 1993; Schell and others 1996), there seems to be no down-

stream pattern to the concentrations (Table 1). Plots show way too much scatter to be significant (Fig. 6).

Influence of the phosphate industry

Phosphorus is not present in elevated levels in the upper reaches of the Rio Tinto but it is in the estuary (Table 1). The huge beneficiation plant in the Huelva industrial complex produces both large volumes of phospho-gyp-

Table 1
Chemical analyses of surface sediment samples. Rio Tinto fluvial/estuarine system. Geochemical data from the 43 surface sediment samples analyzed. Note that they are arranged with

the top of the table representing the mining site and the bottom being the mouth of the estuary. Elevated P_2O_5 values begin near the limit of tidal influence

Distance (km)	Sample	Site description	Al ₂ O ₃ (wt%)	Fe ₂ O ₃ (wt%)	MgO (wt%)	CaO (wt%)	MnO (wt%)	K ₂ O (wt%)	Na ₂ O (wt%)	TiO ₂ (wt%)	P ₂ O ₅ (wt%)	Sr (ppm)	Ba (ppm)	Ni (ppm)	Co (ppm)	Cr (ppm)	V (ppm)	Zn (ppm)	Cu (ppm)
11	3	Spoil pile outwash	5.25	3.86	0.2	0.11	0.006	1.76	0.14	0.62	0.08	76	12660	15	6	8	43	3200	325
3.6	5	Rio Jarama	15.46	1.83	1.9	1.27	0.385	2.66	0.91	0.64	0.13	73	682	34	15	16	111	2500	114
5.2	2	Fluvial	9.49	15.42	1.32	0.32	0.073	1.78	0.49	0.47	0.41	81	5908	48	21	19	107	14200	877
10	4	Open-pit mine	7.47	21.55	2.02	0.37	0.091	1.51	0.32	0.29	0.26	49	1768	63	37	53	109	23200	1090
12	6	Rio Jarama	25.44	2.29	2.27	2.02	0.258	2.5	3.4	1.4	0.15	143	572	49	24	0	158	14000	971
22.2	7 A	Fluvial	14.13	3.55	1.24	1.73	0.061	2.06	1.81	1.31	0.16	153	1380	33	18	27	155	2750	255
22.2	7B	Fluvial	4.94	8.1	0.6	0.26	0.026	0.98	0.34	0.35	0.11	42	444	25	13	61	54	10600	480
42.2	8 A	Fluvial	11.47	10.92	1.02	1.16	0.115	2.51	0.8	0.78	0.21	164	1993	49	24	0	158	14000	971
42.2	8B	Fluvial	6.27	7.64	0.4	0.17	0.022	1.44	0.35	0.27	0.14	38	589	24	9	27	93	8000	4 28
50.4	9 A	Fluvial	9.83	11.59	0.81	0.49	0.066	1.89	0.69	0.44		65	793	32	5	47	74	720	952
50.4	9B	Fluvial	7.03	11.72	0.71	0.35	0.035	1.39	0.46	0.33		49	570	36	6	62	82	10600	1040
50.4	9 C	Fluvial	11.63	13.87	0.72	0.27	0.039	2.05	1.09	0.57	0.29	211	1207	43	18	99	185	8260	241
50.4	9D	Fluvial	8.69	11.77	0.97	0.34	0.08	1.42	0.48	0.32		47	662	37	7	49	86	17800	1080
58.8	10 A	Fluvial	12.21	11.18	1.03	0.65	0.048	2.73	0.79	0.8	0.26	105	2210	36	17	0	165	13100	812
58.8	10B	Fluvial	7.36	18.6	0.49	0.15	0.023	1.56	0.46	0.35		50	748	33	5	46	99	6140	227
61.6	11 A	Fluvial	8.6	9.87	0.92	0.88	0.042	1.52	0.61	0.46	0.15	61	381	30	4	37	53	797	1150
61.6	11B	Fluvial	3.42	13.22	0.46	0.2	0.023	0.55	0.25	0.17		27	220	20	7	25	41	7830	476
61.6	11 C	Fluvial	11.75	9.48	0.89	0.47	0.036	2.51	0.9	0.64		102	1162	44	5	82	114	10000	552
68	12 A	Above tidal limit	10.38	10.77	1.07	1.02	0.046	2.07	0.83	0.65	0.18	83	345	16	2	27	33	233	341
68	12B	Above tidal limit	9.71	10.71	1.23	0.59	0.05	2.26	0.82	0.55		97	702	34	5	51	81	18200	604
71.4	13 A	Within tidal limit	7.87	14.65	0.81	0.84	0.043	1.75	0.61	0.49	0.27	78	333	17	2	27	42	400	317
71.4	13B	Within tidal limit	19.54	4.93	0.72	0.11	0.021	2.86	0.49	0.72	0.74	110	530	36	10	24	141	3250	181
75	15 A	Estuary	14.73	9.36	0.94	0.3	0.03	2.8	0.85	0.47	0.96	169	400	29	3	99	113	259	598
75	15B	Estuary	12.45	9.74	1.09	0.46	0.037	2.77	0.99	0.29	0.61	207	416	35	4	80	108	574	522
75	15C-1	Estuary	15.17	6.25	1.43	0.9	0.053	3.05	1.72	0.76		113	783	34	5	69	84	731	1160
75	15C-2	Estuary	14.74	9.5	1.31	0.34	0.038	3.53	1.74	0.52	0.2	134	758	41	5	84	125	602	775
76	14 A	Estuary	8.31	8.88	1.07	0.87	0.024	3.13	4.71	0.68	0.39	169	1246	32	6	50	73	4470	475
76	14B	Estuary	14.57	9.13	0.97	0.27	0.022	2.03	0.83	0.58	2.42	83	444	31	4	108	109	7410	293
76	14 C	Estuary	17.58	3.37	1.62	0.32	0.028	3.32	0.98	0.89	0.2	77	384	36	4	94	117	493	569
76	14D	Estuary	15.16	8.33	0.7	0.16	0.016	1.98	0.62	0.58	2.95	104	674	270	6	55	57	653	1100
78.2	16 A	Estuary	16.69	6.5	1.1	0.33	0.03	2.14	1.4	0.59	3.28	149	609	41	6	97	131	293	738
78.2	16B	Estuary	8.59	10.4	1.87	0.38	0.056	1.31	0.59	0.17	2.46	144	469	25	4	41	101	774	1020
78.2	16C-1	Estuary	13.9	5.7	1.47	0.69	0.05	2.28	3.03	0.64	0.15	109	354	34	5	89	87	369	275
78.2	16C-2	Estuary	16.97	3.6	2.86	2.21	0.121	2.93	1.73	0.64	0.15	112	379	45	7	102	97	213	213
81	17 A	Estuary	5.43	6.44	2.81	1.46	0.024	2.34	13.82	0.21	1.08	515	216	40	4	204	124	1110	990
81	17B	Estuary	7.59	10.62	2.9	0.38	0.072	0.68	3.39	0.16	1.26	192	652	34	7	46	136	2490	3000
81	17C-1	Estuary	17.69	4.73	2.09	0.34	0.046	2.95	2.44	0.61	0.2	86	388	39	4	92	100	725	2150
81	17C-2	Estuary	10.33	9.7	1.43	0.36	0.023	1.74	5.12	0.43	2.34	228	675	28	3	67	167	276	509
84.8	18 A	Gypsum stacks	15.35	5.28	1.54	0.45	0.035	2.46	2.25	0.66	1.37	96	508	45	5	89	128	5030	1340
84.8	18B-1	Gypsum stacks	8.03	8.16	2.63	0.78	0.047	1.66	9.01	0.22	1.56	397	479	34	7	51	108	1360	2930
84.8	18B-2	Gypsum stacks	12.87	9.81	1.37	0.38	0.036	2	1.08	0.38	2.4	101	384	39	3	71	90	300	496
84.8	18D-1	Gypsum stacks	15.11	3.36	2.56	9.7	0.036	2.25	3.15	0.51	0.27	140	302	56	15	113	74	278	140
92.4	20-A	Iron foundry	1.67	41.64	0.49	0.82	0.101	0.16	0.71	0.04	0.96	171	751	60	16	36	325	14700	3420

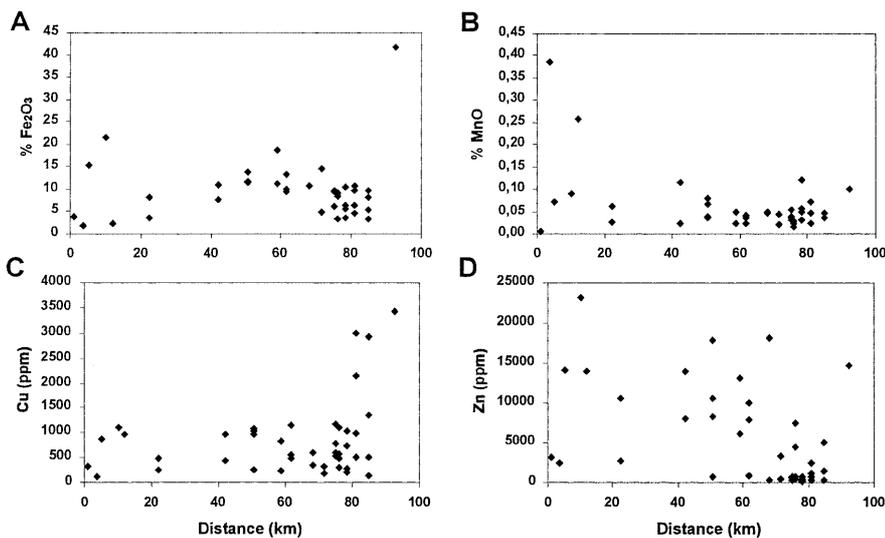


Fig. 6 Plots of the distribution downstream of selected pollutants showing the absence of any geographic trend. The highly elevated values for Fe_2O_3 and Cu near the mouth of the estuary reflect the proximity of the industrial complex where ore was processed

sum waste adjacent to the estuary and discharges fluids into it. The geographic distribution of the elevated phosphate concentrations (Table 1) extends to almost the tidal limit of the estuary at sample site 13B (Fig. 2). This indicates that the phosphate industry is polluting the Rio Tinto throughout the entire estuarine portion. It should also be noted that the analyses of the long core in the Odiel estuary adjacent to the Huelva industrial complex did not show any high levels of phosphate indicating that Rio Tinto waters do not travel into the Odiel estuary.

Rates of sediment accumulation

The four pound cores were collected in order to determine if a chronology could be developed for two important events in the Rio Tinto environments: (1) the expansion of mining to large-scale, open-pit procedures in the late nineteenth century and (2) the development of the major industrial complex at Huelva City beginning in 1967. Cores nearly 1 m long were taken and dated by Pb-210 methods with the expectation that their length would include at least a century of sediment accumulation. Each core was photographed, cut, described and sampled for analysis. Both geochemical analysis and dating were conducted for each of the samples taken.

Although there are individual spurious values, overall the results of the Pb-210 analyses are quite consistent for three of the cores (1–3) which show nearly the same rate of sediment accumulation; about 0.3 cm/year (Fig. 7). The fourth core, which was taken near the limit of tidal influence in the system, did not provide any stratigraphic trends based on the Pb-210 analysis (Fig. 7). This suggests that the sediment in the core accumulated as the result of a major discharge event that reworked sediment at least several decimeters in thickness. Although the most recent important flood events prior to the sampling

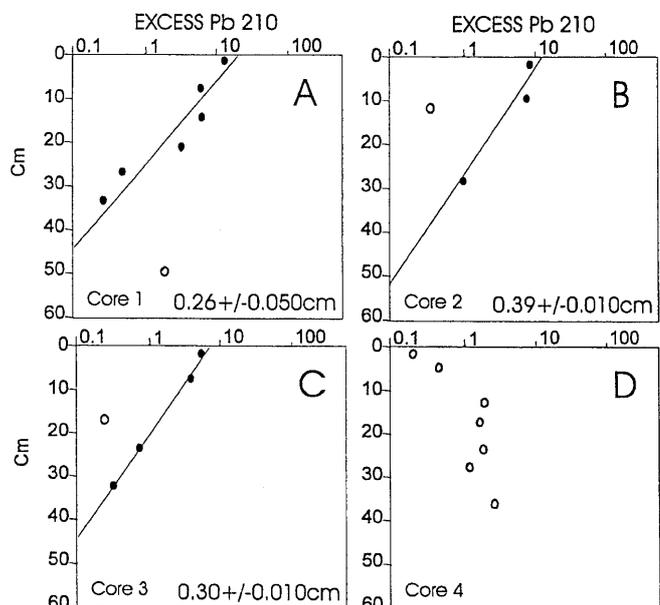


Fig. 7 Plots of Pb-210 analyses for four short-pound cores taken from along the tidal portion of the estuary. See Fig. 2 for locations of the cores. Note that there is no stratigraphic trend for core no. 4 and thus, no sedimentation rate was obtained for it

were in 1988 and 1989, it is likely that little sediment accumulated since that time because of (1) the location near the limit of tidal influence and (2) the absence of sediment discharge in this part of the system except during major flood events.

Using the rates of sediment accumulation determined for each of the cores, it is clear that the cores do represent more than 100 years of the accumulation of sediment in the Rio Tinto system. The lowermost sample analyzed in each of the two cores accumulated in 1830 (2) and 1810 (3), well before the large-scale mining operations began

in the headwaters area. These data compare with the dates of large-scale copper production in the early 1880s (Harvey 1981) and the first occurrence of excess zinc (1840–1890) in shelf cores as determined by van Geen and others (1997).

Of significance is the fact that the geochemical analyses of the push-core samples show that extremely elevated levels of the various pollutants produced by mining activity accumulated before the large-scale mining began in the late nineteenth century (Table 2). These data show that the Rio Tinto was polluted as the result of mining activities in its headwater areas that predate the large-scale, open-pit mining of the United Kingdom operators. Further testimony to this conclusion is provided by geochemical analysis of sediment samples from the vibracores (Fig. 8). Samples from throughout the cores show elevated concentrations of Cu and Zn. Specifically core VT-8, near the mouth of the Rio Tinto, had high concentrations of Cu and Zn to depths of 1.6 m and then a very high level of Cu (970 ppm) near the base of the core (2.4 m) with a 14-C date of 2020 years b.p. Core VT-14 taken from several kilometers upstream showed similar results. High concentrations of Cu and Zn are in the upper 0.5 m, then there is a decrease ending with a large concentration of Cu (978 ppm) at 3.2 m, near the base of the core. A 14-C date from this horizon yielded an age of 840 years b.p. The other core to be dated (15) is from the vicinity of core VT-14 and showed high levels of both Cu and Zn, with the latter remaining about the same throughout the core whereas Cu increased to 2466 ppm near the base (Fig. 8). That horizon was dated at 3640 years b.p. This apparent reverse trend is real. The surface of the location from which this core was taken is an area of erosion indicating that the upper part of the heavily polluted sequence was removed. The radiometric

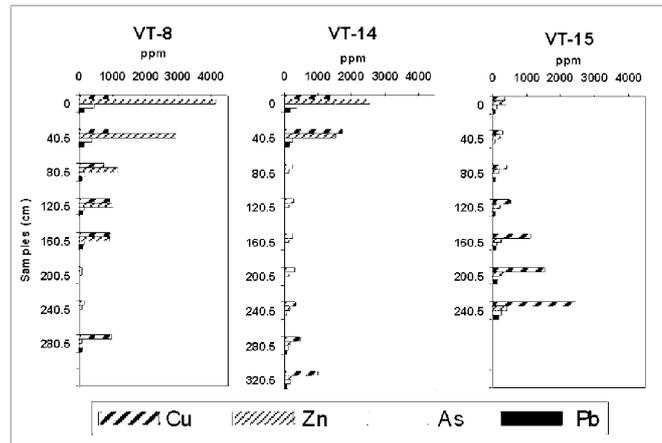


Fig. 8

Stratigraphic geochemical data from three vibracores taken from various locations in the Rio Tinto estuary. (see Fig. 2 for locations)

date (3640 YBP) shows that pollution was present in pre-Roman times.

An important aspect of these stratigraphic data is the fact that abundant shells, including articulated *Cerastoderma* and thick oyster accumulations, are present throughout the range of the high concentrations of Cu and Zn. This means that these organisms must have been able to exist and reproduce under such benthic conditions. Data from other studies indicate that the waters of the current estuary are highly contaminated with Cu and Zn, as well as other metals. It should be expected that if sediment was highly contaminated in the past, the water was also. This raises a significant question: are these taxa typically toler-

Table 2

Elemental analyses from selected vibracores. Geochemical data obtained from analysis of the three vibracores cores shown in

Sample	1	3	5	7	9	11	13	15	17
VT-8 (A)									
Depth (cm)	0	39.5	80.5	120.5	160.5	200.5	240.5	280.5	
Cu (ppm)	863.2	875	729.5	893.6	948.7	73.1	118.2	970	
Zn (ppm)	4122.9	2913.3	1175.3	1004.9	904.5	68.6	65.7	68.6	
As (ppm)	441	366.9	171.2	136	131.7	22.4	22.4	97.1	
Pb (ppm)	122.9	143.1	77.1	87.8	101.5	24.7	25.9	79.7	
VT-14 (B)									
Depth (cm)	0	39.5	80.5	120.5	160.5	200.5	240.5	280.5	320.5
Cu (ppm)	1349.4	1709.9	243.5	259.4	222.8	289.2	340.9	463.3	978.4
Zn (ppm)	2537.8	1508.2	147.9	138.4	119	136.3	150.4	168.4	208
As (ppm)	375.6	218.1	37.6	46.6	37	42.5	57.4	84	158.6
Pb (ppm)	170.2	125.8	47.2	43.9	39.4	47.2	49	54.1	71.6
VT-15 (C)									
Depth (cm)	0	39.5	80.5	120.5	160.5	200.5	240.5		
Cu (ppm)	355	286.7	419.3	513.3	1115.5	1546.9	2465.9		
Zn (ppm)	383	216.3	200.2	213.8	262.9	337.3	425		
As (ppm)	128	65.3	90.4	113.3	141.4	148.7	262.2		
Sample (ppm)	73.1	48	59.3	68.9	104.6	117.8	168.6		

Fig. 7. Elevated levels of pollutants appear much before the large-scale mining operations

ant of such high concentrations or were these populations genetically adapted to these toxic conditions? These core data demonstrate that pollution extended back well before the large-scale mining; at least to before the Roman activities and probably to the beginning of the original small, shaft mines.

Conclusions

Analysis and interpretation of a system-wide suite of surface sediment samples, four pound cores and three vibracores from the Rio Tinto fluvial-estuarine system permits the following important conclusions:

1. The data collected from the mines themselves to the mouth of the estuary corroborate that of other investigators in that there are highly elevated concentrations of numerous pollutant oxides and trace elements in surface sediments.
2. Likewise, our data do not show any downstream trends, high concentrations occur throughout the system.
3. Effluent produced by the phosphate beneficiation system in the Huelva industrial complex is being transported upstream to the tidal limit of the estuary as evidenced by elevated phosphorus concentrations.
4. Benthic fauna, especially oysters and clams, were able to exist and reproduce under very polluted estuarine conditions
5. Most importantly, it has been determined that the Rio Tinto system was polluted by mining activities well before the large-scale, open-pit practices of the late nineteenth century.

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