Historical metal inputs to the western Mediterranean associated with mining activities in SW Spain

J. M. Nieto
E. Jagoutz
Max-Planck-Institut für Chemie, Postfach 3060, 55020 Mainz, Germany

E. Puga
A. Maldonado
Instituto Andaluz de Ciencias de la Tierra, Av. Fuentenueva s/n, 18002 Granada, Spain

It has been recently shown that present trace metal inputs to the western Mediterranean are mainly controlled by atmospheric deposition of European and Saharan aerosols (Guieu *et al.*, 1997). However, fluvial inputs may be locally important, especially near industrialized and mining areas. Cu, Cd and Zn enrichments in the Alboran Sea have been explained as a consequence of inflow into the Mediterranean through the Strait of Gibraltar of metal enriched Atlantic surficial water of the Gulf of Cádiz (van Geen *et al.* 1997 and references therein). The metal enrichment in these shelf waters is related to the acid mine drainage of the Tinto and Odiel rivers (Elbaz-Poulichet and Leblanc, 1996; van Geen *et al.*, 1997). These two rivers drain the eastern part of the Iberian Pyrite Belt (IPB), one of the oldest and most important sulphide mining districts in the world, and their watershed includes giant and supergiant massive sulphide deposits with total reserves exceeding 1400 million tons. The mining activities in the IPB started in the Late Bronze Age, with major development during the Phoenician, Carthaginian and Roman times (from about 800 B.C. until 410 A.D.). After the Romans, mining activities were very limited and discontinuous, until their resurgence in the middle of the 19th century. The aim of this contribution is to evaluate historical and present metal inputs to the Gulf of Cádiz, and consequently to the western Mediterranean, from the mining and smelting activities in the eastern part of the Iberian Pyrite Belt.

Materials and results

We have measured trace metal contents of surface sediment samples from the Tinto and Odiel rivers and two sediment cores from the Gulf of Cádiz. River sediments were collected in September and December 1997. Two representative samples, one from the Tinto river (near Niebla, water pH = 2.7) and the other from the Odiel river (near Calañas, water pH = 3.6), have been included in Table 1. All river sediments show very high concentrations of Cu, Pb, Zn and As relative to average Continental Crust values. The concentrations are higher in clay-rich samples than in quartz-rich samples. Sediment cores were collected in 1986 on board *García del Cid* (campaign M-86-3). Two cores were selected for this study: G-163 (204 cm long) and G-177 (180 cm

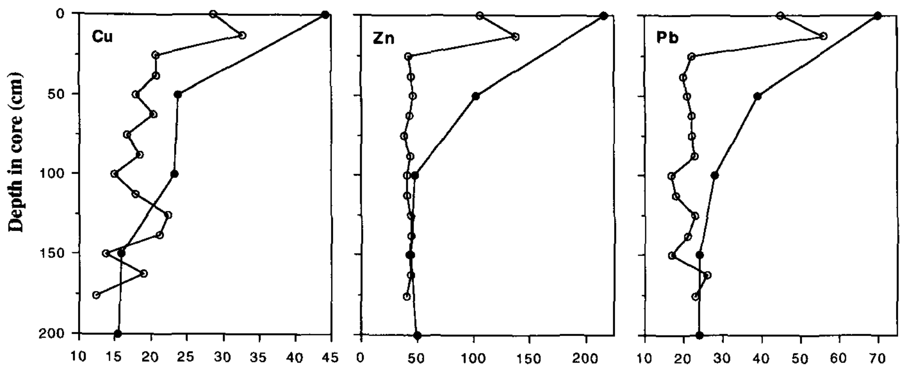

FIG. 1. Open circles: core G-177, filled circles: core G-163.

TABLE 1. Metal content of selected sediment samples (Al in %, others in ppm)

	Al	Cu	Zn	Pb	As
Tinto	0.47	277	334	210	1470
Odiel	0.42	730	205	113	190
G-177/0	1.21	28.7	106	45	17
G-177/180	1.13	12.3	39.3	23	5
G-163/0	1.21	44.2	216	70	14
G-163/200	1.28	15.4	49.9	24	<3

long), both of them from the area of highest metal enrichment in surface waters of the Gulf of Cádiz (van Geen *et al.*, 1997) at about 20 km offshore the city of Cádiz.

The selected cores are located in the mid-shelf Holocene mud facies, for which estimated long-term sedimentation rates range from 74 to 110 cm/ky, although a decrease in the rate is common in the middle to late Holocene (Nelson *et al.*, 1998). Trace metal contents in the top of the cores are high (Table 1), although much lower than in river sediments for Cu, Pb and As. In both cores trace metal contents decrease down-core until reaching background levels (Fig. 1). In core G-163 a progressive down-core decrease until 150 cm can be seen for Cu and Pb, while Zn reaches background levels at around 100 cm. On the other hand, as shown in Fig. 1, core G-177 shows a more complicated picture, which remains similar if the metal content is normalized to the Al content of the sample to take into account small changes in sediment sources or mineralogy. Zn content is at a maximum at 12.5 cm depth, reaching background levels in the next data point at 25 cm. However Cu, and to a lesser extent also Pb, seem to behave in a different way. After a maximum enrichment at 12.5 cm depth, the metal contents decrease until approximately 100 cm, then increase until giving a second relative maximum around 125 cm, and finally decrease to background levels similar to the ones reported by van Geen *et al.* (1997) for Cu (11 ppm) in a core about 25 km south of the Tinto-Odiel estuary.

Discussion

Van Geen *et al.* (1997) reported metal enrichments in the upper 15.5 cm of two cores from the mid-shelf Holocene mud facies of the Gulf of Cádiz and concluded that metal pollution on a regional scale in these sediments was restricted to the resurgence of the mining and smelting activities in the IPB in the middle of the 19th century. However, the data we have obtained so far suggest that metal pollution started well before this time. In fact, it has been estimated that since the Romans abandoned their workings from 70.000 to 80.000 tons of metallic copper must have been carried into the sea by the Tinto river (Checkland, 1967). Furthermore, Pb coming from the Rio Tinto area has been isotopically identified in Greenland ice dated to the Carthaginian and Roman times (Rosman *et al.*, 1997). Therefore, although more sediment cores should be studied, and precise sedimentation rates and/or absolute chronology should be established for each core (work is in progress), it can be concluded that trace metal inputs to the Gulf of Cádiz, and consequently to the western Mediterranean, started in ancient times as a result of extensive mining and smelting operations in SW Spain.

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