PERGAMON

Continental Shelf Research 21 (2001) 1961–1973

CONTINENTAL SHELF RESEARCH

www.elsevier.com/locate/csr

Review article

Metal biogeochemistry in the Tinto–Odiel rivers (Southern Spain) and in the Gulf of Cadiz: a synthesis of the results of TOROS project

Françoise Elbaz-Poulichet[a,*], Charlotte Braungardt[b], Eric Achterberg[b], Nicholas Morley[c], Daniel Cossa[d], Jean-Marie Beckers[e], Philippe Nomérange[e], Antonio Cruzado[f], Marc Leblanc[a]

[a] *Laboratoire Hydrosciences, UMR 5569, CNRS-University of Montpellier II, Place Eugene Bataillon, CCMSE, P.O. Box 057, 34095 Montpellier cedex 5, France*

[b] *Department of Environmental Sciences, University of Plymouth, Plymouth PL4 8AA, UK*

[c] *School of Ocean and Earth Sciences, Southampton Oceanography Center, University of Southampton, Waterside Campus, European Way, Southampton SO14 3ZH, UK*

[d] *IFREMER, Centre de Nantes, BP 21105, 44311 Nantes Cedex 03, France*

[e] *Université de Liège-Geohydrodynamics and Environmental Research (GHER). Sart Tilman B5, B-4000 Liege, Belgium*

[f] *Center d'Estudis Avancats de Blanes, Cami de Sta. Barbara, 17300 Blanes, Spain. CSIC/CEAB, Cami de Santa Barbara S/N, 17300 Blanes, Spain*

Received 7 January 2000; accepted 24 January 2001

Abstract

TOROS (Tinto–Odiel–River–Ocean Study) has been studying the biogeochemical processes which control metals and nutrients cycling in the mixing zone of the Tinto and Odiel rivers (SW Spain) and has established the fate of metals in the Gulf of Cadiz in relation to hydrodynamics and biological activity. The Tinto and Odiel rivers are small, with a combined mean discharge of $18\,m^3/s$. They drain the largest sulphide mineralisation in the world. Predominantly, Zn–Cu–Pb mineralisation has been worked since 2500 yr BC. The estuarine zone includes both an extensive area of salt marsh and an intensively industrialised urban area. As a consequence of pyrite oxidation, the Tinto and Odiel rivers are strongly acidic ($pH < 3$) with extremely high and variable metal concentrations. Transition metals are poorly removed from the water column in the mixing zone. Moreover, drainage from large phosphogypsum waste deposits contributes to As, Hg, U and phosphate contamination of the estuary. The collapse of the tailing reservoir at los Frailes in 1998 had not impacted the chemistry of the coastal waters up to 6 months later. A large plume of metal-rich waters due to the Tinto and Odiel discharges occurs along the coast of the Gulf of Cadiz. This plume affects seasonally the Atlantic inflow through the Strait of Gibraltar. The dispersion of the metal discharges has been simulated by injection of a tracer in the 3-D hydrodynamical model. Both

*Corresponding author. Tel.: +33-467-143931; fax: +33-467-144774.

E-mail address: francoise.elbaz@msem.univ-montp2.fr (F. Elbaz-Poulichet).

PII: S0278-4343(01)00037-1

model and field study clearly show the inflow of metal contaminated Spanish Shelf Water through the Strait of Gibraltar.

1. Introduction

Metals are introduced in waters by present or past mining activities, agriculture, industrial and domestic sewage. Unlike organic compounds or radionuclides, they do not degrade and thus are not expected to lose their toxic potential. In Europe, mining activity is one of the major sources of metals in the coastal zone. Mining activities leave metal-rich wastes which slowly release metals in the rivers. Several small and large rivers are affected by mine drainage: in France—the Dordogne river tributary of the Gironde, the Gardon and the Ardeche, tributaries of the Rhone; in England—the Tamar river, Lake district, etc; and in Spain—rivers discharging on the north-west and south-west coast.

Spain is affected by metal discharges, particularly in Andalucia, where the main rivers flowing into the Atlantic oceans drain metal mineralisation. In this region, mining activity has left enormous metal-rich wastes. Some mines are still active and there is an important risk of accidental metal spill. This risk has been materialised recently by the collapse of the retaining dam of a tailing reservoir in Aznalcollar (25 April 1998). Between 5 and $7 \times 10^6\,m^3$ of acid sludge and water (pH 2) were released into the Rio Agrio, a tributary of the river Guadiamar (Van Geen and Chase, 1998). The released sulphide sludge formed a layer of 1 m thick over a distance of 40 km, covering more than 4000–5000 ha of the river bed and flood plains of the Guadiamar, in addition to surrounding agricultural fields. In order to prevent contamination of the Donana Park (world's biosphere reserve of UNESCO), located at 45 km south of the mine, the waters have been diverted to the river Guadalquivir (40 km from its mouth).

The Gulf of Cadiz represents 5% of fish and shellfish catches for Spain (L. Suarez de Vivero, personal communication) and 10% for Portugal (Bebiano and Machado, 1992). In addition, the waters from the Gulf of Cadiz contribute to 15–20% of the Atlantic inflow to the Mediterranean Sea (Van Geen et al., 1991; Morley et al., 1999).

The aim of TOROS project was to study the fate of metals and nutrients in the Tinto and Odiel estuary and in the Gulf of Cadiz.

This paper summarises the main results obtained to date within this project. In order to evaluate the consequences of metal contamination in the Gulf of Cadiz for the Mediterranean Sea, data from the CANIGO (MAST, DGXII) have also been included in this study.

2. Studied area

The Tinto and Odiel (Fig. 1) are relatively small rivers (83 and 128 km in length, respectively). They have similar drainage basin areas (around $1680\,km^2$). The mean water discharges of the Odiel and the Tinto rivers are 15 and $3\,m^3/s$, respectively. Important variations above and below the mean values have been observed (Borrego-Flores, 1992), with extremely low discharges during dry periods.

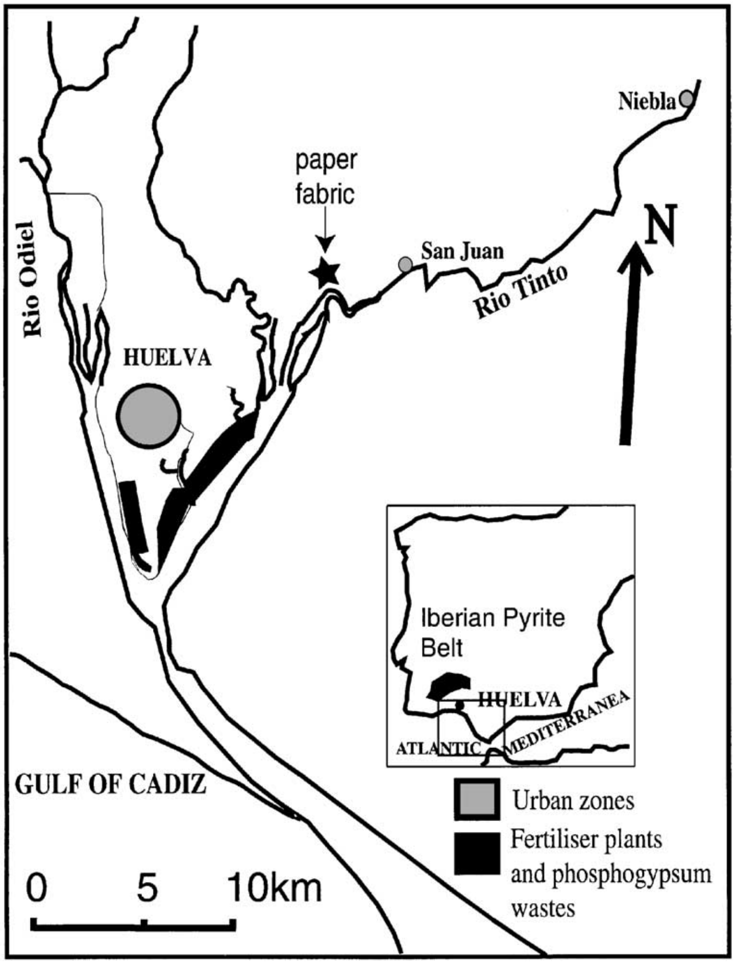

Fig. 1. Map of the study area. The Tinto and Odiel rivers meet in a common estuary (Ria) at Huelva.

Both rivers drain the Iberian Pyrite Belt, which is the largest sulphide deposit in the world and contains 1700 mt of sulphides (Leistel et al., 1998). This predominantly Zn–Cu–Pb mineralisation has been worked continuously since the Phoenician and Roman era (Rothenberg and Blanco Freijero, 1980). Nowadays, mining activity is less intense in the Odiel than in the Tinto catchment, where ore extraction is still taking place. On the upper Odiel river a dam has been built which traps sediments and acid mine wastes from ore processing plants. The oxidation of pyrite in the mining zone produces sulphuric acid and as a consequence, the Tinto and Odiel waters are acidic (pH 2.5, Nelson and Lamothe, 1993; Elbaz-Poulichet and Leblanc, 1996; Van Geen et al., 1997).

Tinto–Odiel estuary is a well- to partially mixed estuary with a maximum tidal amplitude of approximately 3 m. The estuarine zone is a site of major industrial activity. On the east bank of the Odiel are phosphate-based fertiliser plants, which generate important phosphogypsum wastes.

The wastes are dumped on the northern bank of the Tinto near the junction of the two rivers. Furthermore, the industrial area includes a pyrite roasting plant, a Cu smelting plant, an oil refinery and other chemical industries.

3. Methodology

Within the TOROS project, four surveys were carried out: November 1996, June 1997, April 1998 and October 1998. Four surveys of the Strait of Gibraltar were also performed in the framework of the CANIGO project from 1997 to 1999.

The methodology for water sampling, metal and nutrient analyses which involved intercomparison exercises and repeated runs of certified reference standards, has been described in Braungardt et al. (1999) and Elbaz-Poulichet et al. (1999, 2000).

The numerical hydrodynamic model—geohydrodynamics and environment research (GHER-3D) model (Beckers, 1992)—has been used to simulate the fate of metals in the Gulf of Cadiz. In order to get a more precise pattern of the dispersion of the river's plume, a nested model has been implemented in the Gulf of Cadiz. The nesting procedure (Nomerange, 1998) allows a very fine model domain (1.3 km horizontal resolution) to be used.

In order to assess the history of metal contamination, a 15 m deep core has been drilled in the Tinto floodplain (Fig. 1). Sediments have been dated using ^{14}C and analysed for metals.

4. History of metal contamination

The oldest findings indicate that metallurgical activities in the region date from 2500 yr BC (Briard, 1976; Rothenberg and Blanco Freijero, 1980). The drilled core of the Tinto confirms this old mining activity and shows that it also corresponds to an old history of metal inputs to the Tinto river and estuary. In this core, two metal-rich horizons are recognised (Fig. 2). The upper level corresponds to the modern mining; the lower horizon has been dated to 2530 yr BC (^{14}C AMS calibrated age). The presence of small droplets of likely slags (vesicular glasses with Fe–Si or C–Si compositions with up to 0.5% of Cu and sulphur) and fragments of charcoal in the lower horizon is compelling evidence for an active contemporaneous metallurgical activity (Leblanc et al., 2000).

5. Metal biogeochemistry in waters

5.1. Origin and metal (Fe, Ni, Cu, Zn, Cd, Pb, As and Hg) concentrations in the Tinto and Odiel mixing zones

The concentration ranges observed in the Tinto and Odiel are reported in Table 1. These values are variable but extremely high when compared to other European rivers. In the Odiel mixing zone dissolved Hg concentrations reach 0.165 nM. This value is 10 times higher than the

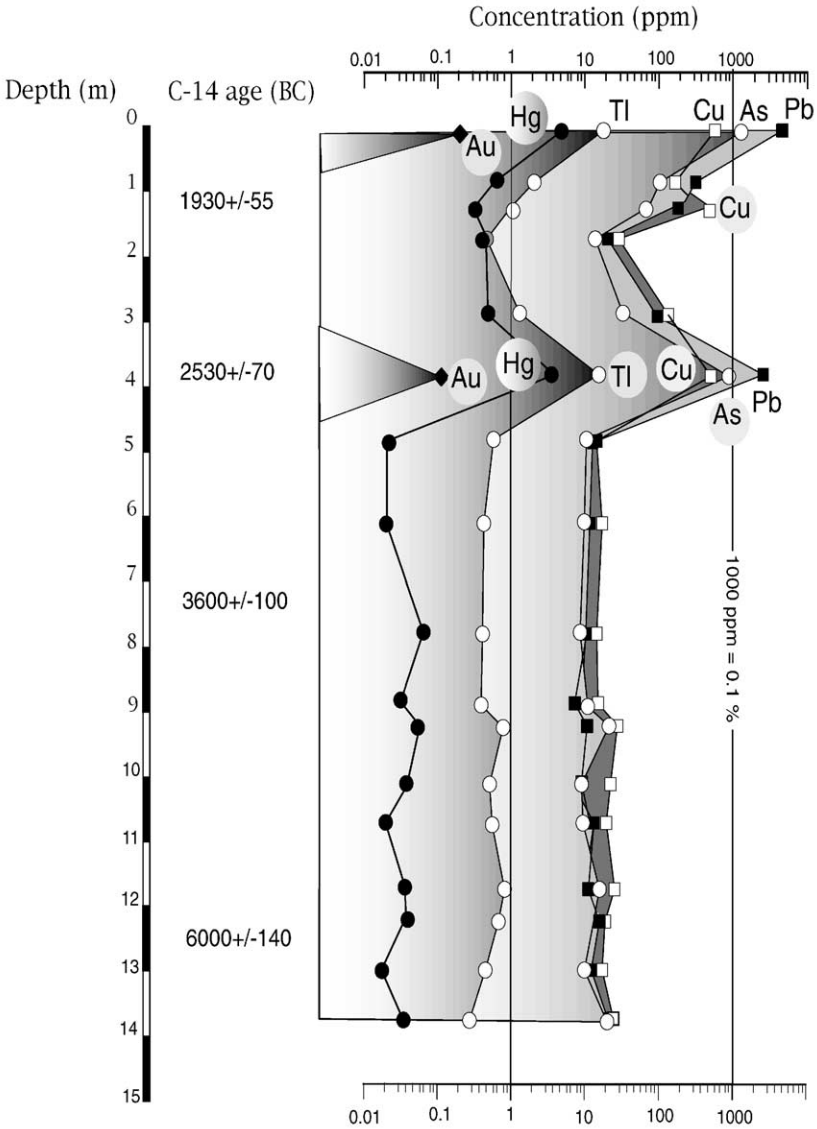

Fig. 2. Metal profiles in the sediments of the Tinto estuary.

maximum value observed in the Seine river which is considered as the most heavily contaminated French river (Cossa and Boutier, 1999).

The primary source of metal is the drainage of mining wastes. However, heavily contaminated sediments and phosphogypsum wastes constitute important secondary sources. The Hg concentration in the phosphogypsum waste is comprised between 1 and 4 ppm. The U concentration is 11 ppm. Assuming that the deposit contains 10^{10} kg of phosphogypsum (Travesi et al., 1997) the stocks on the bank of the Tinto are 10–70 t for Hg and 110 t for U. This stock is important

Table 1
Dissolved metal concentrations (nM) in some contaminated European rivers near their mouths and in the Tinto and Odiel rivers[a]

River	Fe	Ni	Cu	Zn	Cd	Pb	As	Hg
Tinto (1)[b]	1229–12527	1617–2432	142–447559	265–890	682–2617	5555	203–29253	0.042
Odiel (1)[b]	39–734	1722–2491	67–136693	133–418	457–868	307	6–369	0.164
Garonne (2, 3, 4, 5)	139	6	13	18	0.52	0.26	20	0.0025
Seine (6, 7, 8)	40	70	31	200	2	2.5		0.014
Rhone (9, 10)	232	27	35	20	0.27	0.42	26	0.0024
Scheldt (11)			35	352	0.27			
Tagus (12, 13)[b]	210	15	26	230	3.4	3	680	

[a] Sources: (1) Elbaz-Poulichet et al. (1999, 2001); (2) Kraepiel et al. (1997); (3) Elbaz-Poulichet et al. (1987); (4) Seyler and Martin (1990); (5) Cossa and Boutier, (1999); (6) Cossa et al. (1994); (7) Chiffoleau et al. (1994); (8) Huang and Mouchel (1994); (9) Elbaz-Poulichet and Leblanc (1996); (10) Guieu et al. (1993); (11) Zwolsman et al. (1997); (12) Cotte (1997); (13) Seyler (1985).

[b] Fe and Zn concentrations in μM in the Tinto and Odiel rivers.

compared to the mean European Hg consumption estimated to be 400–450 t/yr between 1985 and 1992 (OCDE, 1994).

Using rare earth elements in waters, we have demonstrated that phosphogypsum wastes are leaking (Elbaz-Poulichet and Dupuy, 1999) and supplies the waters with dissolved and particulate As, Hg and U (Elbaz-Poulichet et al., 1999, 2000; Cossa et al., 2001).

5.2. Fate of metals in the Tinto–Odiel estuary

According to their behaviour in the dissolved phase, two groups of metals may be recognised in the estuarine zone of the Tinto and Odiel rivers.

The first group includes Fe, Mn, Cu, Cd, Pb and Ni which are supplied to the rivers by drainage of mining wastes. In the Odiel mixing zone their concentrations in the dissolved phase decrease from the river end-member to the marine end-member (Fig. 3). Contrasting with normal estuaries, (Boyle and Edmond, 1977) where extensive Fe removal occurs in the low chlorinity part of mixing zones, Fe is only slightly removed in the Odiel mixing zone (Fig. 3).

In the Tinto mixing zone, metals increase strikingly in the early stage of mixing (Fig. 2) and then decrease with increasing salinity. The maximum concentration in the low chlorinity region of the Tinto is attributed to the release of Fe from detrital pyrite and Fe-oxyhydroxides, which are abundant in these sterile salt marshes (Elbaz-Poulichet et al., 1999, 2000; Elbaz-Poulichet and Dupuy, 1999).

The second group includes Hg, As, U and P which show a maximum of dissolved concentration (Fig. 4) near the effluent which drains the phosphogypsum waste deposits. They are trapped by sediments in the estuarine zone (Elbaz-Poulichet et al., 1999, 2000; Cossa et al., 2001). The similarity between As and phosphate distribution in waters (Fig. 4) and the concomitant increase of As in suspended matter and chlorophyll-a (Fig. 5) suggest that algae play a role in removing As from the water column.

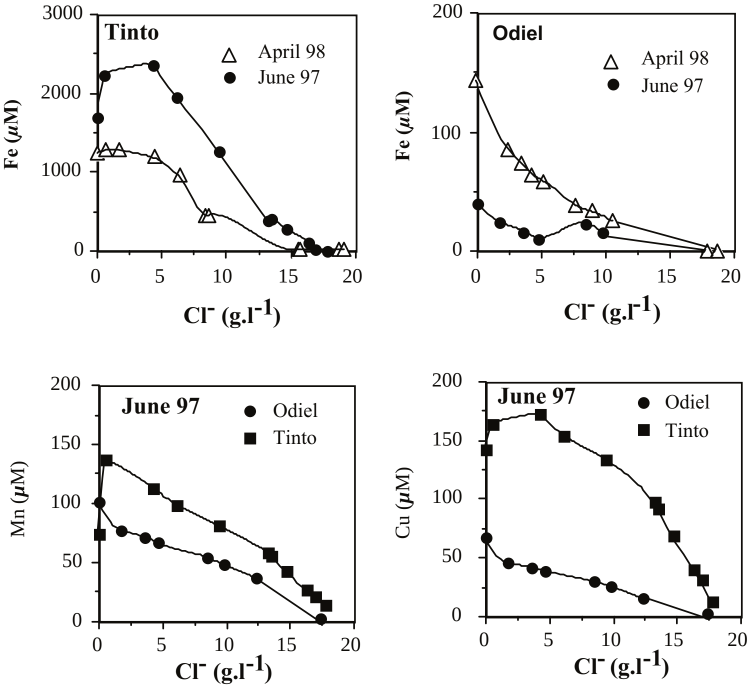

Fig. 3. Distribution of dissolved Fe, Mn and Cu in the waters of the Tinto–Odiel mixing zone as a function of chloride.

5.3. Metal dispersion in the Gulf of Cadiz—consequences of the Aznalcollar spill

From the Tinto and Odiel estuary, where metal concentrations are maximum, and Odiel river a plume of contaminated water follows the north-eastern coast of the Gulf (Fig. 6). This confirms the occurrence of a metal-enriched water mass in the Gulf of Cadiz (Spanish shelf water, SSW), first reported by Van Geen et al. (1991). The coupled hydrodynamical-advection–dispersion model of the Gulf of Cadiz demonstrates that the majority of variations in trace metal concentrations between the Ria de Huelva and the Strait of Gibraltar can be accounted for by advection–dispersion processes of metals discharged by the Tinto and Odiel rivers (Elbaz-Poulichet et al., 2001a).

Continuous in situ monitoring of metal concentrations (Fig. 7) revealed that dissolved metal concentration in the Gulf of Cadiz in the vicinity of the Guadalquivir mouth (Fig. 7) had not changed after the collapse of the tailing reservoir of the Aznalcollar mine (Achterberg et al., 1999).

6. Consequences of the contamination in the Gulf of Cadiz on the Mediterranean Sea

The distribution of dissolved metal concentrations in surface waters of the Gulf of Cadiz indicates that the coastal currents carry the metals discharged from the Tinto and Odiel to the Strait of Gibraltar. With the exception of Hg (Cossa et al., 2001), metal enrichments are observed

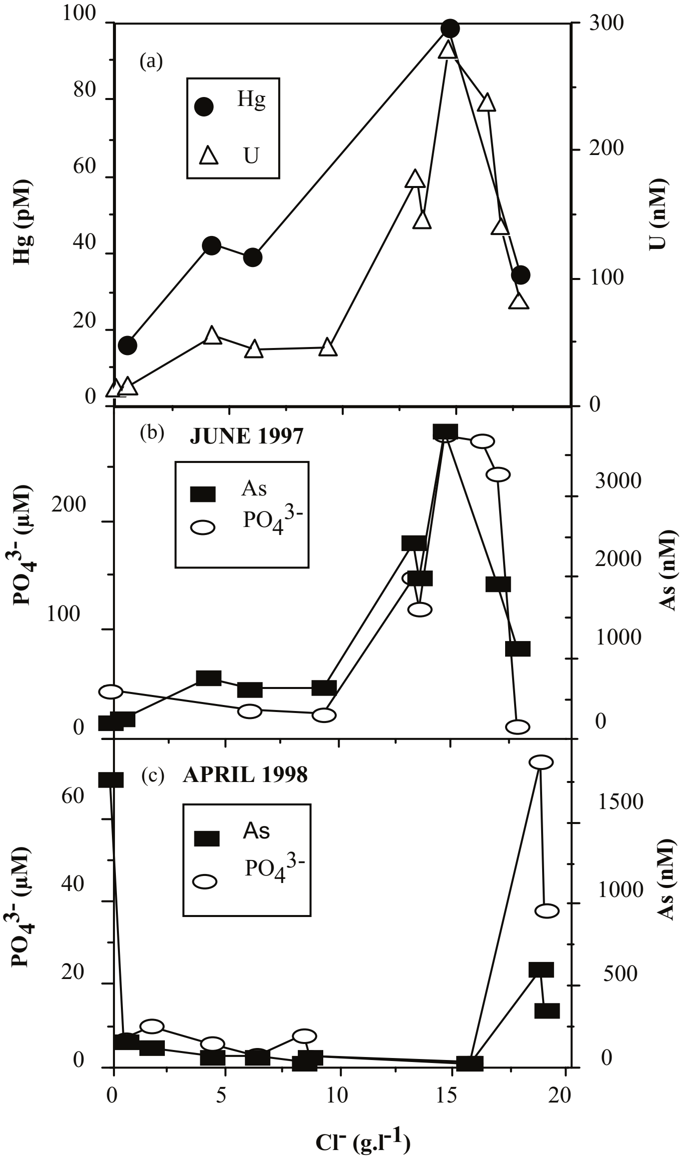

Fig. 4. Distribution of Hg and U (a), and PO_4^{3-} and As in June 1997 (b) and April 1998 (c) as a function of chloride in the Tinto mixing zone.

in the Strait of Gibraltar (van Geen et al., 1988, 1991; Morley et al., 1999; Elbaz-Poulichet et al., 2001a). Arsenic shows limited enrichments compared to transition metals (Cu, Zn, Mn).

The relative contribution of SSW to the Atlantic inflow in the Strait of Gibraltar has been calculated using the GHER hydrodynamical model and an inversion method applied to a mixing model. These two methods give a contribution of $15 \pm 5\%$ for SSW entering in the Mediterranean Sea through the Strait of Gibraltar (Morley et al., 1999; Elbaz-Poulichet et al., 2001a). This value is close to $20 \pm 10\%$ suggested by van Geen et al. (1991).

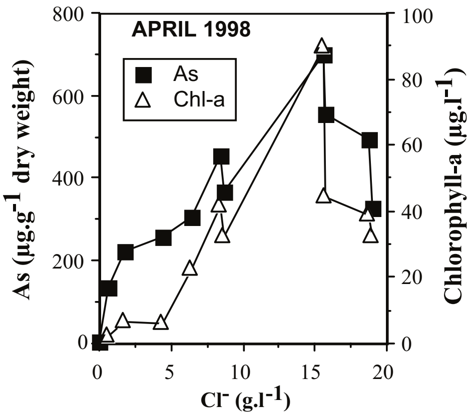

Fig. 5. Distribution of As in the suspended matter and chlorophyll-a in the Tinto estuary as a function of chloride.

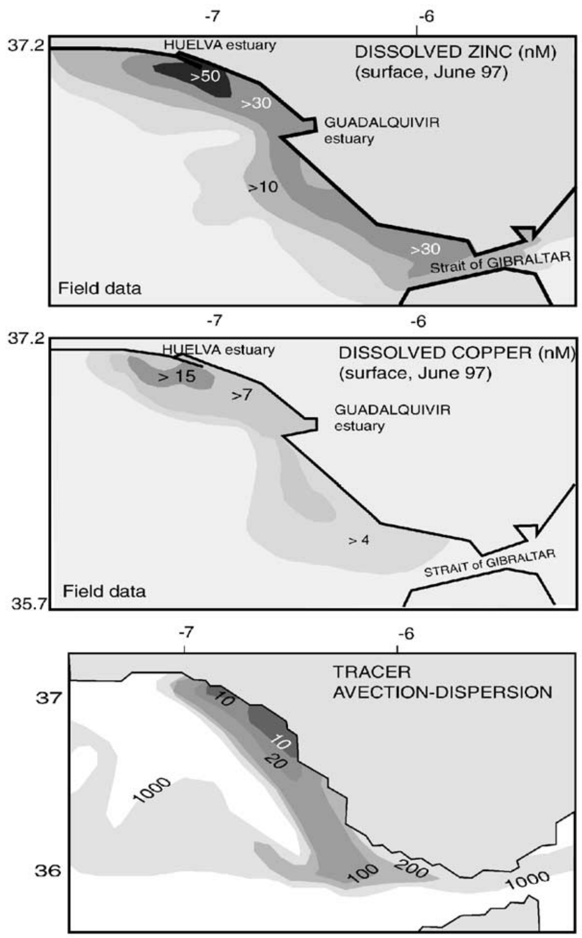

Fig. 6. Distribution of dissolved Cu and Zn concentrations in surface (0–50 m) water of the Gulf of Cadiz. Distribution of the passive tracer injected in the GHER-3D hydrodynamic model. The concentration injected was 1 arbitrary units. Numbers on the contours are dilution factors.

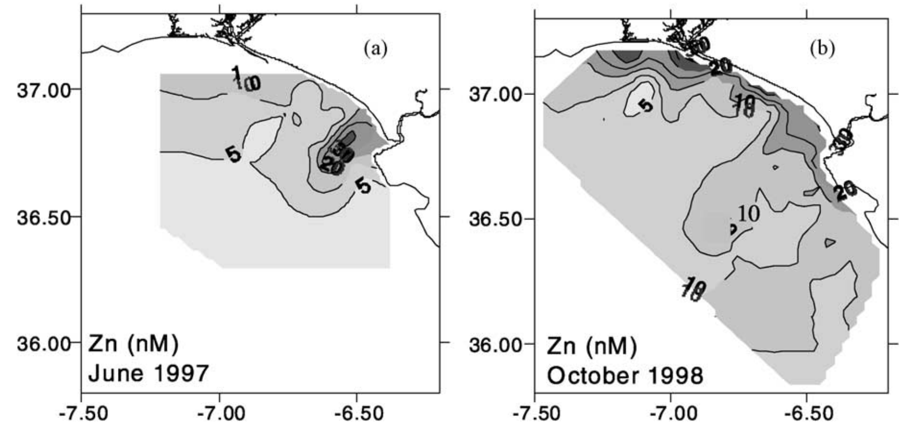

Fig. 7. Dissolved Zn concentrations in the surface waters of the Gulf of Cadiz before and after the Aznalcollar accident. Similar patterns are observed for other metals (Achterberg et al., 1999).

Metal fluxes through the Strait of Gibraltar have been calculated using the new data set acquired during the CANIGO project (Elbaz-Poulichet et al., 2001b). Results are given in Fig. 8. The introduction of SSW systematically increases the metal flux by a factor 2–7 for Mn, Fe, Cu, Zn, Cd and Pb but does not significantly change the Ni, Co and As fluxes in the Mediterranean Sea. Neither Ni nor Co has important source in the Iberian pyrite belt (IPB). Although As is abundant in the IPB and in the Tinto and Odiel rivers, the extensive transfer to the particulate phase, which occurs in the Tinto and Odiel mixing zone, prevents its important dissemination in the Gulf of Cadiz. Cossa et al. (2001) also suggest that the lack of Hg enrichments in the Gibraltar (Cossa et al., 1997) is due to its extensive scavenging by sediments in the Tinto–Odiel estuary and in near-shore waters. With or without SSW, the Atlantic ocean is always a net source of Mn, Cu and Pb for the Mediterranean Sea and conversely the Mediterranean Sea is a net source of Ni, As and Cd for the Atlantic.

7. Conclusion

TOROS study has shown that the Tinto and Odiel rivers have extremely high metal concentrations. The following metals (Mn, Cu, Ni, Co, Fe, Cd, Zn and Pb) are mainly discharged by acid mine drainage whereas the phosphate fertiliser industry constitutes an important source for As, Hg and U. This raises the question of the impact of the dumping of phosphogypsum in estuarine zone.

Metal behaviour in the Tinto and Odiel mixing zone is rather unexpected with a weak removal from the dissolved phase in the Odiel and a release into solution in the Tinto. The metal discharges in the Huelva estuary have a regional impact, and increase significantly, at least seasonally, metal inputs (excepted for As, Hg and U) to the Mediterranean Sea.

The history of metal contamination is recorded in the sediments of the Tinto and we report the oldest metal contamination through mining activity known so far in the world. Despite this old

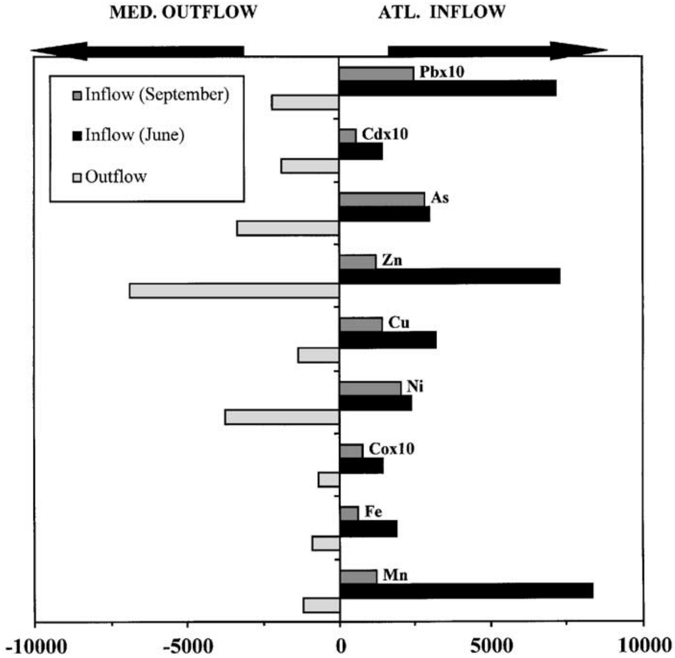

Fig. 8. Metal fluxes through the Strait of Gibraltar. MOW: Mediterranean outflowing water.

metal contamination, the estuarine zone is extremely productive due to important inputs of phosphate from phosphogypsum wastes. In this context, further studies should investigate the interactions between metals and biota, and assess the ecotoxological risk.

Acknowledgements

This research was supported by the European Commission (DGXII) under contract TOROS (ENV4-CT96-0217), Environment and Climate Program (ELOISE). The European Commission is also acknowledged for the support given to the CANIGO (MAS3-PL95-0443). We thank our colleagues of the University of Huelva, especially, Jose Borrego, Juan Antonio Morales and Mercedes Lopez-Guillen for their assistance in the field. We are grateful to the captains and the crew of the research vessels from Spain, UK and France: RV Garcia Del Cid, RV Cornide de Saavedra, RRS Discovery, NO Thalassa.

This is ElOISE contribution number 237.

References

Achterberg, E.A., Braungardt, C., Morley, N.H., Elbaz-Poulichet, F., Leblanc, M., 1999. Impact of los Frailes mine spill on riverine, estuarine and coastal waters in southern Spain. Water Research 33, 3387–3394.

Bebiano, M.J., Machado, L.M, 1992. Concentrations of metals and metallothioneins in mytilus galloprovincialis along the south coast of Portugal. Marine Pollution Bulletin 34, 666–671.

Beckers, J.M., 1992. La Mediterranee Occidentale: de la Modelisation Mathematique a la Simulation Numerique. Ph.D. thesis, University of Liège, Collection des publications, 350pp.

Borrego-Flores, J., 1992. Sedimentologia del estuario del Rio Odiel (Huelva, S.O. Espana). Ph.D. thesis, University of Sevilla, 315pp.

Boyle, E.A., Edmond, J.M., 1977. The mechanism of iron removal in estuaries. Geochimica et Cosmochimica Acta 41, 1313–1324.

Braungardt, C., Achterberg, E.A., Nimmo, M., 1999. On-line voltammetric monitoring of dissolved Cu and Ni in the Gulf of Cadiz, south-west Spain. Analytica Chimica Acta 377, 205–215.

Briard, J., 1976. L'age de bronze en Europe Barbare. Hesperides Publications, Paris, pp. 81–86.

Chiffoleau, J.F., Cossa, D., Auger, D., Truquet, I., 1994. Trace metal distribution, partition and fluxes in the Seine estuary (France) in low discharge regime. Marine Chemistry 47, 145–158.

Cossa, D., Boutier, B., 1999. Le cadmium, le mercure et le plomb dans les eaux des grands fleuves français. ARET Actualité Fascicule 2, 5–9.

Cossa, D., Elbaz-Poulichet, F., Nieto, J.M., 2001. Mercury in the Tinto–Odiel estuarine system (Gulf of Cadix, Spain): sources and dispersion. Aquatic Geochemistry 7, 1–12.

Cossa, D., Martin, J.-M., Takayanagi, K., Sanjuan, J., 1997. The distribution and cycling of mercury species in the western Mediterranean. Deep-Sea Research II 44 (3–4), 721–740.

Cossa, D., Meybeck, M., Idlafkih, Z., Bombled, B., 1994. Etude pilote des apports en contaminants par la Seine. Rapport Int. DEL/93.13/NANTES, Ifremer, F-92138 Issy les Moulineaux, France, 151pp.

Cotte, M.H., 1997. Origines et comportement des metaux dissous dans les eaux de la marge Atlantique Européenne. Ph.D. thesis, University Paris VI. 207pp.

Elbaz-Poulichet, F., Cruzado, A., Velasquez, Z., 2000. Influence of sorption processes by Fe oxides and algal uptake on Arsenic and Phosphate cycle in an acidic estaury (Tinto Rivers, Spain). Water Research 33, 3387–3394.

Elbaz-Poulichet, F., Dupuy, C., 1999. Behaviour of Rare Earth Elements at the freshwater–seawater interface of two acid mine rivers: the Tinto and Odiel (Andalucia, Spain). Applied Geochemistry 14, 1063–1072.

Elbaz-Poulichet, F., Guieu, C., Morley, N.H., 2001b. A reassessment of trace metal budgets in the Western Mediterranean Sea. Marine Pollution Bulletin 42 (8), 623–627.

Elbaz-Poulichet, F., Leblanc, M., 1996. Transfert de metaux d'une province miniere a l'ocean par les fleuves acides (Rio Tinto, Espagne). Comptes Rendus, Academy Science Paris, Serie IIa, Vol. 322, pp. 1047–1052.

Elbaz-Poulichet, F., Martin, J.M., Huang, W.W., Zhu, J.X., 1987. Dissolved Cd behavior in some selected French rivers and estuaries. Consequences on Cd supply to the ocean. Marine Chemistry 22, 125–136.

Elbaz-Poulichet, F., Morley, N.H., Beckers, J.M., Nomerange, P., 2001a. Dissolved metal fluxes through the Strait of Gibraltar: the influence of the Tinto and Odiel rivers (SW Spain). Marine Chemistry 3–4, 193–213.

Elbaz-Poulichet, F., Morley, N.H., Cruzado, A., Velasquez, Z., Achterberg, E.A., Braungardt, C., 1999. Preliminary assessment of trace metal and nutrient concentrations (including metal speciation) in an extremely low pH (2.5) river-estuarine system, the Ria of Huelva (south-west Spain). Science of the Total Environment 227, 73–83.

Guieu, C., Zhang, J., Thomas, A.J., Martin, J.M., Brun-Cottan, J.C., 1993. Significance of atmospheric fallout on the upper layer water chemistry of the north-western Mediterranean. Journal of Atmospheric Chemistry 17, 45–60.

Huang, W.W., Mouchel, J.M., 1994. Concentrations totales et formes chimiques des metaux dissous dans la Seine. Rapport 1994/III, Piren Seine, GDR Analyse et modelisation des systèmes fluviaux anthropisés.

Kraepiel, A., Chiffoleau, J.F., Martin, J.M., Morel, F., 1997. Geochemistry of trace metals in the Gironde estuary. Geochimica et Cosmochimica Acta 70, 1421–1436.

Leblanc, M., Morales, J.A., Borrego, J., Elbaz-Poulichet, F., 2000. A 4500 years old mining pollution in Spain. Economic Geology 95, 655–662.

Leistel, J.M., Marcoux, E., Thieblement, D., 1998. The volcanic hosted massive sulphide deposits of the Iberian Pyrite Belt. Mineralia Deposita 33, 22–30.

Morley, N.H., Elbaz-Poulichet, F., Nomerange, P., 1999. Trace metals in the waters of the Straits of Gibraltar. Oral presentation. 24th General Assembly of the European Geophysical Society in The Hague, April 19–23, Journal of Geophysical Research Abstracts 2, Sec. OA4.

Nelson, C.H., Lamothe, P.J., 1993. Heavy metal anomalies in the Tinto and Odiel river and estuary system, Spain. Estuaries 16, 495–511.

Nomerange, P., 1998. Ecohydrodynamical modelling of the Gulf of Cadiz using nested models. DEA in Modelling of the Marine Environment. Dissertation, University of Liège.

OCDE, 1994. Environment Monography Series No. 98.

Rothenberg, B., Blanco Freijero, A., 1980. Scientific Studies in early Mining and Extractive Metallurgy, Craddok Edition, British Museum Occasion, Vol. 20, pp. 41–56.

Seyler, P., 1985. Formes chimiques et comportement de l'Arsenic en milieu estuarien. Ph.D. thesis, University Paris VI, 194pp.

Seyler, P., Martin, J.M., 1990. Distribution of arsenite and total dissolved arsenic in major French estuaries: dependance on biogeochemical processes and anthropogenic inputs. Marine Chemistry 129, 277–294.

Travesi, A., Gasco, C., Pozuelo, M., Palomares, J., Garcia, M.R., Perez del Villar, L., 1997. Distribution of natural radioactivity within an estuary affected by release from phosphate industry. In: Desmet, G., et al. (Ed.), Freshwater and Estuarine Radioecology. Elsevier, Amsterdam, pp. 267–279.

Van Geen, A., Adkins, J.F., Boyle, E.A., Nelson, C.H., Palanques, A., 1997. A 120-yr record of widespread contamination from mining of the Iberian pyrite belt. Geology 25, 291–294.

Van Geen, A., Boyle, E.A., Moore, W.S., 1991. Trace metal enrichments in waters of the Gulf of Cadiz, Spain. Geochimica Cosmochimica Acta 55, 2173–2191.

Van Geen, A., Chase, Z., 1998. Recent mine spill adds to contamination of southern Spain. EOS 79, pp. 38, 449–445.

Van Geen, A., Rosener, P., Boyle, E.A, 1988. Entrainment of trace metal-enriched Atlantic shelf-waters in the inflow to the Mediterranean Sea. Nature 331, 423–426.

Zwolsman, J., van Eck, B., van der Weijden, C., 1997. Geochemistry of dissolved metals (cadmium, copper, zinc) in the Scheldt estuary, southwestern Netherlands; impact of seasonnal variability. Geochimica Cosmochimica Acta 61, 1635–1652.