

## Trace metal enrichments in waters of the Gulf of Cadiz, Spain

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**Abstract**—Dissolved Cu, Cd, and Zn concentrations in continental shelf waters of the Gulf of Cadiz are much higher than reported for other coastal areas. Direct observations of the metal enrichments in this region were made in March–April 1986 and October 1986; indirect observations (in the Alboran Sea) suggest similar enrichments occurred in June 1982 and September 1980, and it is probable that these enrichments are a persistent feature of the region. Zinc concentrations varied by more than two orders of magnitude between Atlantic water entering the Strait of Gibraltar (<1 nmol/kg) and Spanish shelf water (up to 160 nmol/kg). Copper and cadmium were also highly enriched in Spanish shelf water (up to 47 and 1.3 nmol/kg, respectively), and concentrations of these metals varied co-linearly with Zn. Chemical profiles show that metal enrichments over the Spanish shelf extended from the surface down to about a 45 m depth. In contrast, Ni, phosphate, silicate, and <sup>228</sup>Ra/<sup>226</sup>Ra all occurred at levels typical of other shelf waters. Copper, cadmium, and zinc concentrations in nearby Moroccan shelf water were only a factor of 2 to 3 higher than off-shore surface Atlantic water. A steep surface Cu, Cd, and Zn concentration gradient was observed in the axis of the Strait of Gibraltar denoting the boundary between off-shore Atlantic and Spanish shelf water.

Metal:metal and metal:salinity relationships immediately west of the Strait of Gibraltar show that variations in the composition of surface water can be described by conservative mixing of three sources: (1) metal-depleted surface Atlantic water, (2) Spanish shelf water, highly enriched in Cu, Cd, and Zn, and (3) subsurface North Atlantic Central Water, enriched in Cd and slightly enriched in Ni. Because the Atlantic inflow through the Strait is the main water source for the Mediterranean Sea, enrichments in the Gulf of Cadiz influence metal concentrations of the whole basin. Some temporal metal variation is observed in Spanish shelf water: Zn concentrations decreased by a factor of two between April and October 1986.

Although metal concentrations increase systematically with decreasing salinity over the Spanish shelf, Iberian rivers cannot account for the Cu, Cd, and Zn enrichments. An anthropogenic source of any type seems unlikely because the loss of Cu, Cd, and Zn by entrainment of shelf water through the Strait of Gibraltar is equivalent to a significant fraction of total metal consumption on the Iberian peninsula. A diagenetic shelf sediment source may be more plausible, but it would have to be of much greater magnitude than on other shelves. One mechanism that may enhance metal fluxes from shelf sediments is a coastal “metal trap” driven by an estuarine-type circulation pattern and biological production along the Iberian coast. This process is illustrated here by a simple box model; if this process occurs along the whole Iberian peninsula, Cd enrichments (but perhaps only part of the observed Cu or Zn enrichments) could be sustained against the considerable advective metal sink through the Strait of Gibraltar.

### INTRODUCTION

SHELF WATERS OF THE Gulf of Cadiz were recently reported to be enriched in dissolved Cu, Cd, and Zn relative to offshore waters (VAN GEEN et al., 1988). These enrichments are sufficient to dominate the trace metal composition of the Atlantic inflow to the Mediterranean Sea, because Spanish coastal water is entrained with the inflow through the Strait of Gibraltar. In fact, the composition of the inflow (estimated from western Alboran Sea samples collected in June 1982) indicates that most of the enrichment in these elements for the Mediterranean relative to the surface Atlantic (SPIVACK et al., 1983; BOYLE et al., 1985; SHERRELL and BOYLE, 1988) could be due to this external source. Further documentation of the extent and variability of trace metal concentrations in the Gulf of Cadiz presented here support this finding, including

145 surface samples collected in March–April and October 1986, 8 water column profiles, 20 surface water <sup>228</sup>Ra/<sup>226</sup>Ra activity ratios, and 7 river samples.

Concentrations of trace metals other than highly particle-reactive elements are typically elevated in nearshore waters relative to those of the open ocean. Several mechanisms have been called upon to explain these enrichments. High Cd concentrations in Pacific surface waters near central California were attributed to upwelling of metal- and nutrient-enriched subsurface water (BRULAND et al., 1978). Elevated Cu concentrations in shelf waters north of the Gulf Stream and in the Gulf of Panama, on the other hand, could not be due to upwelling and instead were attributed to remobilization from coastal sediments (BOYLE et al., 1981). Similarly, Bering Sea continental shelf sediments were shown to be significant sources of Cu and Mn to the overlying water column (HEGGIE, 1982; HEGGIE et al., 1987). In the North Atlantic, BOYLE et al. (1981) found Cu, Ni, and Cd enrichments in a single northeast US coastal sample relative to nine samples from

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the Sargasso Sea. These enrichments were confirmed by BRULAND and FRANKS (1983) who found a linear increase in Cu, Ni, Cd, and Zn concentrations with decreasing salinity as fresher coastal waters of the North American shelf mix with Sargasso Sea water (13 samples). BOYLE et al. (1984) added data on another 29 samples from this area that confirmed the salinity trends observed by BRULAND and FRANKS (1983), but that also indicated that there was significant variability about the mean trend. Whether shelf or riverine metal inputs caused such increases could not be determined definitively in this instance. KREMLING (1983) demonstrated that Cu, Ni, Cd, and Mn concentrations also increase in northern European coastal waters relative to the open ocean.

None of the above studies, however, report Cu, Cd, or Zn concentrations as high as observed in Gulf of Cadiz shelf water. The origin of these enrichments is of interest because processes relevant to other coastal areas may be particularly distinct here. In addition, the significant loss of metal-enriched shelf water by entrainment through the Strait of Gibraltar puts a strong constraint on the magnitude of the source that is required. This paper examines possible explanations for the observed enrichments (such as atmospheric deposition, river input, anthropogenic discharges, and shelf sediment diagenesis) and concludes that none of these explanations seem adequate. A simple box-model is therefore constructed to determine to which extent the Spanish shelf concentrates trace metals supplied by upwelling (by a mechanism analogous to the "nutrient-trap" observed in estuaries). It turns out that although the effect of such a "metal-trap" could be dramatic, it cannot explain by itself all of the observed enrichments.

#### SAMPLING AND ANALYSIS

Two cruises (March 26–April 19, 1986, and October 12–17, 1986) of *USNS Lynch* during the Gibraltar Experiment (KINDER and BRYDEN, 1987) offered the opportunity to collect surface samples with a contamination-free underway pumping apparatus (BOYLE et al., 1982). Surface samples from these cruises are listed in the Appendix as Apr. 1 to Apr. 288 and Oct. 1 to Oct. 107, respectively, following the order of collection. Profiles and additional surface samples were collected during *RV Oceanus* cruise 176 between April 14–16th, 1986. These surface samples are listed as Oce. 0.1 to Oce. 15.0. Eight of these surface samples (Oce. 1.0, 2.0, 3.0, 5.0, 6.0, 7.0, 11.0, and 15.0) also correspond to the location of vertical profile stations that are listed as Oce. 1 to Oce. 15. Five-liter Niskin bottles modified and cleaned as described in Boyle et al. (1985) were used to obtain profile samples. Salinity, Si, and P were determined using standard techniques (Guildline Autosol salinometer and colorimetry, respectively) similar to the methods described in STRICKLAND and PARSONS (1968).

Trace metal analyses were performed on 30 mL samples using an automated resin pre-concentration procedure (VAN GEEN and BOYLE, 1990a). Comparison of this procedure for selected samples with modified Co-APDC (cobalt-ammonium pyrrolidone dithiocarbamate) co-precipitation (BOYLE et al., 1981; SHERRELL and BOYLE, 1988) showed good agreement for Cu, Ni, Cd, and Zn (unpubl. data). All sample concentrates were analyzed by graphite-furnace atomic absorption spectroscopy (GFAAS: Perkin-Elmer Zeeman 5000, HGA 500). One-sigma precisions for the data are 5% or 0.1 nmol/kg (whichever is larger) for Cu and Ni, 6% or 0.006 nmol/kg for Cd, and 6% or 0.3 nmol/kg for Zn. Blank corrections and detection limits averaged 0.1 nmol/kg, 0.01 nmol/kg, <0.001 nmol/kg, and 0.3 nmol/kg for Cu, Ni, Cd, and Zn (Zn detection limit based on variability in blank: 0.1 nmol/kg). A number of samples spanning the range of metal concentrations in the Gulf were filtered shipboard through 0.4  $\mu\text{m}$  Nuclepore filters in a laminar flow clean-bench.

Trace metal concentrations were determined for several Iberian rivers by direct injection GFAAS with calibration by standard addition. Results for the Guadalquivir and the Guadiana rivers by this method agree with trace metal concentrations determined by the automated pre-concentration procedure.

Dissolved  $^{228}\text{Ra}/^{226}\text{Ra}$  activity ratios for surface samples collected during *RV Oceanus* cruise 176 were determined using a pumping system that rapidly flushed seawater through Mn impregnated fibers (MOORE, 1976).

#### RESULTS

In April 1986, salinity in Gulf of Cadiz surface waters (outside the region influenced by coastal water) ranged from 36.25 to 36.40‰ (Fig. 1 and Appendix 1). Over the Spanish continental shelf, salinities ranged between 35.6 and 36.0‰. In contrast, salinity in Moroccan shelf water remained above 36.1‰. Extensive CTD coverage obtained during the same cruise indicates an average surface mixed layer depth of 60 m (BRAY, 1986). At six chemical profile stations discussed later (Oce. 1, 3, 5, 6, 7, and 11), there was no significant difference between metal concentrations at the surface and the first subsurface samples (at 20, 5, 58, 15, 40, and 50 m depths, respectively). This shows that surface samples taken with the underway pumping apparatus (with an intake depth between 1 and 3 m) were representative of a significant portion of the water column rather than just a thin surface layer. Phosphate and silicate concentrations ranged between 0.05–1.0  $\mu\text{mol}/\text{kg}$  and between 0.3–3.2  $\mu\text{mol}/\text{kg}$ , respectively (Fig. 2 and Appendix 1). Elevated nutrient concentrations were restricted mainly to fresher water overlying the Spanish continental shelf. Silicate and phosphate concentrations found near the estuary of the Guadalquivir river were typical of other rivers (EDMOND et al., 1981, 1985; BOYLE et al., 1984).

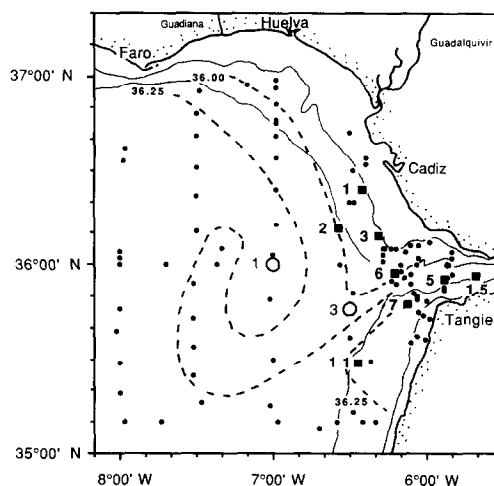


FIG. 1. Location of surface samples (small dots) collected in the Gulf of Cadiz (Spain), the western approaches to the Strait of Gibraltar, and north-east Moroccan shelf waters in March–April 1986. All sample locations and compositions listed in Appendix 1. Also indicated are salinity contours at 36.00 and 36.25‰ interpolated from the same data set. Filled square symbols indicate the location of eight chemical profiles collected between April 14–16th, 1986 (Appendix 3). Two open circles show position of profile stations 1 and 3 of BOYLE et al., (1985) sampled in June 1982. Isobaths at 50 and 200 m depth.

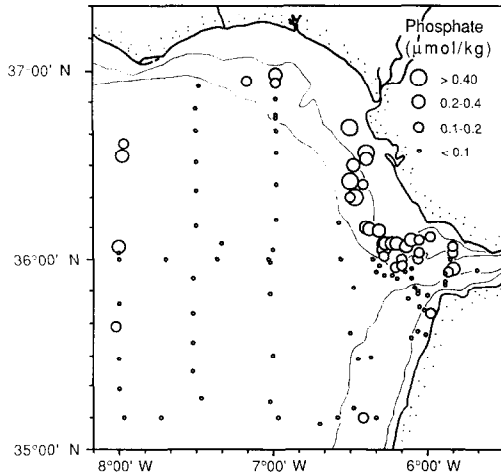


FIG. 2. Phosphate distribution in surface water in March–April 1986. Four symbol sizes indicate concentration ranges. We have no explanation for elevated concentrations in a few offshore stations along 8°00'W.

### Trace Metals in Surface Water

In general, Zn spatial variability in surface waters resembled that of salinity and nutrients, although in detail the patterns differed (Fig. 3 and Appendix 1). For offshore surface samples with salinities above 36.25‰, Zn concentrations ranged from 0.3 to 1 nmol/kg. Zinc levels over the Spanish shelf, on the other hand, were elevated by more than an order of magnitude. Zinc concentrations were greater than 40 nmol/kg over a distance of 40 km from the estuary of the Guadalquivir river (Apr. 1) to shelf water off Cadiz south of the estuary (Apr. 7, 2, 3, and Oct. 0.1). Copper and cadmium concentrations in shelf water were also extremely high in the same region (e.g., Oct. 0.1; Zn, 52 nmol/kg; Cu, 21 nmol/kg; and Cd, 0.40 nmol/kg) and co-varied with Zn (Fig. 4). Nickel

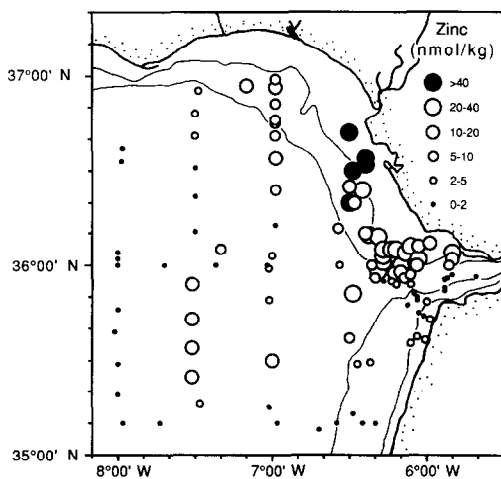


FIG. 3. Zn distribution in surface water in March–April 1986. Samples are subdivided in six concentration ranges. Note that the “tongue” pattern of elevated concentrations (10–20 nmol/kg) in center Gulf of Cadiz corresponds to penetration of the 36.25‰ isohaline (Fig. 1). Western approaches to the Strait of Gibraltar enlarged in Fig. 9a.

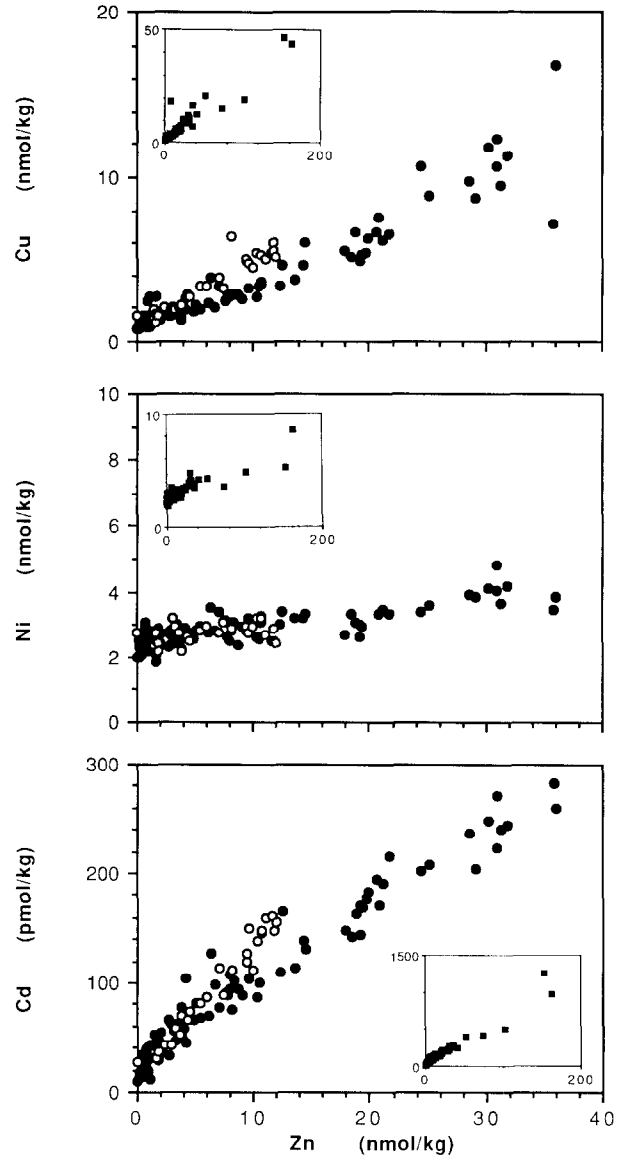


FIG. 4. Co-linear variations in metal concentrations. Filled circles represent all surface samples (Fig. 1) collected in March–April 1986. Insets show near-linear Cu- and Cd-Zn relationships extending over the entire observed concentration range. Also shown are October 1986 surface samples listed in Appendix 2 (open circles, locations in Fig. 9b).

enrichments over the Spanish shelf, on the other hand, were much weaker. A single sample (Apr. 1) reached a Ni concentration above 6 nmol/kg, i.e., only three times higher than typical offshore levels in the Gulf of Cadiz.

The high levels of Cu, Cd, and Zn concentrations found in Spanish coastal water are not due to contamination during sampling or analysis. The same surface sampling procedures followed in the Gulf of Cadiz have yielded consistent results for trace metals such as Cu, Zn, and Pb in Sargasso Sea surface water where metal concentrations are much lower. Furthermore, remarkably constant inter-element ratios between Zn and Cu, Ni, Cd (Fig. 4) for the suite of enriched shelf samples argue against contamination. Samples were collected during

a total of three separate cruises with different personnel and subsequently analyzed in random order. A different concern is the possible contribution of metals from particles. In the open ocean, Cu, Ni, Cd, and Zn concentrations in filtered and unfiltered samples are virtually indistinguishable (BOYLE et al., 1981; BRULAND and FRANKS, 1983). Table 1 compares the composition of five filtered and unfiltered samples from the Spanish shelf and shows that, even for highly metal-enriched samples, differences were negligible within the analytical uncertainty. For this reason, data reported here reflect dissolved Cu, Ni, Cd, and Zn concentrations even though the majority of surface samples were not filtered.

Low metal concentrations in offshore water samples collected in 1986 are consistent with concentrations in surface samples collected in September 1980 (SPIVACK et al., 1983) and profiles collected in June 1982 (BOYLE et al., 1985). A coastal current is thought to follow the coastline over the Spanish shelf in the direction of the Strait of Gibraltar (T. KINDER, pers. comm.). By adjusting a geostrophic balance calculation to current meter data, GRUNDLINGH (1981) calculated a 0.15 cm/s surface current flowing east off the southern coast of Portugal. The curved "tongue" of high Zn concentrations extending beyond the shelf southwest of Cadiz over a distance of 100 km may have been an extension of this coastal current; this feature is also seen in the salinity data. Copper and cadmium ratios relative to Zn in the "tongue" were consistent with conservative mixing of offshore and shelf water. Nutrients within the "tongue" were highly depleted, and salinity in the same samples was approximately 0.2‰ higher than expected from a mixture of shelf and offshore water that would create the observed metal concentrations. These differences suggest that surface nutrients and salinities may not be conservative relative to Cu, Cd, and Zn on the advection time scale of this feature. The potential use of dissolved metals as tracers of cross-shelf circulation is evident from this observation.

#### $^{228}\text{Ra}/^{226}\text{Ra}$

Even though the processes releasing metals and Ra to coastal waters differ, the  $^{228}\text{Ra}/^{226}\text{Ra}$  activity ratio provides

a measure of the extent of water-sediment interactions (MOORE, 1987). Figure 5 shows that  $^{228}\text{Ra}/^{226}\text{Ra}$  activity ratios were elevated in shelf waters, both north and south of the entrance to the Strait of Gibraltar, relative to nutrient-depleted Atlantic water within the Strait. The range of activity ratios is comparable to that measured in earlier work on the South Atlantic Bight (MOORE, 1987) and the Amazon river outflow (MOORE et al., 1986). A plot of  $^{228}\text{Ra}/^{226}\text{Ra}$  vs. salinity shows three groups of samples (Fig. 6): (1) Spanish shelf water with activity ratios up to 0.57, (2) more saline Moroccan shelf water with ratios not exceeding 0.26, and (3) surface Atlantic water within the Strait (<0.2). Higher ratios in Spanish shelf water could be due to both input from the Guadalquivir estuary (there is no freshwater input of comparable magnitude to the Moroccan coast), and the broad portion of continental shelf shallower than 50 m (Fig. 5). The main conclusion to be drawn from the comparison of trace metals and  $^{228}\text{Ra}/^{226}\text{Ra}$  distributions is that, despite particularly elevated metal concentrations over the Spanish shelf, activity ratios in the same region were not exceptional.

#### Trace Metal Profiles

Eight chemical profiles were collected in April 1986 in the Gulf of Cadiz and the Strait of Gibraltar (Fig. 7; see Fig. 1 for locations). Most profile samples were filtered (see Appendix 3). Metal enrichments over the Spanish shelf water extended down to the bottom of the water column at Oce. 1 and 3 (45 and 25 m depth, respectively). At Oce. 6 (further offshore in the direction of the Strait of Gibraltar, ~120 m bottom depth), metal-enriched shelf water was clearly present as a surface layer at least 15 m thick. Apart from the surface sample at Oce. 2, which has an anomalous Cu/Zn ratio of 2.3 relative to other enriched samples (Cu/Zn ~ 0.4) implying that this sample was contaminated, neither of the remaining stations (Oce. 5, 7, 11, and 15) showed metal concentrations comparable to those at Oce. 1, 3, and 6.

Two deep water masses are significant in the Gulf of Cadiz: North Atlantic Central Water (NACW; GASCARD and RICHEZ, 1985) and Mediterranean Outflow Water (MOW).

TABLE 1 Comparison of unfiltered (UF) vs. 0.4  $\mu\text{m}$  Nuclepore filtered (F) samples.

Station	(n)	Cu	Ni	Cd	Zn
F Apr. 1	(3)	40	8.7	1.02	170
UF Apr. 1	(2)	44	8.5	0.97	160
F Apr. 2	(1)	49	5.8	1.29	170
UF Apr. 2	(1)	47	5.2	1.26	150
F Apr. 3	(1)	17	5.1	0.56	93
UF Apr. 3	(1)	20	4.8	0.51	100
F Oce. 0.1	(1)	20	4.0	0.35	50
UF Oce. 0.1	(1)	21	4.3	0.40	52
F Oce. 3(20m)	(2)	7.8	3.4	0.20	25
UF Oce. 3(20m)	(1)	8.8	3.7	0.20	26

Number of replicate analyses (n). Units: nmol/kg.

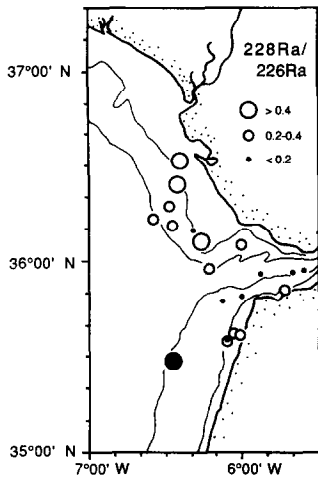


FIG. 5.  $^{228}\text{Ra}/^{226}\text{Ra}$  activity ratio (dpm/dpm) in surface waters west of the Strait of Gibraltar. Samples (collected April 14th–16th, 1986 and listed in Appendix 4) are subdivided in three concentration ranges. Trace metal and radioisotope sample locations do not always overlap. Radioisotope samples at Oce. 3.0 and 11.0 (filled circles) were taken sequentially and labels may have been exchanged inadvertently.

These water masses can be identified by their salinity characteristics. Outside the region of direct influence of Spanish shelf water, subsurface salinity minima at Oce. 2, 6, 15, 5, 7, and 11 (in order of decreasing latitude) are characteristic of NACW. Of the trace metals considered here, only Cd, and to a much lesser extent Ni and Zn, are enriched in this source. Phosphate-, cadmium-, and nickel-salinity relationships for two profiles collected previously in the Gulf of Cadiz (BOYLE et al., 1985) and the new data for April 1986 are consistent with each other (Fig. 8). Stations Oce. 15, 5, and 7 showed the characteristic high-salinity signature of MOW. Salinities

greater than 37.3‰ (approximately 50% MOW contribution) were found at 150 m, 200 m, and 340 m depth at Oce. 15, 5, and 7, reflecting the sinking of this water mass with increasing distance from its source. Copper, nickel, cadmium, and zinc concentrations in the outflow of 2, 5, 0.080, and 5 nmol/kg, respectively (Oce. 15), are compatible with earlier determinations (STATHAM et al., 1985; BOYLE et al., 1985; COPIN-MONTEGUT et al., 1986; SHERRELL and BOYLE, 1988).

DISCUSSION

Endmembers Contributing to the Atlantic Inflow

Surface waters west of the Strait of Gibraltar region were sampled at high spatial resolution in both April and October 1986 (Fig. 9; data in Appendix 1 and 2). Comparison of the salinity distributions shows an increase of 0.2 to 0.3‰ throughout the region between April and October. Spanish shelf water remained enriched in dissolved metals at both times, but there is a significant difference between the two cruises. Although Cu and Cd concentration remained roughly constant at similar locations over the Spanish shelf, Zn concentrations were approximately a factor of two lower in October. Such variations also affect the composition of the Alboran Sea, immediately east of the Strait of Gibraltar (VAN GEEN et al., 1988). Profiles at Oce. 3 and 6, located within the boundaries of Fig. 9a, suggest that elevated concentrations originate from the portion of Spanish shelf shallower than 50 m and are advected south, beyond the 200 m isobath, towards the axis of the Strait of Gibraltar. Stations Oce. 5, 7, and 15 lie too far south to show evidence of metal enrichments originating from the Spanish shelf.

Metal-salinity plots of surface samples from the western approaches to the Strait (Fig. 10) help to distinguish Atlantic sources contributing to the inflow. We follow the approach of VAN GEEN et al. (1988) but redefine the composition of

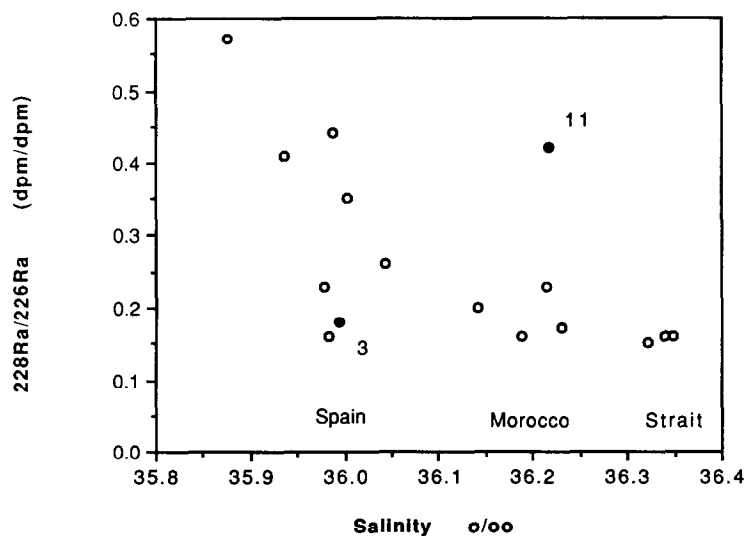


FIG. 6.  $^{228}\text{Ra}/^{226}\text{Ra}$ -salinity relationship for surface samples of Fig. 5, where salinity from nearby trace metal sample is available. Note that salinities may be approximate since the large volume of water pumped through the Mn-impregnated fibers may not correspond exactly to the spot salinity sample. Elevated activity ratios over the Spanish shelf relative to the Moroccan shelf could be due to a combination of greater river input (and estuarine desorption) and a wider shelf shallower than 50 m. Filled circles indicate samples at Oce. 3.0 and 11.0.

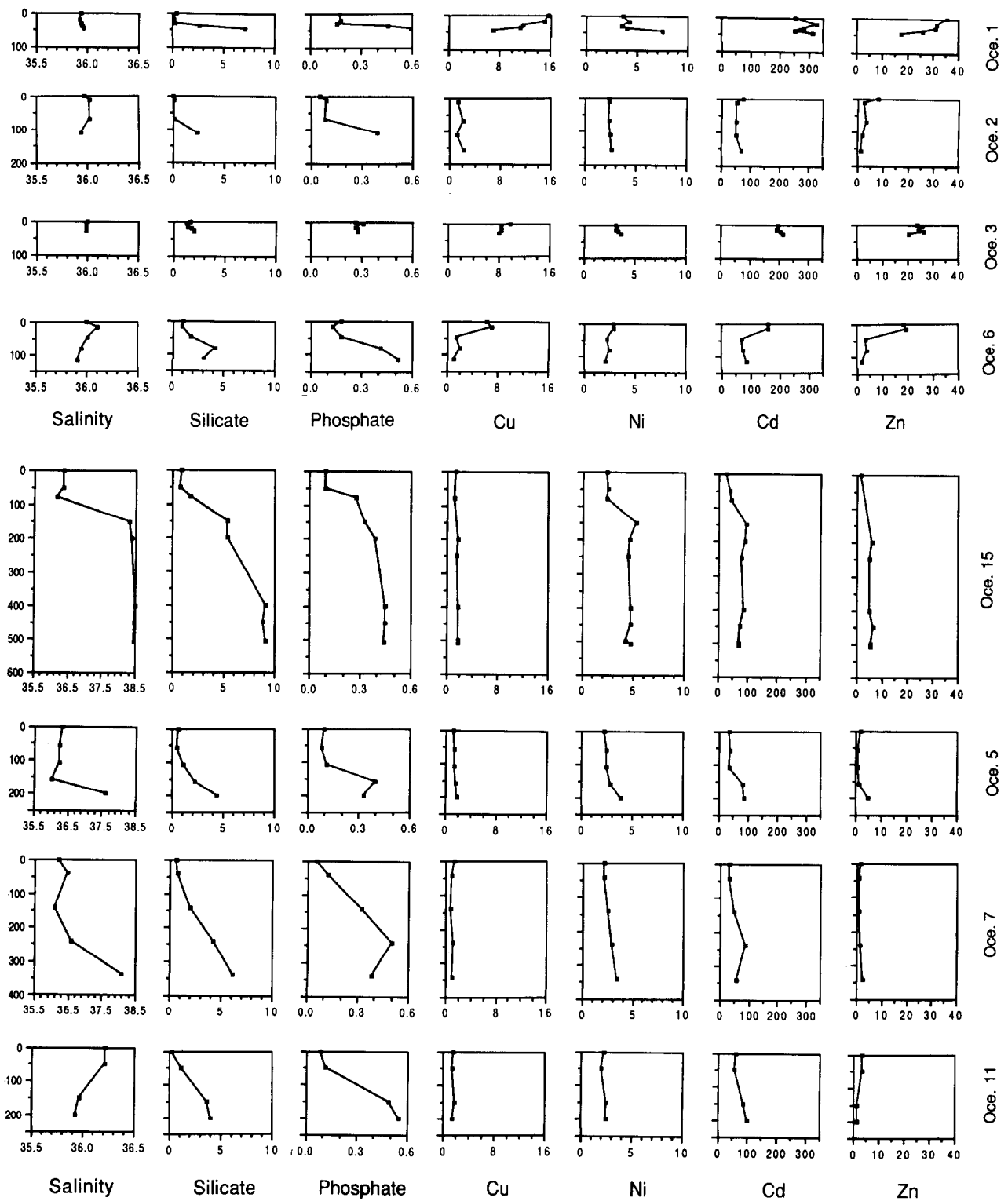


FIG. 7. (a) Chemical profiles at stations Oce. 1, 2, 3, and 6, in order of decreasing latitude (all north of 35°58'N). Stations Oce. 1, 3, and 6 show a strong presence of metal-enriched Spanish shelf water down to 45, 25, 15 m depth, respectively. At Oce. 6, decreasing salinity and increasing Cd and nutrient concentrations below the mixed layer indicate mixing with North Atlantic Central Water. Salinity, silicate, phosphate, Cu, Ni, Cd, and Zn are on the same scale at each station for comparison. Highest metal concentrations are observed at Oce. 1. Surface sample at Oce. 2 probably contaminated, as discussed in text. (b) Chemical profiles at stations Oce. 15, 5, 7, and 11, in order of decreasing latitude (south of 35°58'N). Salinity scale is contracted at Oce. 15, 5, and 7 to show outflow of saline Mediterranean water below 150, 200, and 340 m depth, respectively. Other tracers on same scale as in Fig. 6a for comparison. Salinity decreasing with depth at Oce. 11 and salinity minima above the outflow layer at Oce. 15, 5, and 7 indicate mixing with NACW.

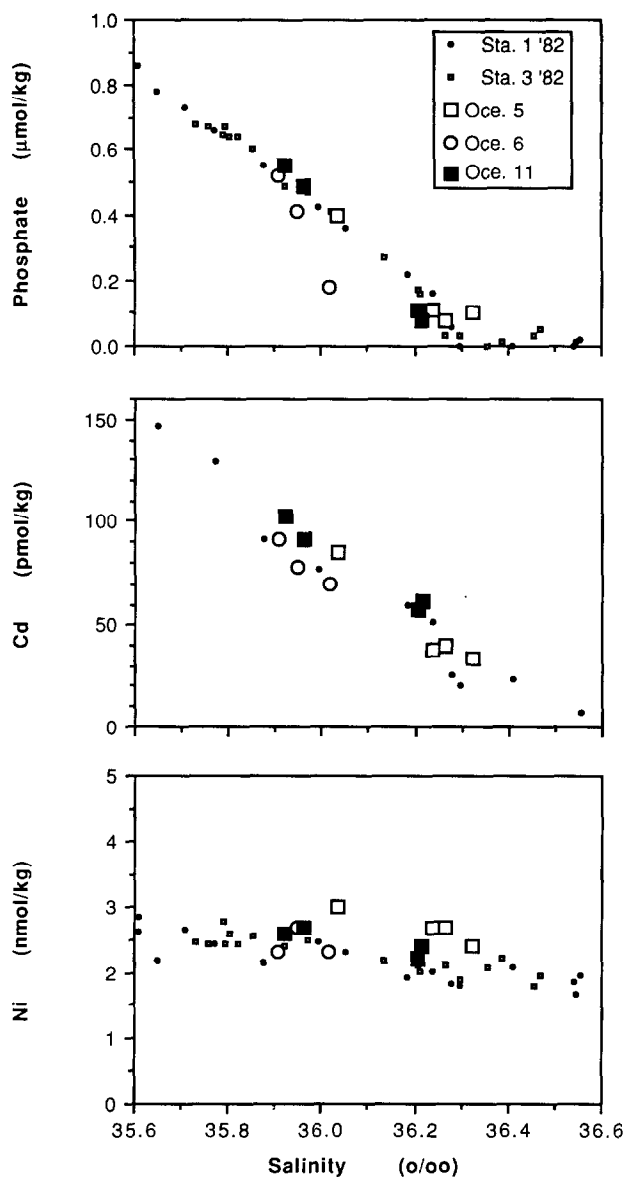


FIG. 8. Phosphate-, Cd-, and Ni-salinity relationships for samples not affected by Spanish shelf water at stations Oce. 5, 6, and 11. Also included are data from offshore Station 1 and Station 3 collected in June 1982 (locations in Fig. 1, data from BOYLE et al., 1985) with deepest samples shown from 430 and 310 m depth, respectively. Results are consistent between the two sampling periods. Note deviation from mixing relationship of phosphate concentration for 45 m deep sample at Oce. 6 which is discussed in text. As shown, Cd and salinity profiles can be described as the result of conservative mixing in different proportions of two sources (surface Atlantic water and NACW, defined in Table 2), despite likely nonconservative behaviour of both tracers in surface water. The gradient in Ni concentrations between 0 and 400 m depth is weak but detectable; Cu and Zn concentrations (not shown) do not change significantly over the same depth range.

three sources based on this more extensive data set: these sources are (1) surface Atlantic water, (2) Spanish shelf water, and (3) NACW. The salinity of metal-depleted surface Atlantic water west of the Strait increased from about 36.30 to 36.45‰ between April and October, although Cu, Cd, and Zn concentrations remained roughly constant at 1, 0.030,

and 0.8 nmol/kg, respectively (Table 2). The 36.25‰ (April) and 36.40‰ (October) isohalines in Fig. 9 suggest penetration of this endmember in the southern part of the Strait of Gibraltar.

With the composition of one source determined, variations in trace metal concentrations with depth *outside* the region of influence of Spanish shelf water can be examined to determine the composition of NACW. The linear Cd-salinity mixing relationship in Fig. 8 shows that these two tracers can be described as if there were conservative mixing of two sources, one at the surface and the other at 400 m depth. This description should not be taken as an assumption that the compositions of the upper 400 m literally are determined by mixing of two endmembers, but rather that the range of compositions can be mathematically described as if there were such a mixture. The change in compositions for salinity and Cd with increasing depth in this range is about  $-0.3‰$  and  $+0.10$  nmol/kg, respectively. For Cu, Ni, and Zn, the change in concentration through the same interval is near the detection limit:  $+0.3$ ,  $+0.4$ , and  $+0.7$  nmol/kg, respectively (only Ni is shown in Fig. 8). Despite the lack of much difference in the concentrations of the other tracers, NACW composition significantly influences Cd and salinity in the

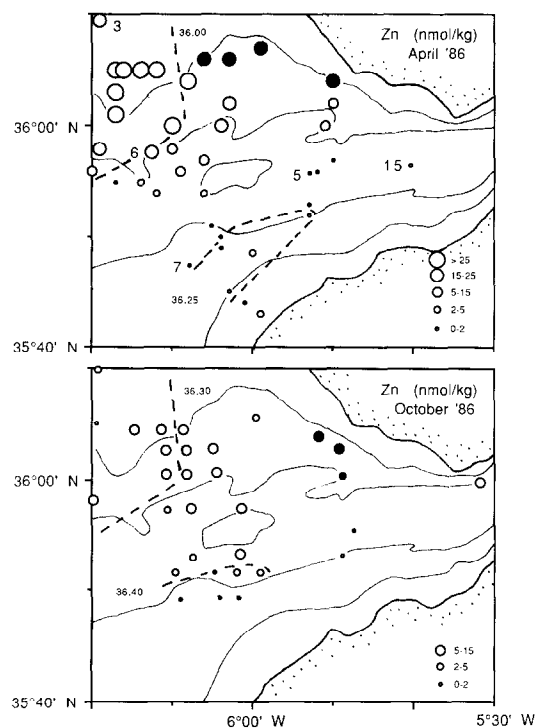


FIG. 9. (a and b) Comparison of Zn concentrations in surface water of western approaches to the Strait of Gibraltar between April and October 1986. Both data sets are subdivided into the same five concentration ranges indicated in the figure. Maximum concentrations in the region are 41 nmol/kg (Apr. 276) and 12 nmol/kg (Oct. 31) in April and October, respectively. Also indicated are surface isohalines at 36.00, 36.25‰ (April), and 36.30, 36.40‰ (October) which delineate roughly regions of predominance of Spanish shelf water and surface Atlantic water, respectively. Surface samples at chemical profiles Oce. 3, 5, 6, 7, and 15 are labelled. Isobaths are at 50 and 200 m depth. Samples deviating from dominant salinity:Zn relation in shelf water are indicated by filled circles for both April and October 1986 (see text).

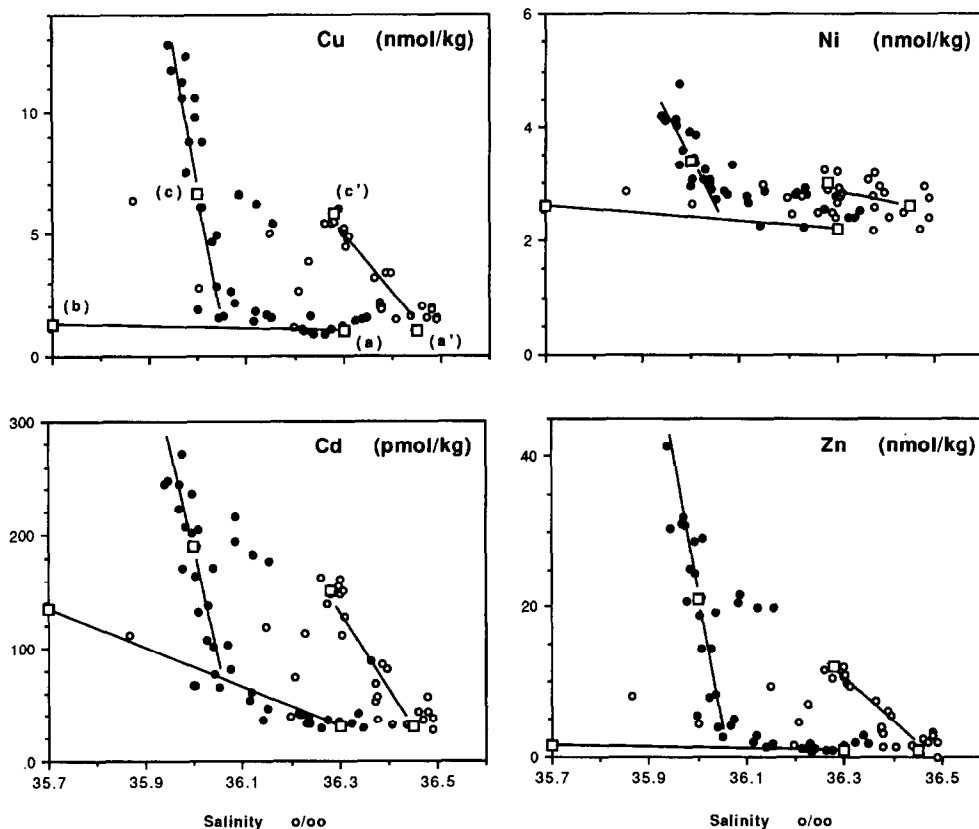


FIG. 10. Metal-salinity relationships for surface samples collected in April (closed symbols) and October (open symbols) 1986 within the boundaries of Fig. 9. Composition of three Atlantic endmembers (Table 2) also indicated: (a) April and (a') October surface Atlantic water; (b) North Atlantic Central Water; (c) April and (c') October Spanish shelf water.

Strait of Gibraltar and Alboran Sea. The definition of the NACW source as water present at 400 m depth in the center of the Gulf of Cadiz (Table 2) is reasonable, as the sill depth across the Strait is 230 m. Also indicated in Table 2 are standard errors in source composition that include the sum of natural variability and analytical uncertainty.

Given the continuum in compositions shown in Fig. 10, Spanish shelf water is more difficult to define. At the same time, this source exerts the strongest control on the distribution of trace metals in the region and shows seasonal variability in composition. The mixing line determined by mixing of surface Atlantic water and NACW is superimposed on the composition of surface samples in Fig. 10; this presentation distinguishes surface enrichments specific to the Spanish shelf from elevated concentrations due to upwelling and vertical mixing. It appears that samples with Cd concentrations up to 0.09 nmol/kg (total of 19 samples in April 1986) could be explained by upwelling of NACW if only salinity and Cd were considered. The number of surface samples within the region covered by Fig. 9 that were truly unaffected by Spanish shelf water is reduced to eight by noting which Cu and Zn concentrations were greater than that of upwelling NACW. Figure 10 also shows a well-defined mixing line between an enriched shelf source and a roughly 60/40% mixture of surface Atlantic water and NACW. Despite non-conservative processes that may be active in the shelf region, it appears that

the composition of metal-enriched surface samples can be described as the result of conservative mixing with a hypothetical Spanish shelf water source. We arbitrarily choose to define the source endmember based on the most prevalent composition of samples west of the Strait between the 50 and 200 m isobaths in April 1986. We define "100%" Spanish shelf water by a salinity of 36.00‰ and Cu, Ni, Cd, and Zn concentrations of 6.6, 3.4, 0.19, and 21 nmol/kg, respectively. Uncertainties in the composition of this source are listed in Table 2. Revised Spanish shelf water Cu, Cd, and Zn concentrations at the same salinity are lower by 34, 27, and 47%, respectively, relative to our first estimate (VAN GEEN et al., 1988).

In October 1986, the 36.30‰ isohaline encompassed roughly the same portion of the Spanish shelf as the 36.00‰ isohaline did in April 1986 (Fig. 9). The composition of the majority of October 1986 samples again showed a linear relationship between two extreme compositions (albeit over a smaller range of metal concentrations): surface Atlantic water (salinity  $\approx$  36.5‰) and shelf water of salinity 36.28‰ and Cu, Cd, Zn concentrations of 5.8, 0.15, and 12 nmol/kg, respectively. If one chooses this composition for Spanish shelf water in October 1986, "100%" Spanish shelf water originated from the same region west of the Strait of Gibraltar on both occasions (even though the definition of source composition between the two periods differs). Nickel did not show evidence



TABLE 2 Composition of end-members observed in the Gulf of Cadiz

	Surface Atlantic	NACW	Mediterranean
Salinity	36.30* (0.05)	35.70 (0.05)	38.45 (0.01)
Cu	1.0 (0.2)	1.3 (0.1)	1.9 (0.1)
Ni	2.2* (0.1)	2.6 (0.2)	4.6 (0.2)
Cd	0.030 (0.01)	0.135 (0.01)	0.077 (0.01)
Zn	0.8 (0.5)	1.5 (0.5)	4.8 (0.5)

\* Salinity of 36.4‰, Ni 2.6 nmol/kg in October '86.

	Spanish Shelf: April '86	October '86
Salinity	36.00	36.28 (0.1)
Cu	6.6	5.8 (0.5)
Ni	3.4	3.0 (0.2)
Cd	0.19	0.15 (0.02)
Zn	21	12 (2)

Trace metal concentrations in nmol/kg.  
Estimate of combined standard deviation  
due to of natural variability and  
analytical uncertainty indicated in parentheses.

of significant Spanish shelf water enrichments (3 nmol/kg at most), but surface Atlantic water concentrations increased from about 2.2 to 2.6 nmol/kg between April and October 1986. Naturally, there were some deviations from this simple picture. Samples near the southern extension of the Spanish shelf (Apr. 259, 271, 272, 273, and Oct. 103, 104, 105 indicated in Fig. 9) deviate from the metal:salinity mixing lines between surface Atlantic water and Spanish shelf water in both April and October, even though Cu/Zn and Cd/Zn ratios were consistent with the definitions of Spanish shelf water in Table 2.

Moroccan shelf surface samples appeared to be enriched in Ni and Cd only by mixing with subsurface Atlantic water. Copper and zinc concentrations in 7 out of 19 samples from Moroccan shelf waters (see Fig. 3, Apr. 260 and Oct. 8.0 to 13.0) were higher than either surface Atlantic water or NACW concentrations (up to 2.8 and 4.8 nmol/kg, respectively). Perhaps some shelf enrichment also occurs here, but to an extent detectable only for Cu and Zn, which are most strongly affected by the shelf enrichment process. It appears that little Moroccan shelf water was entrained with the inflow to the Alboran Sea, because relatively low Zn concentrations (about 1 nmol/kg for most samples) were seen in the southern half of the Strait of Gibraltar (Fig. 9). Given its minor contribution to metal fluxes through the Strait, this water source will be neglected.

With the revised composition of the Spanish shelf end-member, approximately 20 ± 5% of the inflow was contrib-

uted by this source in April 1986 (VAN GEEN and BOYLE, 1990b). Transport of Atlantic water through the Strait of Gibraltar is  $0.70 \cdot 10^6$  m<sup>3</sup>/s (SARMIENTO and TOGGWEILER, 1988, based on data of BRYDEN and PILLSBURY, 1988). Metal fluxes through the Strait corresponding to a  $0.14 \cdot 10^6$  m<sup>3</sup>/s loss of Spanish shelf water are listed in Table 3 and put a strong constraint on the origin of Spanish coastal enrichments.

#### An Atmospheric Source of Enrichments?

The regional impact of Spanish metal enrichments does not extend far beyond the shelf in Atlantic Ocean surface waters. Apart from metal enrichments in the Gulf of Cadiz that are due to mixing with shelf water (we include the offshore Zn "tongue" in this category), offshore concentrations of nutrient-depleted surface waters in this region are comparable to metal concentrations in "typical" open-ocean nutrient-depleted water. Concentrations of Cu, Ni, Cd, and Zn (0.8, 2.1, 0.013, and 0.2 nmol/kg, respectively) in 4 samples from the western margin of Fig. 3 (Apr. 39, 40, 44, 46) were very similar to levels in the surface Sargasso Sea (0.8, 2, 0.002, and 0.06 nmol/kg) determined by BRULAND and FRANKS (1983) and VAN GEEN and BOYLE (1990a). The sharp geographical boundaries of trace metal enrichments observed in this region argue against a significant atmospheric source because the pattern expected from such an input would be more diffuse and unrelated to salinity. A comparison of atmospheric

TABLE 3 Comparison of potential metal inputs to coastal waters with flux due to shelf water entrainment by the inflow through Gibraltar. Fluxes given in mol/sec.

	Shelf water entrainment	Iberian consumption	River flux at S=0‰/‰	Oxic sediments	Anoxic sediments	Fjord sediment
Cu	0.92	87	6.0	0.011/0.1	0.05	0.006/0.027
Cd	0.027	0.08	0.083	0.00013	0.0008	0.025/0.030
Zn	2.9	56	17	-	-	0.43/0.32

Shelf water flux based on entrainment of  $0.14 \cdot 10^6 \text{ m}^3/\text{s}$  (20% of total Atlantic inflow) and April 1986 composition of end-member (Table 2)

Iberian metal consumption estimate based on global consumption estimate 1971-80 (Nriagu, 1979) and Spanish+Portuguese share of world GDP (2.0%, World Bank, 1988)

Hypothetical river flux calculated by extrapolating Cu, Cd and Zn concentration to zero salinity (see text) and multiplying by the combined yearly averaged discharges of the Guadalquivir, Guadiana, Tejo and Douro rivers ( $1.2 \cdot 10^6 \text{ m}^3/\text{s}$ , UNESCO, 1969).

Oxic sediments, from Klinkhammer et al., 1982/Heggie et al., 1987.

Anoxic sediments, from Gaillard et al., 1986.

Fjord sediments, from Westerlund et al., 1986.

Benthic fluxes calculated for area of shelf box ( $2 \cdot 10^{10} \text{ m}^2$ )

input (particulate and dissolved) to the whole Western Mediterranean basin (1.1 and 0.096 moles/sec, respectively; MARTIN et al., 1989) also shows that Cu and Cd shelf water fluxes through Gibraltar (0.92 and 0.027 mol/s) could not easily be supported by atmospheric input over the limited area of the Iberian shelf.

#### A Riverine Source?

Linear metal-salinity relationships over the Spanish shelf (Fig. 10) cannot be attributed to simple conservative mixing with high-metal river water (VAN GEEN et al., 1988). Linear extrapolation to zero salinity shows that unreasonably high dissolved metal concentrations would be required in the rivers (5, 0.07, 14  $\mu\text{mol}/\text{kg}$  for Cu, Cd, and Zn, respectively) even for this active mining region (STENNER and NICKLESS, 1975). Spot samples were taken from the major rivers reaching the Atlantic flank of the Iberian peninsula (Table 4). Dissolved Cu, Cd, and Zn concentrations in both Guadalquivir and Guadiana rivers were not significantly different from levels found in the Mississippi, or for that matter, in the relatively unperturbed Amazon river (SHILLER and BOYLE, 1987; data in Table 4). While these spot samples do not prove that high metal concentrations *never* occur in Iberian rivers, it is unlikely that occasional episodes of high metal concentrations in these rivers could account for the persistent occurrence of metal anomalies in Spanish shelf waters. In contrast to the other metals, enrichments of Ni over the Spanish shelf (that are not pronounced) could be due to river input because extrapolation of the Ni-salinity relationship to zero salinity yields a river source concentration comparable to levels observed in both the Guadalquivir and the Tejo rivers.

Even if metals are not transported by rivers in dissolved

form, they might instead be carried on the river-borne particulates and released into solution later when they encounter saline waters or during shelf diagenesis. If the composition of riverine suspended matter was typical of "average crustal" concentrations (TAYLOR, 1964), complete dissolution of Cu, Cd, and Zn from an unrealistic suspended load of 5, 40, and 13 g/l (respectively) would be required to account for dissolved metal concentrations extrapolated to zero salinity. Even if the suspended particles in this region are heavily contaminated by anthropogenic inputs (and note here that Zn in Mississippi river particles does not appear to be greatly affected by anthropogenic inputs; SHILLER and BOYLE, 1985), desorption from riverine particles cannot easily account for Spanish shelf metal enrichments. It is conceivable that extraordinary erosional events supply a large quantity of particulate metals to the shelf, which are now being slowly released. This possibility is difficult to evaluate.

#### An Anthropogenic Source?

Another scenario for the metal-salinity correlation would have metals injected downstream of the river sampling sites, most likely in the relatively more saline regions of the estuaries. In this case, implausibly high metal concentrations would not be necessary, because only moderately high metal concentrations would have to exist at salinities of about 30‰. While this scenario avoids the problem of unreasonably high metal concentrations, it does not avoid the problem of the total metal flux needed to maintain the metal-salinity relationships. As shown by BOYLE et al. (1974), the flux of non-conservative components through estuaries can be calculated by extrapolation of the concentration-salinity relationship to zero salinity and multiplying this number by the river flow.

TABLE 4 Dissolved trace metal concentrations in major Iberic rivers (nmol/kg).

River	Location/date	Cu	Ni	Zn
Guadalquivir	downstream of Sevilla /8-25-88	9.5	21.3	13.0
Guadalquivir #1	60 km north of mouth /3-28-88	15.7	64.1	33.2
Guadalquivir #2	60 km north of mouth /3-28-88	14.3	78.6	40.2
Guadiana	downstream of Merida /8-26-88	10.1	7.0	3.1
Tejo	North of Trujillo /8-26-88	0.6	58.8	7.0
Tejo #1	upstream of Lisboa /10-21-88	9.6	20.8	418
Tejo #2	upstream of Lisboa /10-21-88	7.5	14.0	392
-----				
Amazon *		24	5	4
Mississippi *		23	23	3

\* Shiller and Boyle (1987)

Analysis of 0.4  $\mu\text{m}$  Nuclepore filtered samples by GFAAS direct injection and standard additions.  
Cd concentrations below detection limit of  $\approx 0.1$  nmol/kg.  
Seawater contribution estimated from Mg concentration and determined by flame AA: below detection limit ( $\sim 1\%$ ) for Spanish rivers and 2% for the Tejo.

In this scenario, the flux of metals would still have to be as high as if they had been released in the river itself. Shelf water enrichments seen in the Gulf of Cadiz were recently traced as far north as Lisbon along the Iberian coast (VAN GEEN et al., 1990). The corresponding metal fluxes required to sustain the observed salinity:metal relationships for the whole peninsula therefore can be estimated from the combined annual discharge of the Douro, Tejo, Guadiana, and Guadalquivir rivers ( $1.2 \cdot 10^3$  m<sup>3</sup>/s; UNESCO, 1969) and coastal metal concentrations extrapolated to zero salinity. As indicated in Table 3, these fluxes correspond to 7% (Cu), 103% (Cd), and 30% (Zn) of a rough (GNP-based) estimate of total metal consumption in Spain and Portugal. Despite the uncertainty in these estimates, it seems unlikely that industrial effluents could cause such large metal inputs to rivers in one form or another.

It is also instructive to compare metal fluxes through the Strait of Gibraltar with local dumping activities by a nearby titanium dioxide production plant (Tioxide Espana, SA). Acidic waste effluents are discharged daily at 36°30'N, 07°00'W from two 750 m<sup>3</sup> capacity tankers and have been the subject of environmental concern (unpubl. manuscripts presented by Spain to the 12th meeting of the Oslo Commission, Madrid, June 1986). Copper and zinc inputs calculated from the reported composition of the effluent at Huelva could account only for a minimal fraction (Cu, 1/15000; Zn, 1/700) of the metal flux due to shelf water entrainment.

### Shelf Sediments?

Shelf sediment diagenesis is more difficult to evaluate as a potential source of metals, and we can only address it indirectly. The unusual nature of such a source in this area, if it exists, can be seen by comparing coastal water enrichments in the Gulf of Cadiz with metal concentrations determined in shelf waters elsewhere (Table 5). Clearly, Zn, Cu, and to a lesser extent Cd enrichments off Cadiz were outside the range of most previously reported shelf water concentrations. Only metal concentrations in the German Bight (KREMLING and HYDES, 1988) approach those of the Gulf of Cadiz. This comparison suggests that a shelf sediment source, if significant, would have to be considerably stronger than in other coastal regions that have been studied (with perhaps the exception of the German Bight). Copper concentrations in the Bering Sea do not rise above 5 nmol/kg even though the continental shelf in this region is much wider than the Spanish shelf ( $\sim 200$  vs. 20 km width to the 50 m isobath). A more revealing difference between the two regions is that Mn concentrations over the Spanish shelf were considerably higher than in the Bering Sea. Total dissolvable Mn concentrations as high as 160 nmol/kg (Oce. 0.1) were measured by G. KLINKHAMMER (pers. comm.) for the unfiltered Spanish shelf water, with offshore concentrations in the Gulf of Cadiz under 2 nmol/kg. Because Mn concentrations in the Bering Sea do not exceed 20 nmol/kg, particularly intense Mn reduction must occur in sediments of the Gulf of Cadiz.

TABLE 5 Survey of trace metal concentrations reported for shelf waters. (Salinity: ‰, metal concentrations: nmol/kg)

Location	Salinity	Cu	Ni	Cd	Zn	Mn
Cadiz (1)	35.42	40	8.7	1.02	170	160*
Morocco (1)	36.20	1.9	2.4	0.06	4.2	
NW Atlantic (2)	30.00	4.0	6.0	0.20	2.5	20
NE Atlantic (3)	35.00	2.5	-	0.25	-	12
Calif. Bight (4)	33.50	-	-	0.15	-	-
Bering Sea (5)	31.50	5.0	-	-	-	30
German Bight (6)	29.00	30	20	0.80	-	55
French Coast (6)	33.00	9	10	0.30	-	32

\* unfiltered sample

- (1) this work  
 (2) Bruland and Franks (1983)  
 (3) Kremling (1983)  
 (4) Martin et al. (1976)  
 (5) Heggie et al. (1987)  
 (6) Kremling and Hydes (1988)

On the other hand, profiles collected in shallow waters west of the Strait did not show the higher metal concentrations indicative of a strong pore water source. At station Oce. 3 (25 m deep), potential evidence of a bottom source probably was obscured by vertical mixing, while at Oce. 1, slightly deeper (45 m) and closer to the Guadalquivir estuary, Cu and Zn concentrations were significantly higher in the upper water column rather than towards the sediment. A sedimentary source could nevertheless be masked by the flow pattern on the shelf if low metal open-ocean water accumulates metals in shallow bottom waters until it reaches the coast, upwells, and moves offshore at the surface.

Copper and cadmium pore water concentrations measured in a few locations can be used to estimate the magnitude of such a diagenetic source over an area 1000 km long by 20 km wide that corresponds roughly to the shelf region covered by metal-enriched waters within the 50 m isobath up to the Douro river. Benthic fluxes corresponding to data of KLINKHAMMER et al. (1982) for oxic sediments from the equatorial Pacific, HEGGIE et al. (1987) for suboxic sediments from the Bering Sea shelf, and GAILLARD et al. (1986) for a shallow bay on the French Mediterranean coast are listed along with metal fluxes through the Strait of Gibraltar in Table 3. Given the uncertainty in these calculations, Cu fluxes through the Strait could conceivably be sustained only by diagenetic fluxes comparable to those found on the Bering Sea shelf. Considerably higher diagenetic metal fluxes (that were measured with benthic chambers in a Swedish fjord) are also included in Table 3 (WESTERLUND et al., 1986). Only the latter estimates of benthic Cd and Zn fluxes fall within an order-of-magnitude of fluxes required to sustain the loss of Cd and Zn through the Strait of Gibraltar. Metal diagenesis required to sustain the loss of Spanish shelf water by entrainment

through the Strait are clearly at the upper limit of what has been observed elsewhere. For this reason, we suggest one mechanism analogous to the "nutrient trap" observed in estuaries (REDFIELD et al., 1963) that could significantly enhance diagenetic fluxes in this region.

#### A Shelf Metal Trap

This scenario can be illustrated by a simple box-model constrained by water, salt, and metal fluxes. For this mechanism to operate, there must be upwelling onto the shelf, metal removal by plankton from upper waters, and finally regeneration of this metal flux within the shelf region. The section perpendicular to the coastline shown in Fig. 11 illus-

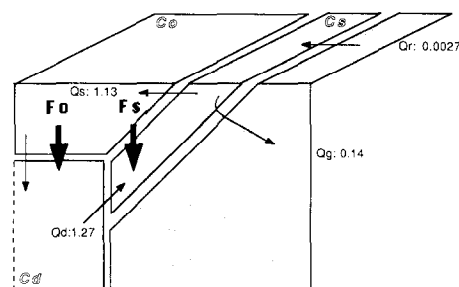


FIG. 11. Section of box model showing "metaltrap." Compartments identified by metal concentrations:  $C_0$ , offshore surface box;  $C_s$ , shelf box;  $C_d$ , offshore deep box. Thick arrows represent particulate metal fluxes from box of origin and redissolution into destination box. Trapping efficiency  $f$  is defined as  $(F_s)/(F_0 + F_s)$ . Advective water fluxes are indicated by thin arrows:  $Q_r$ , river input;  $Q_g$ , shelf water loss through Gibraltar;  $Q_d$ , upwelling of deep water;  $Q_s$ , offshore surface advection of shelf water ( $10^6 \text{ m}^3/\text{s}$ ).

trates the role of these processes. The first step of the trapping cycle is upwelling of subsurface Atlantic water containing Cu, Ni, Cd, and Zn at (relatively low) concentration  $C_d$  onto the shelf by a water transport  $Q_d$ . Plankton production stimulated by upwelling strips trace metals from solution onto biogenic particles and generates particle fluxes  $F_s$  and  $F_o$ . A fraction of these particles remains within the shelf box (e.g., by sinking to shelf sediments:  $F_s$ ). As shelf water is advected further offshore ( $Q_s$ ), concentrations are reduced to  $C_o$  by particle flux  $F_o$  into the deep offshore box. The offshore surface box extends only over the region of the surface ocean where the particulate metal flux is sufficient to compensate for any metals supplied by upwelling that are not trapped within the shelf box. The final step of the enrichment process is plankton decomposition in the shelf box, which releases metals to the water column and raises metal concentrations of the shelf water to  $C_s$ .

Based on the distribution of metal enrichments in Iberian shelf waters, a 50 m depth is added to the dimensions (20 by 1000 km) of the shelf box defined above. The boundary between the offshore surface and deep boxes is also set at 50 m. Based on the CTD survey of the Gulf of Cadiz made by BRAY (1986) in April 1986, the salinity of the shelf box is set at  $S_s = 36.0\%$  (indices for salinity follow the description of metal concentrations ( $C_x$ ) in Fig. 11). At the southern end of the shelf box, water is lost to entrainment with the Atlantic inflow through the Strait of Gibraltar. Shelf water loss through the Strait of Gibraltar  $Q_g$  and river input  $Q_r$  are added to the model (Fig. 11). The following derivations assume steady state with respect to volume and metal concentrations for both the shelf and offshore surface boxes. In addition, conservation of salt is assumed for the shelf box. The composition of the deep box is a boundary condition and mass balance is not used as a constraint here, which is equivalent to assuming that the net export of water and metals through the Strait of Gibraltar (ultimately sustained by upwelling) does not significantly reduce the size or metal concentrations of the deep ocean. For mass balance in the shelf box, water fluxes must satisfy

$$Q_d + Q_r = Q_s + Q_g \quad (1)$$

Two terms of this equation ( $Q_r$ ,  $Q_g$ ) are reasonably well known. Because metal enrichments were highest in April,  $Q_r$  is set at  $2.7 \cdot 10^3 \text{ m}^3/\text{s}$  which is the total peak discharge (February–March) of the four main rivers on the Atlantic coast of the Iberian peninsula (Guadalquivir, Guadiana, Tejo, and Douro; UNESCO, 1969).  $Q_g$  was estimated at  $0.14 \cdot 10^6 \text{ m}^3/\text{s}$  above. Salt balance for the shelf box is a second constraint from which  $Q_d$  (the driving force of the metal-trap) can be derived:

$$S_d \cdot Q_d = (Q_s + Q_g) \cdot S_s \quad (2)$$

Combining Eqn. (1) and (2) yields

$$Q_d = \frac{Q_r \cdot S_s}{(S_d - S_s)} \quad (3)$$

Because the average salinity of subsurface water between 60 and 300 m (the estimated depth range of the offshore deep box) is  $36.10 \pm .05\%$ , the estimate of  $Q_d$  ranges between

$0.65\text{--}1.9 \cdot 10^6 \text{ m}^3/\text{s}$ . Most of the upwelling flux returns offshore to the surface box because Eqn. (1) dictates  $Q_s = 1.13 \cdot 10^6 \text{ m}^3/\text{s}$  given the average value of  $Q_d$  ( $1.27 \cdot 10^6 \text{ m}^3/\text{s}$ ). An independent estimate of the upwelling rate shows that this flux is reasonable. MAY (1982) presented data showing that the wind stress along the Portuguese coast varies between 0.3 and 1.0 dyne/cm<sup>2</sup> from the north. From the Ekman transport equation:

$$U = \frac{\tau \cdot L}{\rho \cdot f} \quad (4)$$

where  $\rho$  is the density of sea water ( $\sim 1 \text{ g/cm}^3$ ),  $L$  the length of coastline ( $10^8 \text{ cm}$ ),  $f$  the Coriolis parameter ( $9.3 \cdot 10^{-3}/\text{s}$  at  $40^\circ$  latitude), and  $\tau$  the wind stress; the corresponding wind-driven upwelling rate ( $U$ ) is 0.36 to  $1.1 \cdot 10^3 \text{ m}^3/\text{s}$ . For this simplified picture of circulation in Iberian coastal waters, there is adequate agreement between estimates of upwelling from salt balance and wind stress.

Trace metal trapping can be estimated using the shelf box mass balance (Eqn. 2) and modifying this expression to incorporate particulate metal fluxes  $F_s$  and  $F_o$ , as well as any unknown input to the shelf box  $I$ :

$$C_r \cdot Q_r + C_d \cdot Q_d + F_s + I = (Q_s + Q_g) \cdot C_s \quad (5)$$

and by assuming that trace metals advected into the offshore surface box are removed by the particle fluxes and sinking of surface water back into the deep box:

$$Q_s \cdot C_s - (F_o + F_s) - Q_s \cdot C_o = 0. \quad (6)$$

A shelf *trapping efficiency*  $f$  can be defined as the proportion of the total particulate flux supported by upwelling that is recycled back into the shelf box:

$$f = \frac{F_s}{(F_s + F_o)}. \quad (7)$$

This expression assumes that the total metal flux sequestered by biogenic particles in the shelf box is re-mineralized either in the water column or underlying sediments. While some sedimentary metal removal may occur, the model equations would become more complicated by addition of a "re-mineralization efficiency" without gaining any significant insight. Solving for the offshore particulate flux  $F_o$  from Eqn. (7) and substitution in Eqn. (6) yields

$$F_s = f \cdot Q_s \cdot (C_s - C_o). \quad (8)$$

By substituting this expression for  $F_s$  into Eqn. (5), the metal mass-balance expression for the shelf box becomes

$$C_r \cdot Q_r + C_d \cdot Q_d + f \cdot Q_s \cdot (C_s - C_o) + I = C_s \cdot Q_s + C_s \cdot Q_g \quad (9)$$

Metal concentrations for both the shelf and the offshore surface box are taken from Table 2.  $C_d$  is the average subsurface water concentration between 50 and 300 m depth (not that of NACW at 400 m): 1.3, 2.6, 0.075, and 1.5 nmol/kg for Cu, Ni, Cd, and Zn, respectively. The average composition of Guadalquivir samples #1 and #2 is taken for  $C_r$  (Table 4). An upper limit of 1 nmol/kg is chosen for riverine Cd concentration taking into account the effect of desorption in

estuaries. Rearranging Eqn. (9) yields an expression for shelf enrichment:

$$C_s = \frac{C_r \cdot Q_r + C_d \cdot Q_d - f \cdot Q_s \cdot C_o + I}{Q_s \cdot (1 - f) + Q_g} \quad (10)$$

The trapping efficiency  $f$  is highly significant; if the loss through Gibraltar ( $Q_g$ ) were zero,  $f$  approaching unity could drive shelf water metal concentrations  $C_s$  towards infinity. Even with loss through the Strait of Gibraltar and  $I = 0$ , complete trapping efficiency on the shelf enhances Cu, Ni, Cd, and Zn concentrations to 4.0, 7.2, 0.46, and 8.0 nmol/kg, respectively, relative to the non-trapping case: 1.3, 2.7, 0.077, and 1.6 nmol/kg.

#### Is the Metal Trap a Reasonable Hypothesis?

The relative magnitude of metal fluxes in Eqn. (9) (Table 6) shows that metal input to the shelf box by upwelling ( $C_d \cdot Q_d$ ) is at least as large as loss through Gibraltar ( $C_s \cdot Q_g$ ), except in the case of Zn. The role of rivers as metal sources ( $C_r \cdot Q_r$ ) is relatively minor even though the river input of fresh water helps create the estuarine circulation pattern. Observed Ni and Cd enrichments (i.e.,  $C_s$ ) could be sustained with 61 and 80% trapping efficiencies, respectively. But the metal trap cannot account for observed Cu and Zn enrichments because losses through the Strait of Gibraltar are too high. Even with 100% trapping efficiency, additional inputs ( $I$ ) equal to about half the Cu and Zn strait fluxes are required to satisfy mass balance. Note, however, that the additional Cu and Zn inputs ( $I$ ) are on the order of the uncertainty in metal fluxes through the strait (since entrainment of shelf water—20% of total inflow—is known to  $\pm 5\%$ ).

An independent constraint on the metal-trap mechanism is provided by the required magnitude of biological production. Data in Table 6 also indicate the particulate metal fluxes ( $F_s = f \cdot Q_s \cdot (C_s - C_o)$ ) reaching the shelf box: e.g., for Cd,  $F_s = 0.14$  mol Cd/sec given an 80% trapping efficiency. Assuming that the metal content of plankton relative to carbon determined by COLLIER and EDMOND (1984) off the Galapagos (also a high productivity area) is appropriate to this

environment, a total carbon flux of  $1.2 \cdot 10^4$  mol C/sec would be required. Over the area of the shelf box, this corresponds to a total production rate of  $0.2 \cdot 10^3$  gC/m<sup>2</sup>·a. By comparison, production in the Peru upwelling region is on the order of  $2 \cdot 10^3$  gC/m<sup>2</sup>·a (EPPLEY and PETERSON, 1979). Therefore, the magnitude of productivity over the Spanish shelf required for Cd is reasonable. But for Cu and Zn (6.3 and 22.8 mol/s for 100% trapping efficiencies), primary production would have to be on the order of 20 and  $8 \cdot 10^3$  gC/m<sup>2</sup>·a, respectively. Unless plankton are strongly enriched in Cu and Zn in this region (which may occur in response to the elevated dissolved metal concentrations), the productivity constraint suggests that the metal trap alone cannot account for Cu and Zn shelf water enrichments, even under the most favorable conditions. This limitation of the box model compounds the difficulty in sustaining Cu and Zn mass-balances in the shelf water.

In summary, the metal-trap model shows that significant enhancements to shelf metal concentrations can be produced by this mechanism. In the case of Zn and Cu, this mechanism does not account for all of the enrichment, so that other factors may play a role. This model also does not account for some of the features of our data. It is not clear that the variability in trace metal enrichments is related to seasonality in the driving forces of the metal trap. The two physical forcing mechanisms of the metal trap are of opposite phase: river discharge decreases by an order of magnitude along the Iberian coast between February and August, but wind stress along the Portuguese coast is much stronger during summer months. Although the decrease of Zn shelf water enrichments observed between April and October 1986 may be seasonal, its cause is unknown.

#### CONCLUSIONS

Copper, cadmium, and zinc concentrations over the continental shelf of the Gulf of Cadiz are higher than enrichments generally reported for other coastal waters. Systematic metal-metal and metal-salinity relationships were observed immediately west of the Strait of Gibraltar in April and October 1986 over a wide range of metal concentrations. In contrast,

TABLE 6 Metal fluxes corresponding to the mass-balance of eq.(9). Flux units are moles/s. Details of water and metal flux calculations in text.

	river + upwelling +	part. + unknown	-	offshore	+ Gibraltar	
	$C_r \cdot Q_r$	flux	input	advection	loss	
	$C_d \cdot Q_d$	$f \cdot Q_s \cdot (C_s - C_o)$	I	$C_s \cdot Q_s$	$C_s \cdot Q_g$	
Cu	0.04	1.65	1.00·6.33	0.36	7.46	0.92
Ni	0.19	3.30	0.61·1.36	-	3.84	0.48
Cd	0.003	0.095	0.80·0.181	-	0.215	0.027
Zn	0.13	1.90	1.00·22.83	1.81	23.73	2.94

nutrient levels,  $^{228}\text{Ra}/^{226}\text{Ra}$  activity ratios, and Ni concentrations in coastal water of the Gulf of Cadiz were not exceptional for coastal environments. The mechanism underlying such metal enrichments in Spanish coastal water is of interest because this region feeds the Atlantic inflow through the Strait of Gibraltar and therefore has a basin-wide influence on metal concentrations in the Mediterranean Sea. In addition, high metal fluxes through the strait require high fluxes from the presumed source of metals to this region.

Despite a systematic increase in metal concentrations with decreasing salinity over the Spanish shelf, metal input from Iberian rivers cannot explain observed Cu, Cd, and Zn enrichments. A diagenetic shelf source may be more plausible but would have to be of unprecedented magnitude. Metal concentrations could also be enhanced by an estuarine "metal trap" in the coastal region, although this mechanism can account for only part of the observed enrichments. At the same time, weak Ni enrichments suggest that fluxes for this element cannot be as strong despite crustal abundances comparable to Cu and Zn. Tentatively, we suggest this may be related to the contrasting behavior of Ni relative to Cu, Zn, and Cd in anoxic systems. JACOBS et al. (1985) report that Cu, Cd, and Zn concentrations decrease sharply in anoxic waters in the water column of Framvaren Fjord (Norway), a permanently anoxic basin, while Ni is unaffected. Oxidation of sediments deposited under anoxic conditions would produce a similar pattern to that observed in Spanish shelf water: high Cu, Zn, and Cd fluxes relative to Ni. A few sediment cores and pore water measurements off Spain and Morocco might be sufficient to determine whether dissolved metal enrichments in the Gulf of Cadiz are due to the erosion of metal-rich deposits in Iberian shelf waters or to a circulation and productivity-dependent "metal trap."

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Appendix 1: Surface samples, March–April 1986. Salinity (‰), silicate and phosphate ( $\mu\text{mol/kg}$ ), Cu, Ni, Cd, and Zn (nmol/kg).

Station	Latitude	Longitude	Salinity	Si	PO <sub>4</sub>	Cu	Ni	Cd	Zn		
Apr. 1	36	42	6	30	35.418	3.22	0.45	43.7	8.5	0.966	162.8
Apr. 2	36	30	6	29	35.763	0.45	0.30	46.6	5.2	1.256	153.2
Apr. 3	36	20	6	30	35.630	0.18	0.12	19.6	4.8	0.506	103.1
Apr. 4	35	51	6	29	35.939	0.25	0.06	7.2	3.5	0.283	35.9
Apr. 5	35	37	6	30	36.278	0.80	0.05	3.4	3.4	0.077	7.0
Apr. 6	35	13	6	29	36.341	0.93	0.05	2.7	1.8	0.052	1.6
Apr. 7	35	10	6	20	36.291	1.05	0.05	2.4	2.4	0.041	0.9
Apr. 8	35	10	6	25	36.287	1.07	0.11	1.6	2.1	0.051	1.6
Apr. 9	35	10	6	35	36.350	1.25	0.05	1.2	2.0	0.015	0.3
Apr. 10	35	8	6	42	36.392	0.84	0.04	1.5	2.6	0.018	0.5
Apr. 11	35	10	6	58	36.357	0.85	0.05	2.7	2.7	0.011	1.0
Apr. 12	35	15	7	1	36.382	0.75	0.05	1.5	2.6	0.035	0.5
Apr. 13	35	30	7	0	36.220	0.65	0.07	5.2	3.0	0.168	19.4
Apr. 14	35	49	7	1	36.284	0.84	0.07	1.9	2.8	0.062	2.9
Apr. 15	36	3	7	0	36.302	0.89	0.08	2.0	3.0	0.052	3.5
Apr. 16	36	13	6	59	36.321	0.89	0.08	1.8	2.5	0.039	1.6
Apr. 17	36	24	6	59	36.214	0.85	0.04	2.3	2.7	0.069	6.1
Apr. 18	36	34	6	59	36.113	0.49	0.07	3.4	3.0	0.109	12.4
Apr. 19	36	41	6	59	36.164	0.87	0.04	2.5	3.0	0.088	9.1
Apr. 20	36	45	6	59	36.152	1.04	0.04	2.0	2.8	0.098	6.7
Apr. 21	36	46	6	59	36.087	0.95	0.05	2.5	3.1	0.091	7.6
Apr. 22	36	51	6	59	35.962	0.80	0.08	3.2	3.2	0.104	9.5
Apr. 23	36	56	6	59	35.862	1.25	0.15	3.4	3.3		10.6
Apr. 24	36	59	6	59	35.903	3.07	0.40	3.9	3.6	0.127	6.4
Apr. 25	36	57	7	10	35.870	1.07	0.12	4.6	3.4	0.165	12.5
Apr. 26	36	5	7	20	36.039	0.93	0.08	2.8	2.6	0.088	7.8
Apr. 27	36	55	7	29	36.168	1.11	0.06	1.9	2.8	0.048	3.8
Apr. 28	36	48	7	30	36.248	0.85	0.09	1.2	2.7	0.037	2.0
Apr. 29	36	41	7	30	36.254	0.91	0.06	1.3	2.3	0.050	3.8
Apr. 30	36	31	7	30	36.305	0.93	0.05	1.1	3.1	0.032	0.8
Apr. 31	36	22	7	30	36.254	0.93	0.07	1.1	2.6	0.034	0.5
Apr. 32	36	11	7	30	36.297	1.02	0.07	1.5	2.6	0.032	1.3
Apr. 33	35	54	7	31	36.222	0.58	0.06	4.8	2.6	0.144	19.2
Apr. 34	35	43	7	31	36.248	0.71	0.07	5.2	3.3	0.142	18.4
Apr. 35	35	34	7	31	36.261	0.67	0.05	2.7	2.6	0.086	10.4
Apr. 36	35	25	7	31	36.248	0.58	0.05	3.7	3.2	0.113	13.6
Apr. 37	35	16	7	28	36.371	0.80	0.07	1.5	2.3	0.033	2.7
Apr. 38	35	10	7	44	36.398	0.85	0.05	1.0	2.4	0.019	0.8
Apr. 39	35	10	7	58	36.378	0.96	0.07	0.8	2.5	0.017	0.2



## Appendix I (Continued)

Station	Latitude	Longitude	Salinity	Si	PO4	Cu	Ni	Cd	Zn		
Apr. 40	35	19	8	0	36.420	0.87	0.04	0.8	2.0	0.009	0.1
Apr. 41	35	29	8	0	36.418	0.82	0.05	1.6		0.016	0.7
Apr. 42	35	39	8	1	36.408	0.87	0.13	1.0	2.2	0.017	0.8
Apr. 43	35	46	8	0	36.387	0.96	0.05	1.1	2.6	0.014	0.3
Apr. 44	36	0	8	0	36.391	0.84	0.07	0.8	2.1	0.013	0.2
Apr. 46	36	2	8	0	36.361	0.87	0.08	0.8	2.0	0.013	0.2
Apr. 47	36	33	7	59	36.276	1.09	0.25	1.0	2.3	0.024	0.7
Apr. 48	36	37	7	58	36.222	1.15	0.17	1.5	2.4	0.031	0.6
Apr. 49	36	4	8	0	36.057	1.62	0.26	1.4	2.2	0.052	1.5
Apr. 50	36	0	7	42	36.399	0.76	0.09	0.8	2.0	0.013	0.1
Apr. 52	36	0	7	22	36.399	1.20	0.09	1.0	2.3	0.013	0.2
Apr. 53	35	59	7	1	36.359	1.13	0.10	1.9	2.5	0.044	4.1
Apr. 54	36	0	7	2	36.317	1.15	0.09	1.3	2.5	0.034	1.7
Apr. 56	36	0	6	34	36.054	0.51	0.08	1.6	2.5	0.047	3.3
Apr. 57	36	0	6	21	35.992	0.51	0.09	2.7	2.5	0.095	8.0
Apr. 58	36	0	6	21	36.005	0.67	0.10	2.8	2.3	0.094	8.8
Apr. 70	36	10	6	24	36.043	0.40	0.40	5.5	2.7	0.148	17.9
Apr. 71	36	20	6	28	35.954	0.49	0.49	3.5	3.1	0.146	10.6
Apr. 72	36	25	6	30	35.937	0.64	0.64	3.3	2.6	0.100	10.4
Apr. 73	36	34	6	24	35.887	0.98	0.98	15.6	3.6	0.415	73.9
Apr. 253	35	52	5	53	36.298	0.00	0.00	1.2	2.8	0.035	1.6
Apr. 254	35	53	5	53	36.214	0.00	0.06	1.1	2.8	0.042	1.2
Apr. 255	35	56	5	52	36.234	0.00	0.20	0.9	2.9	0.039	0.7
Apr. 256	35	57	5	50	36.153	0.83	0.24	1.5	2.9	0.046	1.7
Apr. 257	36	0	5	51	36.074	0.83	0.07	2.2	2.8	0.082	5.0
Apr. 258	36	2	5	50	36.029	1.32	0.20	4.6	3.2	0.138	14.4
Apr. 259	36	4	5	50	36.086	1.46	0.15	6.6	3.3	0.215	21.7
Apr. 260	35	43	5	59	36.119	0.60	0.11	1.8	2.7	0.061	2.8
Apr. 261	35	44	6	1	36.141	0.63	0.07	1.7	2.3	0.036	1.3
Apr. 262	35	45	6	3	36.276	0.99	0.06	1.1	2.5	0.037	0.8
Apr. 263	35	49	6	4	36.262	0.89	0.04	0.9		0.029	0.9
Apr. 264	35	50	6	4	36.238	0.70	0.03	0.9	2.8	0.034	1.2
Apr. 265	35	51	6	5	36.219	0.73	0.03	1.0	2.8	0.041	1.1
Apr. 266	35	54	6	6	36.067	0.60	0.04	2.6	2.9	0.103	4.2
Apr. 267	35	57	6	6	36.038	0.79	0.07	2.8	3.1	0.101	8.3
Apr. 268	36	0	6	4	36.038	1.39	0.19	5.0	3.0	0.170	19.2
Apr. 269	36	2	6	3	36.007	1.46	0.15	6.1	3.5	0.190	21.3
Apr. 271	36	7	5	59	36.123	1.06	0.11	6.2		0.183	19.8
Apr. 272	36	6	6	3	36.156	1.06	0.11	5.4		0.177	19.8
Apr. 273	36	6	6	6	36.085	1.69	0.34	6.6		0.195	20.6
Apr. 274	36	5	6	12	35.976	2.42	0.31	12.3	4.8	0.271	30.9
Apr. 275	36	5	6	14	35.969	2.28	0.26	10.6	4.0	0.223	31.0
Apr. 276	36	5	6	16	35.938	1.59	0.27	12.8	4.2	0.245	41.4
Apr. 277	36	5	6	17	35.946	1.82	0.23	11.8	4.1	0.248	30.3
Apr. 278	36	3	6	17	35.970	1.72	0.21	11.3	4.1	0.245	31.9
Apr. 279	36	1	6	17	35.983	1.23	0.17	8.8	3.6	0.207	25.1
Apr. 280	35	58	6	19	35.977	0.46	0.08	7.5	3.3	0.170	20.8
Apr. 281	35	56	6	20	35.999	0.63	0.06	1.9	3.0	0.067	5.4
Apr. 282	35	55	6	17	36.114	0.73	0.09	1.4	2.8	0.053	1.9
Apr. 283	35	55	6	14	36.052	0.66	0.10	1.6	2.7	0.065	2.7
Apr. 284	35	54	6	12	36.042	0.70	0.07	1.6	2.9	0.077	3.9
Apr. 285	35	56	6	9	36.025	0.66	0.09		3.1	0.107	7.9
Apr. 286	35	58	6	10	36.009	0.89	0.13	6.1	3.4	0.132	14.4
Apr. 287	36	0	6	10	35.996	1.29	0.17	9.8	3.9	0.237	28.6
Apr. 288	36	4	6	8	36.010	1.75	0.24	8.8	3.9	0.204	29.1
Oce. 0.1	36	32	6	24	35.876	1.13	0.31	21.2	4.3	0.403	52.0
Oce. 1.0	36	24	6	25	35.935	0.33	0.17	16.8	3.8	0.260	36.0
Oce. 2.0	36	12	6	35	35.979	0.04	0.05	18.6	2.8	0.074	8.2
Oce. 3.0	36	10	6	19	35.995	1.63	0.26	10.6	3.4	0.202	24.5
Oce. 5.0	35	56	5	53	36.323	0.66	0.10	1.4	2.4	0.034	1.9
Oce. 6.0	35	58	6	13	36.003	1.05	0.18	6.7	3.1	0.163	18.9
Oce. 7.0	35	47	6	8	36.231	0.62	0.05	1.6	2.2	0.033	1.7
Oce. 8.0	35	37	6	1	36.142	0.46	0.06	2.0	2.5	0.063	3.8
Oce. 9.0	35	37	6	4	36.215	0.33	0.08	2.0	2.6	0.058	3.9
Oce. 10.0	35	35	6	6	36.188	0.41	0.04	1.8	2.6	0.066	4.8
Oce. 11.0	35	29	6	27	36.217	0.28	0.08	1.7	2.4	0.062	3.4
Oce. 11.1	35	29	6	22	36.165	0.74	0.10	1.6	2.7	0.053	3.5
Oce. 13.0	35	49	6	0	36.339	0.50	0.04	1.5	2.4	0.042	2.9
Oce. 14.2	36	10	6	23	35.982	1.37	0.24	9.5	3.7	0.240	31.3
Oce. 15.0	35	56	5	40	36.349	0.82	0.10	1.6	2.5	0.029	1.7

Appendix 2: Surface samples, October 1986. Same units as in Appendix 1.

Station	Latitude	Longitude	Salinity	Si	PO4	Cu	Ni	Cd	Zn		
Oct. 1	36	10	6	19	36.207	0.40	0.05	2.7	2.5	0.073	4.5
Oct. 2	36	5	6	19	36.197	0.33	0.03	1.2	2.8	0.040	1.6
Oct. 3	35	58	6	20	36.228	0.33	0.10	3.8	2.8	0.113	7.0
Oct. 5	35	49	6	9	36.490	0.33	0.06	1.5	2.8	0.028	0.0
Oct. 7	35	49	6	4	36.436	0.46	0.05	1.6	2.5	0.032	1.6
Oct. 8	35	49	6	2	36.490	0.46	0.04	1.6	2.4	0.038	1.9
Oct. 10	35	52	5	59	36.481	0.40	0.08	1.9		0.043	2.9
Oct. 11	35	52	6	2	36.461	0.43	0.06	2.0		0.043	2.3
Oct. 12	35	52	6	5	36.470	0.43	0.05	1.5	2.2	0.036	1.9
Oct. 13	35	52	6	10	36.378	0.36	0.05	2.0	3.2	0.056	3.1
Oct. 15	35	53	6	7	36.374	0.33	0.10	2.0	2.8	0.052	3.6
Oct. 17	35	53	6	2	36.396	0.36	0.12	3.4	2.9	0.081	5.4
Oct. 19	35	57	6	1	36.387	0.46	0.09	3.4	3.0	0.086	6.0
Oct. 21	35	57	6	8	36.365	0.43	0.09	3.2	3.1	0.089	7.4
Oct. 22	35	57	6	10	36.376	0.46	0.06	2.2	2.2	0.068	3.9
Oct. 23	36	1	6	11	36.280	0.53	0.14	5.5	2.9	0.148	11.7
Oct. 24	36	1	6	8	36.260	0.40	0.19	5.4	2.5	0.162	11.6
Oct. 25	36	1	6	4	36.304	0.30	0.12	4.5	2.9	0.112	9.9
Oct. 26	36	3	6	5	36.308	0.17	0.15	4.8	2.8	0.150	9.6
Oct. 27	36	3	6	8	36.300	0.20	0.14	5.2	3.2	0.148	10.7
Oct. 28	36	3	6	11	36.301	0.07	0.14	5.0	2.7	0.160	11.0
Oct. 30	36	4	6	15	36.291	0.13	0.15	6.0	2.5	0.149	11.7
Oct. 31	36	4	6	11	36.298		0.14	5.1	2.4	0.155	12.0
Oct. 32	36	4	6	9	36.311		0.15	4.9	2.9	0.128	9.4
Oct. 81	36	6	6	0	36.481		0.02	1.9	3.0	0.057	3.3
Oct. 90	36	0	5	32	36.276		0.14	5.4	3.2	0.139	10.4
Oct. 103	36	4	5	52	36.148		0.12	5.0	3.0	0.118	9.5
Oct. 104	36	3	5	49	35.865		0.11	6.4	2.9	0.111	8.2
Oct. 105	36	0	5	49	36.002		0.07	2.8	2.6	0.066	4.3
Oct. 106	35	56	5	48	36.378		0.02	1.9	2.6	0.037	1.4
Oct. 107	35	53	5	49	36.406		0.02	1.5	2.4	0.032	1.4

Appendix 3: Profile data, April 1986. Same units as in Appendix 1. Filtered (F) and unfiltered (UF) samples indicated.

	Depth m	Salinity	Si	PO4		Cu	Ni	Cd	Zn
Oce. 1	0	35.935	0.33	0.17	UF	16.8	3.8	0.260	36.0
36°24' N	20	35.931	0.18	0.18	F	16.1	4.5	0.335	32.2
6°25' W	30	35.932	0.21	0.16	F	12.6	3.7	0.290	31.7
	40	35.945	2.63	0.46	F	12.0	4.2	0.258	26.7
	45	35.963	7.12	0.59	F	7.5	7.9	0.323	18.1
Oce. 2	0	35.979	0.04	0.05	UF	18.6	2.8	0.074	8.2
36°12' N	10	36.020	0.07	0.09	F	1.6	2.5	0.055	2.5
6°35' W	70	36.024	0.18	0.08	F	2.3	2.6	0.055	3.6
	110	35.941	2.34	0.39	F	1.3	2.6	0.055	2.1
	155					2.3	2.7	0.071	1.5
Oce. 3	0	35.995	1.63	0.26	UF	10.6	3.4	0.202	24.5
36°10' N	5	35.983	1.29	0.31	F	9.1	3.5	0.202	26.4
6°19' W	15	35.984	1.32	0.26	F	9.0	3.3	0.195	25.2
	20	35.984	1.78	0.28	F	7.8	3.4	0.205	24.6
	25	35.984	1.94	0.28	F	8.6	3.9	0.217	20.7
Oce. 5	0	36.323	0.66	0.10	UF	1.4	2.4	0.034	1.9
35°56' N	58	36.267	0.49	0.08	F	1.5	2.7	0.040	1.3
5°53' W	108	36.236	1.13	0.11	F	1.5	2.7	0.038	1.2
	158	36.035	2.20	0.40	F	1.8	3.0	0.085	1.6
	200	37.613	4.33	0.33	F	1.9	4.1	0.089	5.1
Oce. 6	0	36.003	1.05	0.18	UF	6.7	3.1	0.163	18.9
35°58' N	15	36.117	0.82	0.13	F	7.6	3.1	0.165	19.7
6°13' W	45	36.017	1.79	0.18	F	1.6	2.3	0.070	3.8
	80	35.949	4.14	0.41	UF	2.2	2.7	0.078	4.1
	115	35.907	3.03	0.52	F	1.1	2.3	0.091	2.2
Oce. 7	0	36.231	0.62	0.05	UF	1.6	2.2	0.033	1.7
35°47' N	40	36.471	0.80	0.12	UF	1.1	2.3	0.031	1.1
6°08' W	140	36.101	1.95	0.32	F	0.9	2.7	0.048	1.3
	240	36.600	4.29	0.50	F	1.3	3.0	0.090	1.8
	340	38.072	6.09	0.38	F	1.2	3.6	0.060	2.8

## Appendix 3 (Continued)

	Depth m	Salinity	Si	PO4		Cu	Ni	Cd	Zn
Oce. 11	0	36.217	0.28	0.08	UF	1.7	2.4	0.062	3.4
35°29' N	50	36.207	1.11	0.11	F	1.5	2.2	0.057	3.5
6°27' W	150	35.963	3.62	0.49	F	1.9	2.7	0.091	1.7
	200	35.920	3.94	0.55	F	1.4	2.6	0.103	1.4
Oce. 15	0	36.349	0.82	0.10	UF	1.6	2.5	0.029	1.7
35°56' N	50	36.365	0.72	0.10	UF		2.6	0.041	
5°40' W	75	36.174	1.75	0.28	UF	1.3	2.5	0.044	
	150	38.303	5.42	0.33	UF		5.5	0.099	
	200	38.372	5.37	0.39	UF	1.9	4.9	0.096	6.1
	250				UF	1.8	4.7	0.080	5.3
	400	38.517	9.18	0.45	UF	1.9	5.1	0.089	5.1
	450	38.450	8.93	0.45	UF		5.1	0.074	6.5
	500				UF	1.9	4.6	0.070	5.8
	510	38.450	9.15	0.44	F	1.8	5.1	0.073	5.4

Appendix 4:  $^{228}\text{Ra}/^{226}\text{Ra}$  activity ratios (dpm/dpm) for samples collected April 14–16, 1986. Nearby trace metal surface sample indicated in most cases. Propagated errors in activity ratios due to counting statistics also indicated.

Ra Station	TM Station	Latitude	Longitude	Act. ratio	Counting Error	
1	Oce. 0.1	36	32 6	24	0.57	0.05
2	Oce. 1.0	36	24 6	25	0.41	0.01
3		36	17 6	29	0.27	0.01
4	Oce. 2.0	36	12 6	35	0.23	0.02
5		36	11 6	27	0.24	0.01
6	Oce. 3.0	36	10 6	19	0.18	0.01
7	Oce. 3.1	36	6 6	16	0.44	0.03
8	Oce. 4.0	35	65 6	0	0.26	0.01
9	Oce. 5.0	35	56 5	53	0.15	0.01
10	Oce. 6.0	35	58 6	13	0.35	0.01
11	Oce. 7.0	35	47 6	8	0.17	0.02
12	Oce. 8.0	35	37 6	1	0.20	0.01
13	Oce. 9.0	35	37 6	4	0.23	0.02
14		35	35 6	6	0.26	0.02
15	Oce. 10.0	35	35 6	6	0.16	0.02
16	Oce. 11.0	35	29 6	27	0.42	0.05
17	Oce. 13.0	35	49 6	0	0.16	0.01
18	Oce. 14.0	35	57 5	35	0.16	0.01
19	Oce. 15.0	35	56 5	40	0.16	0.01
20		35	51 5	43	0.23	0.02