

## Zinc, chromium, vanadium and iron in the Mediterranean Sea

ROBERT M. SHERRELL\* and EDWARD A. BOYLE\*

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**Abstract**—Mediterranean surface waters contain elevated levels of zinc and chromium and slightly lower levels of vanadium compared to similar nutrient-depleted open ocean waters. A detailed mapping of surface concentrations in the Alboran Sea (immediately east of the Strait of Gibraltar) reveals that maximum total dissolvable concentrations of Zn ( $9.4 \text{ nmol kg}^{-1}$ ), Cr ( $3.9 \text{ nmol kg}^{-1}$ ), V ( $35 \text{ nmol kg}^{-1}$ ) and total Fe ( $53 \text{ nmol kg}^{-1}$ ) occur in the core of the Atlantic inflow jet.

These distributions imply that a portion of Mediterranean trace metal enrichment occurs during passage of surface water through the coastal region and into the Strait, as observed previously for Cu and Cd. Mass balance indicates that about half of the Mediterranean Zn enrichment, and most of the Cr enrichment, is due to sources within the basin itself. High concentrations of particulate Fe in the Alboran Sea suggest eolian input or recent sediment resuspension, but in general metal sources are difficult to identify and could be fluvial or anthropogenic as well as eolian and sedimentary.

Chromium and V levels in Mediterranean deep water are similar to surface water concentrations near deep-water formation regions, but Zn is enriched in deep water, implying some vertical transport by biological cycling. A simple steady-state box model indicates that about 30% of the Zn transport is particulate and that the Zn : nutrient ratio in sinking particulate matter is similar to that in open ocean particulates.

### INTRODUCTION

IT WAS recently discovered that Mediterranean surface waters are enriched in the trace metals Cu, Ni and Cd relative to similar nutrient-depleted waters in the open ocean (SPIVACK *et al.*, 1983). This observation could be attributed to anthropogenic metal sources within the densely populated and industrialized countries surrounding this restricted basin. However, consideration of potential sources shows that such an assumption is not yet justified, because natural sources and processes may be important in producing elevated metal levels. In fact BOYLE *et al.* (1985) subsequently discovered that inflowing waters near Gibraltar are highly enriched in Cu and Cd, thus a large fraction of excess metals may originate *outside* of the Mediterranean basin. While sources exterior to the basin may be natural or anthropogenic, a simple box model for geochemical cycling in the Mediterranean showed that flow-through circulation and limited recycling of nutrients in the Mediterranean could produce elevated surface concentrations for these elements *without* anthropogenic effects.

The natural or anthropogenic origin of Mediterranean trace metal enrichments has larger implications concerning geochemical processes in the ocean. If the enrichment is natural, then study of the Mediterranean may be useful in resolving the complex

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\* Department of Earth, Atmospheric, and Planetary Sciences, Massachusetts Institute of Technology, Rm E34-200, Cambridge, MA 02139, U.S.A.

processes responsible for maintaining steady-state oceanic profiles. The present study was undertaken to extend understanding of Mediterranean geochemical processes to other trace elements (Zn, Cr, V and Fe). By measuring a variety of elements with diverse geochemical properties, it is possible to learn more about potential sources and relevant processes. Data for these metals in the Mediterranean and adjacent North Atlantic are presented here with special emphasis on inflowing waters in the Alboran Sea.

#### SAMPLE COLLECTION AND ANALYSIS

Samples were collected in the Alboran Sea and in Atlantic waters immediately west of the Strait of Gibraltar on cruise 1309-80 of the U.S.N.S. *Bartlett*, 25 August-12 September 1980, and on cruise 1309-82 of the same vessel, 22-29 June 1982. A few samples from the west and central Mediterranean, collected on the earlier cruise, were also analysed. Surface samples were obtained using the pole sampling method (BOYLE *et al.*, 1981). Profile samples were collected using both modified Niskin bottles (BOYLE *et al.*, 1984) and "vane" samplers specifically designed for contamination-free trace element sampling (BOYLE *et al.*, 1986). No systematic differences were found between results obtained with each sampler type. A single Sargasso Sea surface water sample collected on 21 June 1983 from a rubber raft at Sta. S (32°12'N, 64°30'W) was analysed repeatedly as a consistency standard and as a representative sample of central gyre nutrient-depleted surface water.

All samples were acidified to pH 1.8 with purified HCl within a few days of collection. A few samples were filtered (0.4  $\mu\text{m}$  Nuclepore) prior to acidification to determine the particulate contribution to the total concentration. Since the particulate trace element fraction is small for many elements, and because each additional procedure increases the potential for contamination, most samples were left unfiltered. The data indicate that this strategy was warranted for Zn, V, and Cr, but not for Fe, for which the dominant fraction in these samples proved to be particulate.

Sample aliquots (18 g) were analysed for total dissolvable Zn, Cr, V and Fe by graphite-furnace atomic absorption spectrometry (Perkin-Elmer HGA 400 and AA 5000) following a modified cobalt-APDC coprecipitation (BOYLE *et al.*, 1981; BOYLE and EDMOND, 1975, 1977). Recoveries for these metals were optimized by buffering at pH  $\sim$ 4.8 with addition of 6 M ammonium acetate to a final concentration of 80 mM. Addition tests were used to monitor recovery efficiencies, which averaged 92% for Zn, 75% for Cr, 97% for V and  $\sim$ 100% for Fe.

Estimates of one-sigma precision based on replicate analyses are: Zn,  $\pm$ 5% or 50 pmol  $\text{kg}^{-1}$ , whichever is larger (the latter value is the approximate detection limit; blanks were generally lower); Cr,  $\pm$ 6% or 100 pmol  $\text{kg}^{-1}$ ; V,  $\pm$ 4% or 1 nmol  $\text{kg}^{-1}$ ; and Fe,  $\pm$ 5% or 400 pmol  $\text{kg}^{-1}$ . Accurate and precise analysis of Fe in seawater is a most difficult problem (GORDON *et al.*, 1982; LANDING and BRULAND, 1987). In 10 of 23 pairs of Fe analyses on simultaneously collected duplicate surface samples, duplicates differed more than 10% from the means. Replicate analyses on aliquots from individual bottles, however, were always within 5% of the mean. Poorer reproducibility of replicate samples compared with that of replicate analyses of the same sample is probably the result of a slight degree of random contamination during sampling. In this work, when the two replicate samples differed by more than 10%, the lower value was used, on the

presumption that contamination had caused the higher result. Analysis of filtered samples showed that most of the Fe represented by our analysis of unfiltered acidified samples was particulate.

Chromium exhibits a variable oxidation state in natural marine waters (CRANSTON and MURRAY, 1978; MURRAY *et al.*, 1983). Cr(VI) is rapidly reduced to Cr(III) during acid storage of seawater samples (CAMPBELL and YEATS, 1981). Concentrations reported here represent total chromium.

Salinity, temperature, oxygen and nutrient data for these samples have been published previously (BOYLE *et al.*, 1985).

## RESULTS

### Alboran Sea surface waters

Hydrographic data and infrared satellite imagery indicate that the shallow circulation of the Alboran Sea during the sampling period was characterized by an anticyclonic gyre (BOYLE *et al.*, 1985). The gyre is a consistent feature, though its position and strength are highly variable (DONDE VA GROUP, 1984; GASCARD and RICHEZ, 1985). Distributions of surface temperature and salinity generally reflect the gyral circulation, and high silicate and phosphate concentrations occur in the center of the inflowing jet (Fig. 1a). Surface

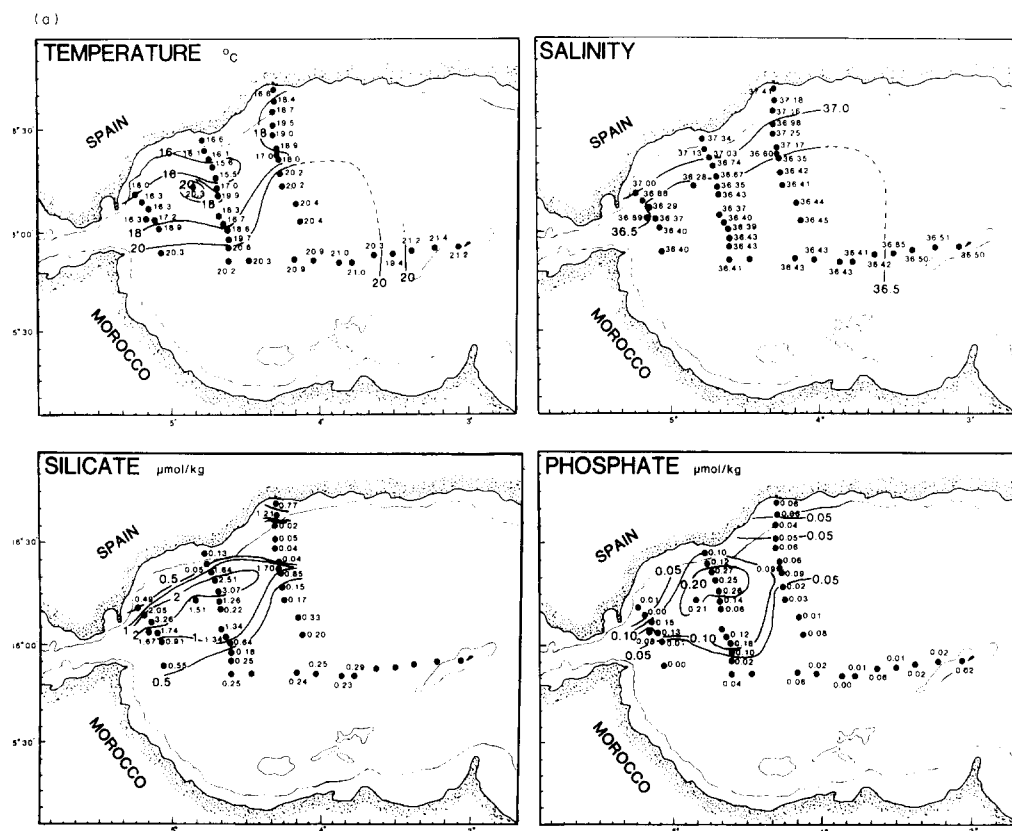


Fig. 1a.

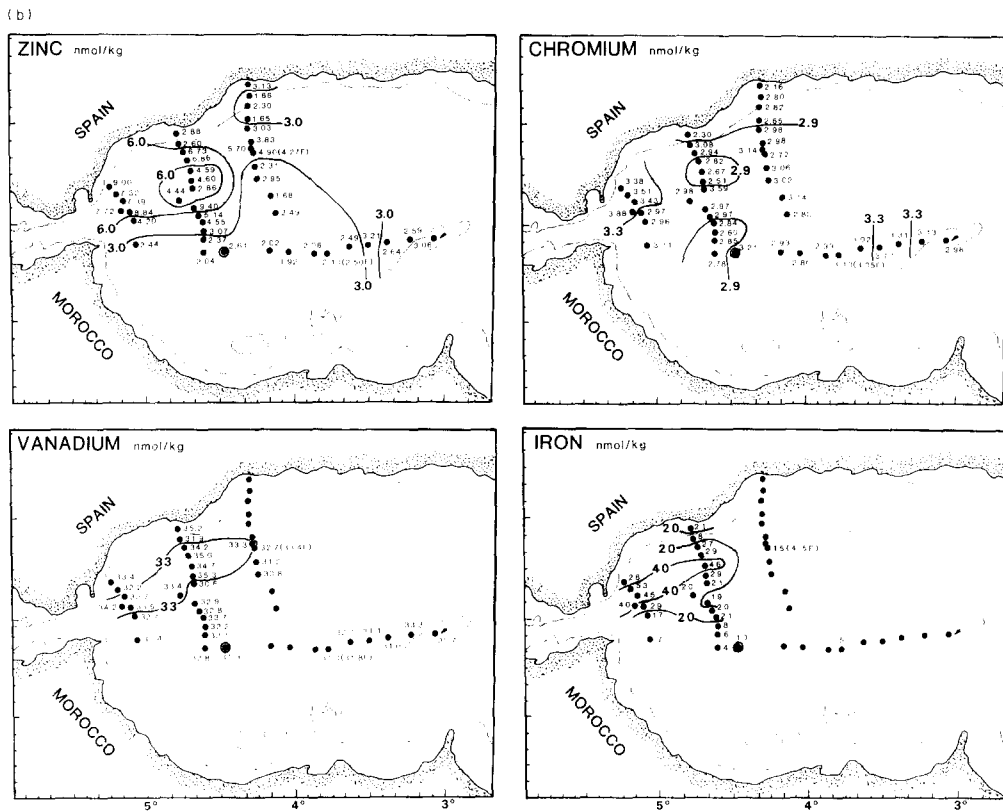


Fig. 1. (a) Hydrographic parameters and nutrient data from Alboran Sea surface waters, U.S.N.S. *Bartlett*, 22–29 June 1982 from BOYLE *et al.* (1985). (b) Trace metal distributions in Alboran Sea surface waters, *Bartlett* cruise 1309–82, 22–29 June 1982. Values in parentheses are filtered replicates. Circled symbol is Sta. 5 profile location.

concentrations of all four metals were elevated within a plume which follows the inflow jet (Fig. 1b). The highest Alboran Sea values (observed in the jet core) were: Zn,  $9.4 \text{ nmol kg}^{-1}$ ; Cr,  $3.9 \text{ nmol kg}^{-1}$ ; V,  $35 \text{ nmol kg}^{-1}$ ; and Fe,  $53 \text{ nmol kg}^{-1}$ .

The Zn distribution is characterized by high variability. Plume values are 10 times higher than surface concentration at nearby Atlantic Stas 1 and 3 (Fig. 2; BOYLE *et al.*, 1985) and 100 times higher than similarly nutrient-depleted waters in the North Pacific (BRULAND, 1980) or the Sargasso Sea (Table 1; BRULAND and FRANKS, 1983).

Chromium, in contrast to Zn, has a limited range of concentrations in the Alboran Sea. Values in the jet core are similar to those in the adjacent Atlantic, but are somewhat higher than Sargasso Sea surface values (Table 1) or Alboran Sea concentrations outside the plume.

Vanadium concentrations exhibit little variation; the highest measurement differs from the lowest by only slightly more than the three-sigma analytical precision of the measurement. However, the average of values within the  $33 \text{ nmol kg}^{-1}$  contour, which approximately delineates the core of the inflow jet (Fig. 1b), is 6% higher than the mean of all remaining Alboran Sea measurements. This difference is statistically significant at

Table 1. Trace metal concentrations (nmol kg<sup>-1</sup>) in North Atlantic surface waters

Metal	Sargasso Sea	Eastern North Atlantic (near Gibraltar)		
	Sta. S	Sta. 1*	Sta. 3*	1980 Samples (mean ± 1σ, n = 3)
Zn	0.06	1.49	0.80	0.99 ± 0.32
Cr	2.90	3.65	3.34	3.86 ± 0.12
V	34.4	34.5	34.9	33.9 ± 0.8

\* See BOYLE *et al.* (1985) for station locations.

the 99% confidence limit. Hence V appears to be slightly higher in the inflow plume relative to the surrounding Alboran Sea waters. On the other hand, concentrations in the jet core are about equal to those in Atlantic waters west of the Strait and in Sargasso Sea surface water (Table 1). Relatively higher values in the plume may thus be caused by depletion of V within the Alboran Sea rather than an additional source for the plume.

Iron was analysed in a subset of the samples. The Fe distribution is consistent with inflowing plume enrichment as demonstrated for other metals. Concentration values are quite high, up to 53 nmol kg<sup>-1</sup>, although the few samples outside the plume approach the previously reported value of ~5 nmol kg<sup>-1</sup> for Mediterranean surface waters further east (KREMLING and PETERSEN, 1981). Open ocean surface concentrations have been reported at 0.15–0.40 nmol kg<sup>-1</sup> (GORDON *et al.*, 1982; LANDING and BRULAND, 1987), another order of magnitude lower. The Fe concentration of a filtered sample was 70% lower than a simultaneously sampled but unfiltered replicate, suggesting that most of the Fe is particulate. High particulate Fe suggests that the plume may have been influenced by a recent aerosol input or interaction with a high-energy shelf resuspension environment.

BOYLE *et al.* (1985) showed that high nickel concentrations near the Spanish coast are consistent with coastal upwelling of deeper Mediterranean waters as evidenced by the salinity distribution. No clear upwelling signature is observed for metals investigated here, though the data suggest slightly elevated Zn concentrations near the Spanish coast, Chromium concentrations are slightly lower in the upwelling zone.

#### *Atlantic and Mediterranean surface waters*

Surface samples collected in 1980 at locations from the Atlantic, through the Strait of Gibraltar, to the central Mediterranean, are shown in Fig. 2.

Surface Zn concentrations increase from less than 1 nmol kg<sup>-1</sup> outside of the Strait to about 3.5 nmol kg<sup>-1</sup> in the western and central Mediterranean. Chromium concentrations vary little (averaging ~4 nmol kg<sup>-1</sup>) on either side of the Strait, although most 1982 Alboran Sea values are less than 3 nmol kg<sup>-1</sup>. These values agree within 25% with the recent Gibraltar and central Mediterranean Cr data of JEANDEL and MINSTER (1987). Vanadium concentrations decrease slightly from about 34 nmol kg<sup>-1</sup> in Atlantic waters to about 32 nmol kg<sup>-1</sup> in the Mediterranean. East of the Alboran Sea, no longitudinal trend in any of these metals is observed. However, Zn and Cr are substantially enriched (25%) in a single sample from the Tyrrhenian Sea, about 175 km southwest of Naples, Italy. SPIVACK *et al.* (1983) also found elevated Cu, Ni and Cd levels in this region.

A comparison of surface concentrations in the central Mediterranean and similarly nutrient-depleted Atlantic (Sargasso Sea) surface waters (Table 1) reveals that the

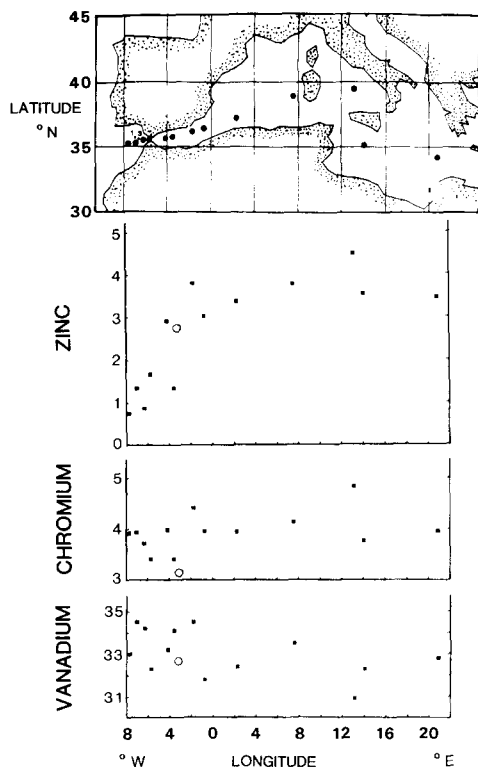


Fig. 2. Station locations and corresponding surface water metal data for Mediterranean and Atlantic waters, *Bartlett* cruise 1309-80, 25 August-12 September 1980. Concentration data for Atlantic Stas 1 and 3 (see map) are not plotted (see Table 1). Open symbol is average of three easternmost 1982 Alboran Sea surface values, used in flux balance estimates. See text for explanation.

Mediterranean is enriched by almost two orders of magnitude in Zn and by about 40% in Cr, but is slightly depleted in V (by 10% when normalized to constant salinity). We are confident that these elevated Zn levels are not due to contamination during sampling and analysis, since low Zn levels were determined on samples from the Sargasso Sea collected by the same personnel, using the same sampling techniques, and analysed by the same individual (RMS). It should be noted that the high Zn levels found in this study are still significantly lower than previously published values. KREMLING and PETERSEN (1981) reported surface values of 4.6-8.6 nmol kg<sup>-1</sup> for six central Mediterranean stations, compared to 3.0-4.5 nmol kg<sup>-1</sup> observed in this work.

#### *Profile data near Gibraltar*

Vertical profiles on each side of the Strait were obtained for Zn, Cr and V. At Alboran Sea Sta. 5 (Fig. 3), all three metals show approximately constant values in deep water, and depletion above 200 m. However, detailed structure of the profiles is unique to each element.

Alboran Sea Zn concentrations decrease with depth from the surface to 150 m. Because pole-sampled replicate surface samples show systematic variations and no

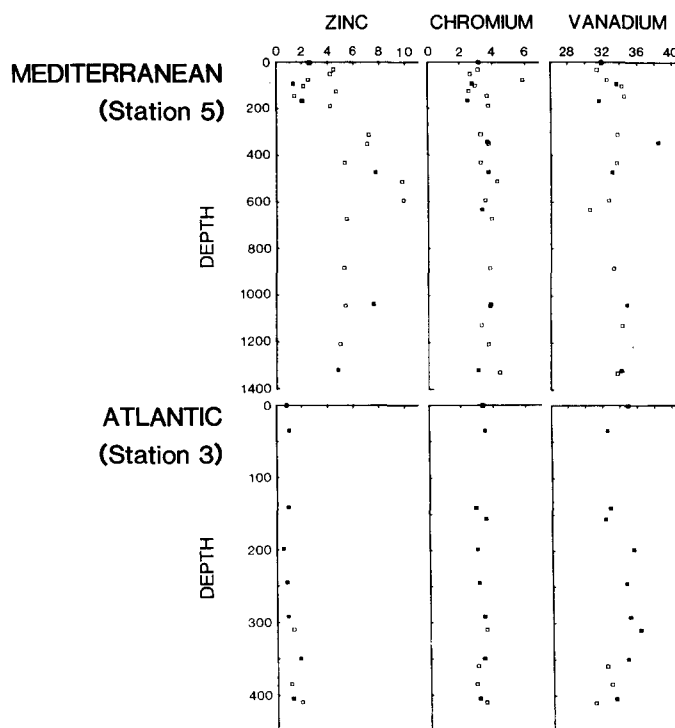


Fig. 3. Profiles of trace metals at Alboran Sea Sta. 5, 35°52.3'N, 4°27.8'W, 25 June 1982 and Atlantic Sta. 3, 35°45.8'N, 6°29.8'W, 30 June 1982. Open symbols are collected by Niskin bottle, closed symbols by "vane" sampler. Surface sample collected by "pole" technique. Concentrations in nmol kg<sup>-1</sup>, depths in meters. Anomalously high values not plotted; see Appendix for full data tables.

anomalously high values (Fig. 1), we are confident of the surface datum. Measured values between 75 and 150 m are about 1 nmol kg<sup>-1</sup> lower than the surface water value; thus it appears that Zn has a significant subsurface minimum. The profile data also show a Zn maximum from 300 to 600 m, although less confidence can be placed in this feature in view of possible contamination. A few profile samples do appear to be contaminated, having high values relative to adjacent samples (Appendix).

The Cr profile in the Alboran Sea is nearly invariant, with slightly lower values in low salinity waters in the upper 200 m. Vanadium also has a slight surface depletion, but increased deep-water concentrations occur at a shallower depth than the halocline. Normalizing the profile to salinity, a small V/S maximum appears at about 150 m, indicating that the cause of the vertical distribution may not be simply related to salinity.

Atlantic Sta. 3 is located 35 km off the Moroccan coast southwest of Gibraltar. Trace element data (Fig. 3) indicate essentially featureless profiles for Cr and V, similar to profiles from other regions of the North Atlantic (CAMBELL and YEATS, 1981; HUIZENGA and KESTER, 1982; JEANDEL *et al.*, 1987). Chromium concentrations at this station are about equal to those found in the deep Alboran Sea. Zinc levels are considerably lower, however, with a broad minimum to 0.5 nmol kg<sup>-1</sup> at 200 m, increasing to 1.9 nmol kg<sup>-1</sup>

near the bottom. The increase with depth is similar to that expected from Zn-Si correlations from the western North Atlantic (BRULAND and FRANKS, 1983).

#### DISCUSSION

##### *Sources of Alboran Sea metal enrichments*

These new data, combined with previously published results, demonstrate clearly that the inflow plume within the Alboran Sea is enriched, to varying degrees, in Zn, Cu, Ni, Cd and particulate Fe. Inflow waters appear to be an important source of trace elements to the Mediterranean.

The trace metal distributions help to constrain the approximate location of enrichment sources, but as yet the data do not uniquely determine the nature of the source (eolian, fluvial or sedimentary; natural or anthropogenic). While Zn is about an order of magnitude more concentrated in Atlantic surface waters west of the Strait than in Sargasso Sea surface waters (Table 1, Fig. 2), elevated Zn levels also have been observed in slope and shelf waters in similar proximity to the east and west coasts of North America (BRULAND, 1980; BRULAND and FRANKS, 1983). East of the Strait, Zn is 10-fold further enriched in the core of the inflow jet. Thus, if observed distributions are indicative of steady-state conditions, a large input of Zn must occur as Atlantic surface water moves closer to the coast and through the Strait. Entrainment of some deeper Atlantic water or outflowing Mediterranean water may occur, but Zn levels in these water masses (Fig. 3) are insufficient to account for the observed enrichment. Zinc and Cu are linearly correlated in Alboran Sea surface waters (Fig. 4), suggesting that these two elements have a similar source location and subsequent mixing/removal behavior. (Two points that fall off the trend correspond to nearshore waters northeast of Gibraltar, and may indicate local input of Zn.) Release of Cu during early diagenesis of sediments, inferred from water column modeling (BOYLE *et al.*, 1977) and demonstrated in pore water studies (KLINKHAMMER, 1980; KLINKHAMMER *et al.*, 1982), may be an important source to the Mediterranean flow. Substantial sedimentary diagenesis sources have not yet been demonstrated for Zn, although coastal enrichments observed for this metal indicate that such a process is plausible. VAN GEEN *et al.* (1988) have shown that the

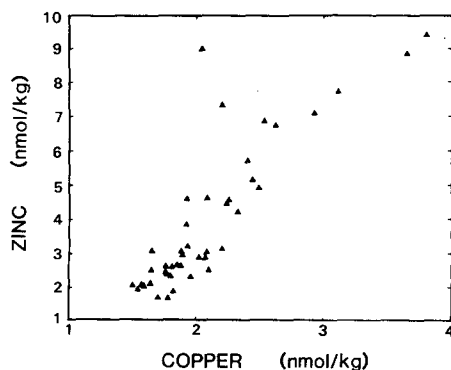


Fig. 4. Zinc vs Cu in Alboran Sea surface waters, June 1982. Copper data from BOYLE *et al.* (1985).



salinity, Cd, Cu, Ni and Zn distribution in the Alboran Sea is consistent with a conservative mixture of four water types: (1) "normal" Atlantic surface water, low in S, Cd, Zn, and Ni; (2) deeper North Atlantic Water, higher in Cd, slightly higher in Ni and Zn, and low in S; (3) Spanish shelf water, low in S, and highly enriched in Cu, Cd and Zn; and (4) deep Mediterranean Water, high in S, somewhat higher in Cd, Zn and Ni. For Zn, the dominant source is the enriched Spanish coastal waters, which therefore are a major source of Zn for the Mediterranean.

Biological removal of Zn in surface waters could mask some of the excess input. The Zn maxima observed at 300–600 m in the Alboran Sea (Fig. 3) require greater sampling resolution for accurate delineation, but coincide roughly with the oxygen minimum at this station (BOYLE *et al.*, 1983) and might be interpreted as surface biological removal and consequent regeneration at depth. However, Levantine Intermediate Water (WUST, 1961; PARILLA *et al.*, 1986) in the 200–600 m interval may be an equally plausible advective source for this maximum. To evaluate the latter possibility, data on the Zn concentration distribution in the eastern Mediterranean (where this water mass is formed) would be necessary.

Chromium concentrations in the inflow jet are somewhat higher than average Alboran Sea surface values (Fig. 1b), but about equal to Atlantic surface values. Thus Cr, in contrast to Zn, does not appear to be significantly enriched during passage through the Strait.

#### *Biological cycling of trace elements in the Mediterranean*

Measurements of Cu, Ni and Cd in deep Alboran Sea waters (BOYLE *et al.*, 1985) have demonstrated the validity of the assumption that these trace metals in Mediterranean deep water are largely "preformed" during deep-water formation events (SPIVACK *et al.*, 1983); only Ni appears significantly enriched by deep-water remineralization of sinking biogenic particulate matter. The profile data for Cr and V (Fig. 3) are generally consistent with a preformed deep-water concentration. Central Mediterranean surface waters and deep Alboran Sea waters both have about 4 nmol kg<sup>-1</sup> Cr. Likewise, the similarity for V is within analytical precision (32–34 nmol kg<sup>-1</sup>). However, Sta. 5 data indicate deep Mediterranean Zn concentrations of about 5 nmol kg<sup>-1</sup>, a 50% enrichment over the levels observed in deep-water formation regions further east. As observed for Ni, vertical transport may play a significant role in the movement of Zn through the Mediterranean.

A rough quantification of the contribution of biological cycling of Zn can be accomplished using a simple steady-state flux balance model similar to that employed by BOYLE *et al.* (1985) (Fig. 5). Phosphorus is assumed to be the limiting nutrient and is used to trace the cycling of organic matter. Recycling fractions ( $f$ ) are calculated from the whole ocean residence times [taken as 160,000 for P (BOYLE *et al.*, 1985) and 50,000 for Zn (SHILLER and BOYLE, 1985)] and the oceanic mixing time [1600 years (BROECKER and PENG, 1982)]. Obviously, a very large fraction of both the P and Zn particulate flux ( $F_P$ ) is regenerated in the deep ocean. In the open ocean, the recycling fraction sets the upwelling flux ( $F_U$ ), the loss to the sediments ( $F_S$ ), and thus the continental input ( $F_R$ ) for phosphorus, normalized to  $F_P$  (phosphorus) = 1000. For zinc,  $F_U$  is determined from measured deep-water P and Zn (Pacific values are used). Other fluxes are calculated using  $f_{Zn}$  and flux balance.

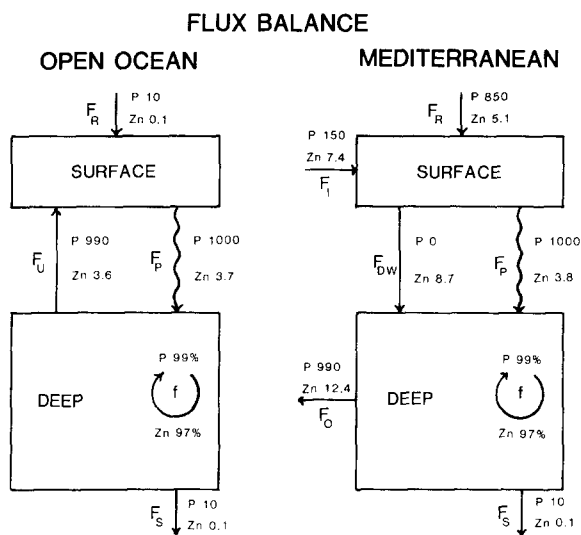


Fig. 5. Flux balance model for Zn in the open ocean and Mediterranean. Symbols defined in text. Net fluxes only are indicated, and are normalized to  $F_P$  (phosphate) = 1000.

The Mediterranean box model assumes the same recycling fractions as for the open ocean, but makes the simplification that no nutrients are upwelled to the surface reservoir. Measurements of P and Zn in Alboran Sea deep water (Fig. 3; BOYLE *et al.*, 1985) are used to compute the P-normalized outflow flux ( $F_O$ ) for Zn. Central Mediterranean values (Fig. 2; BOYLE *et al.*, 1985) set the deep-water formation flux ( $F_{DW}$ ). The inflow flux of Zn is calculated from estimated average Zn concentrations in the inflow plume and water balance. Phosphorus input to the surface reservoir is divided between Gibraltar inflow and river flux after BOYLE *et al.* (1985). [Recent evidence suggests that the Atlantic inflow may contribute close to 100% of the phosphorus input to the Mediterranean (COSTE *et al.*, 1988; J. SARMIENTO, personal communication). This does not affect the interpretations which follow.] Particulate Zn flux is determined by the flux balance for the deep reservoir and river flux by balance for the surface reservoir.

Two significant features of the model are: (1) the particulate flux of Zn within the Mediterranean basin accounts for about 30% of the total transport to the deep waters; and (2) the Zn : P ratio in falling particulate matter is very similar to that in the open ocean ( $3.8$  vs  $3.6 \times 10^{-3}$ ), despite surface dissolved Zn : P ratios that are 100 times that in the open ocean.

The Zn : P value in particulate matter is somewhat sensitive to uncertainties in the measurements and model assumptions. For example, a 20% error in the Mediterranean deep-water Zn value would force  $F_P(\text{Zn})$  to increase or decrease by 70%. If non-steady state anthropogenic Zn input has influenced central Mediterranean surface values, or if average mixed-layer Zn concentrations are lower than surface values, as in the Alboran Sea, Zn : P in particulates would be higher than the model indicates. Relaxing the assumption of zero upwelling flux would have a similar effect. The particulate Zn : P ratio is ultimately determined by relative values of  $F_O$ ,  $F_{DW}$  and  $F_S$  in this steady-state model. The magnitude of  $F_O$  is well constrained by the data, and  $F_S$  is a negligible term,

unless  $f$  is much smaller than the open ocean value. Making the unreasonable assumption that  $F_{DW}$  is zero (forcing all vertical Zn flux to be particulate) creates an extreme particulate Zn : P that is three times the open ocean value. This conclusion is robust even if the steady-state assumption is not strictly correct because the average particulate Zn : P depends on balance equations for the long residence time deep box, while non-steady state processes would mostly affect the more rapidly exchanged surface box. Thus, accounting for the probable magnitude of these uncertainties, the ratio appears to be within a factor of two to three of the open ocean value.

The model therefore suggests that organisms living in metal-enriched surface waters do not incorporate Zn to a much greater degree than in Zn-depleted oligotrophic open ocean waters. This is consistent with auto-regulation of planktonic elemental compositions (COLLIER and EDMOND, 1984), either by metabolic controls or simple chemical means (e.g. saturation of binding sites). Because nutrients are limited, biological removal cannot significantly reduce Mediterranean Zn enrichments.

While Zn and P show no correlation in oceanic cycling behavior, P is chosen in the above model as the general geochemically limiting nutrient for biological activity. In the open ocean, Zn and silicate are linearly correlated in a given ocean basin (BRULAND, 1980; BRULAND and FRANKS, 1983), which indicates common regeneration behavior (mainly on the seafloor) but could also be interpreted as consistent with a common uptake mechanism. If the box model is reformulated using Si as the reference nutrient (less directly related to total biological production), the Zn : Si version of the model yields the same interpretation with respect to the Zn : Si ratio of open ocean and Mediterranean biological materials. A better understanding of biologically mediated trace metal removal in the Mediterranean would require higher precision profile data and analysis of suspended and sinking particulate matter compositions.

Slight depletion of V in Mediterranean surface waters relative to North Atlantic surface waters may be caused by biological removal. In open ocean surface waters, V uptake by labile biogenic phases creates a 10–40% depletion relative to approximately constant deep-water values (ZHOU *et al.*, 1982; COLLIER, 1984). Surface depletion and increasing concentrations to ~150 m observed in the Alboran Sea and in Atlantic Sta. 3 are consistent with this interpretation. East of the inflow region, surface levels are lower but approximately constant with longitude (Fig. 2). Vanadium depletion of Mediterranean surface waters appears to occur soon after entering the Strait, with little change thereafter.

#### *Mediterranean trace element flux balance*

Magnitudes of trace metal enrichment fluxes can be estimated from the inflow/outflow mass balance. This balance can be expressed as

$$Q_O C_O - Q_I C_A = X_T, \quad (1)$$

where  $Q_O$  and  $Q_I$  are fluxes of outflowing Mediterranean water and inflowing Atlantic water,  $C_O$  is the concentration in outflowing Mediterranean water,  $C_A$  is the concentration in Atlantic surface water before entering the Mediterranean, and  $X_T$  is total net input, i.e. the imbalance between advective inflow and outflow terms. Total net input is the sum of inputs near the Strait and input to the Mediterranean basin itself:

$$X_T = X_I + X_M, \quad (2)$$

where

$$X_I = Q_I(C_I - C_A) \quad (3)$$

and  $C_I$  is the average inflow concentration to the Alboran Sea. It is assumed that inflowing waters initially have trace metal concentrations ( $C_A$ ) observed in nearby Atlantic stations (Table 1), which may be modified to  $C_I$  before entering the Alboran Sea. It may be difficult to estimate  $C_I$  because of spatial and temporal variability of the inflow plume (DONDE VA GROUP, 1984). Here it is assumed that an average of the three easternmost 1982 Alboran Sea samples and two 1980 eastern Alboran Sea samples (Fig. 2) represents the average inflow concentration. Because of uncertainty in this value, total net input is a more reliable estimate than its subdivision into components.

Values of  $C_O$  are average deep-water concentration for each metal. For Zn, the fairly constant values at >600 m were assumed representative of average outflow concentration, though the average depth of outflow waters is uncertain to some extent (BRYDEN and STOMMEL, 1982). Single point maxima in the Zn profile (Appendix), almost certainly a result of contamination, were rejected. This calculation gives the current net flux imbalance between Atlantic and Mediterranean, and neglects sedimentation within the Mediterranean basin (which is expected to be negligible for long residence time elements like Zn and Cr).

Results of the mass balance are presented in Table 2. Since concentration differences are slight for V, the Mediterranean is neither a strong source nor sink for this metal, and fluxes were not estimated. Flux estimates for Cr are necessarily approximate because of small relative differences in values for  $C_A$ ,  $C_I$  and  $C_O$ . The Mediterranean is clearly a source for Zn and (to a much lesser extent) Cr to the eastern North Atlantic. Inflow waters and sources within the basin itself contribute about equally to Mediterranean Zn enrichment, while Cr is probably added only within the basin. Total net input of Zn is similar in magnitude to the estimate of ARNOLD *et al.* (1982) for atmospheric particulate flux, but uncertainties in their flux values and the degree of solubilization of Zn from particles argues against concluding that the enrichment is solely due to an aerosol source. It remains uncertain whether metal inputs are natural or anthropogenic, and whether the dominant sources are river input, aeolian particulate flux, or diffusion from nearshore sediments. Evaluation of sources requires extensive measurements of each of the potential inputs; this would be a useful complement to the broader distributions presented here.

Table 2. Trace element inflow/outflow mass balance for the Mediterranean

Metal	Eastern North Atlantic surface concentration	Average inflow conc.	Med. deep- water conc.	Excess inflow flux	Excess Med. basin flux	Total excess flux
	$C_A$	$C_I$ (nmol kg <sup>-1</sup> )	$C_O$	$X_I$	$X_M$ (mol y <sup>-1</sup> )	$X_T$
Zn	1.0	3.0	5.0	$8.2 \times 10^7$	$7.2 \times 10^7$	$15 \times 10^8$
Cr	3.6	3.6	3.8	—*	$6.0 \times 10^5$	$6.0 \times 10^5$

\* No significant excess.

Inflow flux =  $4.1 \times 10^{16}$  kg y<sup>-1</sup>, outflow =  $3.9 \times 10^{16}$  kg<sup>-1</sup> after BOYLE *et al.* (1985).

## CONCLUSIONS

The Mediterranean Sea is greatly enriched in Zn, somewhat enriched in Cr, and slightly depleted in V compared to similar nutrient-depleted open ocean waters.

Alboran Sea trace metal distributions show that highest concentrations of Zn, Cr, V and particulate Fe occur in the Atlantic inflow jet, indicating that metal enrichments can occur outside the Mediterranean. The presence of particulate Fe is evidence for recent eolian particle deposition or proximity to a high-energy shelf environment.

Chromium and V concentrations in Mediterranean deep waters are approximately equal to levels in surface waters from which they are formed, and therefore are largely "preformed". Zinc is somewhat higher in deep water, indicating a significant contribution from vertical particulate transport and regeneration during passage of this water toward the outflow. A simple box model for steady-state fluxes in the Mediterranean suggests that biological removal of Zn does not occur at unusually high Zn : nutrient ratios, despite greatly elevated Zn concentrations in surface waters.

A chemical mass balance for the Mediterranean, and comparison of average inflow concentrations with those in nearby Atlantic surface waters, indicate that Mediterranean Zn enrichment is derived from sources both outside and within the basin. Excess Cr input may occur mainly within the basin. Surface V depletion is probably due to biological removal.

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#### APPENDIX

##### *Data tables for Mediterranean trace metals*

Latitude (Lat.) and longitude (Long.) are given as degrees and minutes (N and E, respectively; negative longitudes signify degrees W). Zinc (Zn), chromium (Cr), vanadium (V), and iron (Fe) in  $\text{nmol kg}^{-1}$ . F, filtered sample; ?, questionable data. Other data pertaining to these samples published in BOYLE *et al* (1985).

Table A1. Surface water data from U.S.N.S. Bartlett cruise 1309-80. 25 August-12 September 1980

Sample*	Lat.	Long.†	Zn	Cr	V
4	39 52.6	13 10.1	4.50	4.84	30.9
14	34 35.8	20 52.2	3.46	3.96	32.8
19	35 30.5	14 04.5	3.55	3.78	32.3
29	39 17.0	07 33.0	3.79	4.14	33.5
37	37 37.6	02 16.8	3.38	3.95	32.4
40	36 50.5	-00 45.0	3.04	3.96	31.8
41	36 36.1	-01 48.7	3.82	4.41	34.5
42	36 11.6	-03 37.3	1.35	3.42	34.1
43	36 04.7	-04 12.8	2.93	3.99	33.2
44	35 57.3	-05 44.9	1.67	3.42	32.3
45	35 56.3	-06 17.5	0.88	3.73	34.2
47	35 37.2	-07 41.6	0.75	3.92	33.0
48	35 43.0	-07 01.0	1.35	3.94	34.5

\* Samples were selected from complete sample set, see BOYLE *et al.* (1985).

† Negative longitudes published in Appendix 1 of BOYLE *et al.* (1985) were incorrect. Correct coordinates are listed here.

Table A2. Alboran Sea surface water data, U.S.N.S. Bartlett, 22-29 June 1982

Sample*	Lat.	Long.	Zn	Cr	V	Fe
1	35 54.6	-05 03.0	2.44	3.11	30.4	6.7
2	36 00.7	-05 04.7	4.20	2.96	32.7	16.5
3	36 03.3	-05 05.9	8.84	2.97	33.5	29.2
4	36 06.0	-05 09.6	7.09	3.43	33.7	44.8
5	36 09.0	-05 11.2	7.32	3.51	32.2	53.0
6	36 12.0	-05 13.0	9.00	3.38	33.4	28.0
7	36 14.7	-05 14.0	7.72	3.88	34.2	40.1
8	36 07.0	-04 47.5	4.44	2.98	33.4	19.5
9	35 52.3	-04 27.8	2.61	3.21	31.9	9.5
10	36 10.8	-04 39.9	2.86	3.59	30.6	21.2
11	36 04.7	-04 39.6	9.40	2.97	32.9	19.3
12	36 03.1	-04 36.4	5.14	2.97	32.8	19.8
13	36 00.7	-04 36.4	4.55	2.84	33.7	21.2
14	35 57.7	-04 36.1	3.07	2.60	32.2	8.3
15	35 55.2	-04 35.8	2.37	2.85	32.1	6.1
16	35 51.5	-04 35.8	2.04	2.78	32.8	3.7
17	36 12.3	-04 40.4	4.60	2.51	35.3	28.7
18	36 15.7	-04 40.8	4.59	2.67	34.7	46.0
19	36 19.6	-04 42.2	6.86	2.82	35.0	29.0
20	36 20.7	-04 43.4	6.73	2.94	34.2	26.6
21	36 24.0	-04 45.1	2.60	3.08	31.9	7.9
22	36 27.8	-04 45.7	2.88	2.30	35.2	20.5
23	36 41.0	-04 16.8	3.13	2.16		
24	36 37.8	-04 17.5	1.86	2.80		
25	36 34.7	-04 17.8	2.30	2.82		
26	36 31.7	-04 18.2	1.65	2.65		
27	36 27.2	-04 18.7	3.03	2.98		
28	36 24.5	-04 16.2	3.83	2.98		
29	36 22.4	-04 15.5	5.70	3.14	33.3	
30	36 20.1	-04 15.2	4.90	2.72	32.7	14.6
			4.27F		33.4F	4.5F
31	36 15.9	-04 15.2	2.31	3.06	31.2	
32	36 12.8	-04 14.5	2.95	3.02	30.8	
33	36 08.0	-04 09.2	1.68	3.14		
34	36 03.2	-04 07.7	2.49	2.80		

Continued

Table A2. Continued

35	35 52.2	-04 09.0	2.02	2.93		
36	35 52.7	-04 02.4	1.92	2.80		
37	35 50.7	-03 53.3	2.06	2.99		
38	35 51.5	-03 50.1	2.10	3.10	31.0	5.1
			2.50F	3.50F	31.8F	
39	35 54.0	-03 39.7	2.49	3.02	32.7	
40	35 54.2	-03 31.2	3.21	3.72	31.1	
41	35 53.8	-03 23.5	2.64	3.31	31.0	
42	35 55.2	-03 15.4	2.59	3.13	33.3	
43	35 55.3	-03 06.9	3.06	2.98	33.7	

Table A3. U.S.N.S. Bartlett chemical Sta. 3, 30 June, 1982,  
35°45.8'N, 6°29.8'W

z	Zn	Cr	V
0	0.80	3.34	34.9
35	1.03	3.48	32.5
141	0.89	2.88	32.8
156	6.08?	3.54	32.3
198	0.54	2.99	35.5
245	0.79	3.05	34.6
292	0.86	3.39	35.0
310	1.31	3.49	36.2
350	1.82	3.34	34.7
360	5.33?	2.97	32.3
385	1.08	2.88	32.8
405	1.22	3.07	33.3
410	1.90	3.45	30.9

Table A4. U.S.N.S. Bartlett chemical Sta. 5, 25 June, 1982,  
35°52.3'N, 4°27.8'W

z	Zn	Cr	V
0	2.61	3.21	31.9
33	4.46	3.15	31.4
51	4.21	2.66	
76	2.50	5.86?	32.5
93	1.35	2.77	33.6
102	2.15	2.96	34.2
124	4.66	2.57	
145	1.44	3.66	34.5
166	2.05	2.50	31.6
188	4.20	3.74	
311	7.18	3.27	33.7
343	20.91?	3.65	38.4
351	7.05	3.75	
432	5.29	3.26	33.6
472	7.70	3.71	33.1
512	9.78	4.26	
593	9.88	3.52	32.7
633	23.39?	3.33	30.5
673	5.42	3.91	
884	5.21	3.77	33.2
1039	7.53	3.83	34.8
1047	5.35	3.80	
1128	16.75?	3.26	34.2
1209	4.94	3.66	
1320	4.75	3.05	34.1
1331	13.96?	4.35	33.6