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# Particulate trace metal chemistry in the open ocean and the Western Mediterranean : a comparative study\*

by

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## Abstract

Preliminary data show the importance of particulate transport in the biogeochemical cycle of trace-metals in the Western Mediterranean.

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Active and passive scavenging by suspended particles which subsequently settle is the single most important mechanism for the rapid transfer of metallic pollutants from the surface layers to the deeper parts of the open ocean (BUAT-MÉNARD, 1979; BUAT-MÉNARD & CHESSELET, 1979; CHESSELET, 1979). We present here a comparison of trace metal concentrations in suspended matter collected through the entire water column in the North and South Atlantic and the South Pacific Ocean (BUAT-MÉNARD, 1979) and recent data from the semi-enclosed Ligurian Sea (Fig. 1).

Sampling and analytical techniques have been described (BREWER *et al.*, 1976; BARON, 1977; BENARD, 1979; BUAT-MÉNARD, 1979; BUAT-MÉNARD *et al.*, 1980). Briefly, ~30 l sea-water samples were collected with PVC Niskin bottles fitted with stainless steel springs coated with Teflon. The sea-water was filtered under pressure on pre-weighed 0.4 µm pore, 47 mm diameter Nuclepore membranes, using ultra-clean procedures. The filters were analysed for elemental composition using a combination of instrumental neutron activation analysis and flameless atomic absorption spectrometry.

The 200 samples collected in the deep waters of the Atlantic and the Pacific show the following:

1. Particulate Al, Sc, and Th are entirely associated with suspended aluminosilicates.

2. Ni, Cu, Zn, As, Se, Ag, Cd, Sb, Au, Hg and Pb are present in world ocean particles in concentrations at least an order of magnitude higher than can be accounted for by terrigenous particles of crustal composition or biogenic particles of planktonic composition. Except for lead, enrichments of these trace metals in oceanic suspended matter were shown to be of natural origin and to reflect internal oceanic processes, primarily the formation of biogenic detritus in surface waters.

Table 1 presents the geometric mean concentrations of particulate trace metals in the various oceanic regions investigated.

From the comparison between the data in Sections A and B in Table 1, the following discussion can be offered with respect to the chemistry of particulate trace elements in North-western Mediterranean deep waters:

1. The mean particulate concentrations of trace elements in North-western Mediterranean waters are of the same order of magnitude as those of the open ocean. However, on the average, Al, Sc, V, Mn, Fe, As and Th exhibit somewhat higher concentrations in the Mediterranean.

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In *Marine Pollutant Transfer Process*, M. Waldichuk, G.N. Kuilenberg and M.J. Orren, editors, Elsevier, Amsterdam *in press*.

2. There is also a trend in Mediterranean waters for higher values at St. 1, closer to the French Riviera, than at St. 2 and St. 3. However, the mean weight of total suspended matter is the same for the three Mediterranean stations and for the open ocean.

Scanning electron microscope and electron microprobe observations of suspended particles have shown that, as is the case for the open ocean, particulate Al in Mediterranean waters is entirely associated with continentally derived aluminosilicates. We have therefore used Al as reference element of crustal weathering products transported into the Mediterranean waters. Assuming that such particles have

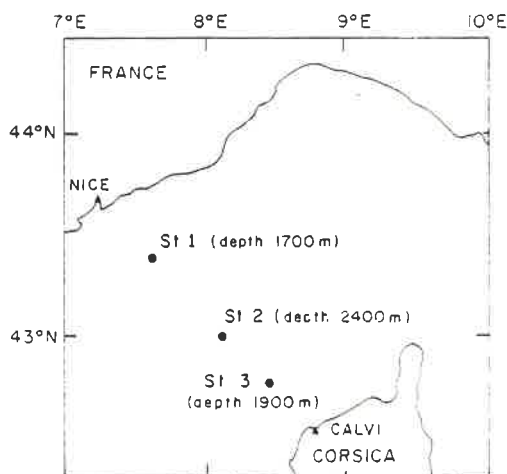


Fig. 1. — Sampling stations in the Northwestern Mediterranean Sea.

a crustal composition (BUAT-MÉNARD & CHESSELET, 1979), we have calculated, for any element X in Mediterranean suspended matter, an enrichment factor relative to the crust as follows:

$$EF_{\text{crust}}(X) = (X/Al)_{\text{suspended matter}} / (X/Al)_{\text{crust}}$$

The  $EF_{\text{crust}}$  values for the three Mediterranean stations are plotted in Fig. 2 together with mean  $EF_{\text{crust}}$  values for the North Atlantic (BUAT-MÉNARD & CHESSELET, 1979). From this figure the following conclusions can be drawn:

1.  $EF_{\text{crust}}$  values for Sc and Th in Mediterranean and North Atlantic suspended matter are close to unity. These elements are also strongly correlated with Al for each of the three Mediterranean stations. Thus, as is the case for the North Atlantic, the particulate concentrations of these elements in Mediterranean waters can be entirely explained by the presence of suspended aluminosilicates.

2. The other elements show  $EF_{\text{crust}}$  values higher than 1 and up to  $10^4$ , both for Mediterranean and North Atlantic waters. For a given enriched element Fig. 2 shows that the order of magnitude of the  $EF_{\text{crust}}$  values in suspended matter is the same for the Mediterranean and North Atlantic waters. Also, as is the case for the North Atlantic, the enriched elements do not show a significant correlation with Al. Thus a major fraction of the particulate concentrations of these elements in Mediterranean waters is associated with phases other than aluminosilicates.

Fig. 3 presents the relative abundances ( $\mu\text{g/g}$  dry weight) of the elements in the non-crustal component of marine suspended matter for both Mediterranean and North Atlantic waters. Similar to open ocean waters, the data in this figure indicate that these relative abundances are too high to be explained by biogenic particles of planktonic composition. Consequently, as is the case for the open ocean, sources other than crustal weathering and particles of planktonic composition are responsible for the particulate concentrations of V, Cr, Mn, Fe, Co, Cu, Zn, As, Cd, Sb, Au, Hg, and Pb in Mediterranean waters. Multiple correlation analysis of the data has shown no clear association pattern for the enriched elements, except for V, Fe, and As, which are highly correlated in Mediterranean waters. This has also been observed at one of our stations in the Tropical North Atlantic. This suggests that there are similar types of associations for particulate trace metals in Mediterranean suspended matter and in open ocean suspended matter. However, it is also clear from Fig. 3 that the relative abundances of Fe, Mn, V, As, and Cu are up to 10 times higher in Mediterranean waters than in the open ocean. This is even more pronounced at St. 1 than at St. 2 and 3. This could be interpreted as the result of riverine and

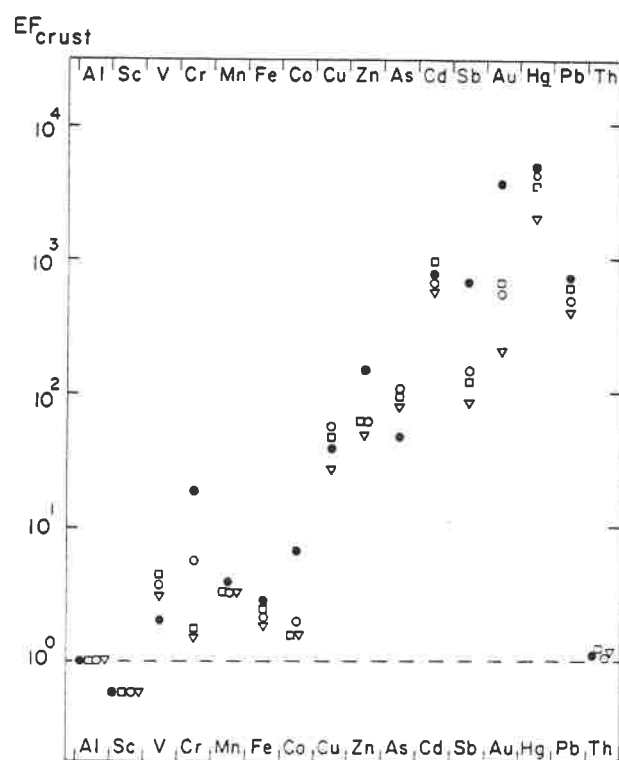


Fig. 2. — Geometric mean crustal enrichment factors of particulate trace elements in Northwestern Mediterranean sea-water : Station 1 [□], Station 2 [○], Station 3 [▽] and in North Atlantic sea-water [●].

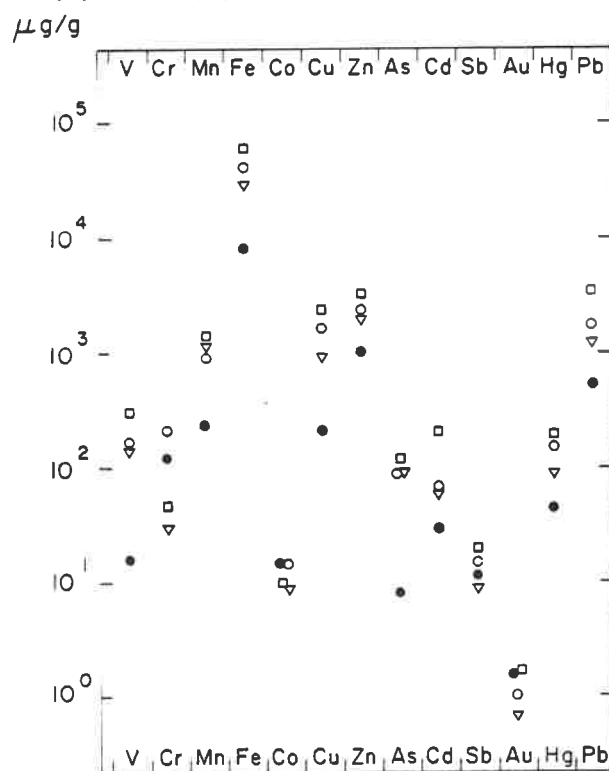


Fig. 3. — Mean relative abundances ( $\mu\text{g/g}$  dry weight) of trace elements in the non-terrigenous component of oceanic suspended matter from the Northwestern Mediterranean Sea : St. 1 [□], St. 2 [○], St. 3 [▽] and from the North Atlantic Ocean [●].

coastal inputs of these elements which indeed might be pollution derived. Such inputs could also account for the high relative abundances of Fe, Mn, V, As, and Cu at St. 2 and 3. However, we must consider the influence of atmospheric inputs on the trace metal particulate chemistry of Mediterranean waters, since we have demonstrated that atmospheric fallout is a major primary source of dissolved and particulate trace metals in open ocean surface waters (BUART-MÉNARD & CHESSELET, 1979). Unfortunately, the present lack of accurate data on the riverine and atmospheric deliveries of trace metals to the Western Mediterranean precludes evaluation of mass balances and budgets such as those which we have made for the North Atlantic.

TABLE 1  
Geometric mean particulate concentrations of trace metals in the open ocean  
and the Northwestern Mediterranean (ng/l)

Element	A						B		
	South Pacific	South Atlantic		North Atlantic			Northwestern Mediterranean (4)		
	(1)	(1)	(2)	(1)	(2)	(3)	St.1	St.2	St.3
Number of samples	19	25	18	50	170	35	11	12	13
Al	72	156	66	124	167	113	523	318	388
Sc	0.021	0.035	0.015	0.022	0.052	0.020	0.10	0.059	0.069
V	0.42	0.69	0.34	0.39	0.82	0.39	3.9	1.9	2.0
Cr	2.1	24	13	12	20	2.6	1.1	2.1	0.8
Mn	4.6	4.7	3.7	6.5	9.2	4.8	19.4	11.5	14.3
Fe	249	362	194	289	330	205	940	508	517
Co	0.13	0.39	0.13	0.09	0.25	0.24	0.26	0.21	0.19
Cu	10	22	5.3	11	14	3.0	18	13	7.6
Zn	10	24	15	13	21	15	20	19	17
As	—	—	—	—	—	0.12	1.1	0.73	0.74
Cd	—	—	—	—	—	0.40	2.0	0.60	0.40
Sb	—	—	—	—	—	0.15	0.17	0.13	0.073
Au	0.020	0.11	0.016	0.012	0.26	0.021	0.015	0.008	0.004
Hg	13	7.5	—	2.5	—	0.40	1.9	1.3	0.7
Pb	—	—	—	—	—	8.6	34	14	11
Th	—	—	—	—	—	0.017	0.085	0.040	0.056
TSM	10	10	12	14	16	15	15	11	12

(1) Samples from the GEOSECS expeditions analyzed by our group.

(2) Samples from the GEOSECS expeditions analyzed by Woods Hole Oceanographic Institution (GEOSECS-NSF/IDOE - 1972-1978 SHORE BASED DATA).

(3) Samples from R/V *Jean Charcot* 1974 Midlante Cruise and R/V *Le Noroit* 1975 Transat cruise (BUAT-MÉNARD and CHESSELET, 1979).

(4) Samples collected in March 1976 on board R/V *Korotneff*.

— No data.

TSM Total Suspended Matter ( $\mu\text{g/l}$ ).

In this context, we need to assess the sources and fluxes on trace metals to the Mediterranean waters, both natural and/or anthropogenic. Indeed, with respect to the atmospheric sources and fluxes, we have previously shown for several metals which are usually enriched in atmospheric particulate matter over oceanic areas that not only industrial activity but also volcanic activity must be taken into account in the atmospheric cycle of these elements in the Mediterranean atmospheric environment (BUAT-MÉNARD & ARNOLD, 1978). More information about the specificity of the internal cycle of trace metals in the Mediterranean Sea is also clearly required. The enrichment of trace metals in suspended matter of the Mediterranean waters could be controlled by processes such as the formation of biogenic detritus in surface waters (FOWLER, 1977). However it is still unclear if it is active and passive scavenging by settling particles which is the single most important mechanism for the rapid transfer of reactive elements from Mediterranean surface waters to Mediterranean deep waters, as it was shown to be for the North Atlantic. The behavior in the Mediterranean Sea of radioactive  $^{239} + ^{240}\text{Pu}$  derived from atmospheric fallout indicates that the rate of removal of dissolved reactive elements by settling biogenic particles is apparently lower in the Mediterranean Sea than in the North Atlantic (LIVINGSTON *et al.*, 1977; FUKAI *et al.*, 1979). These data seem to be supported by very recent results on the vertical

distribution of dissolved trace metals in the Mediterranean Sea (KREMLING, *personal communication*). They show no significant depletion of dissolved Cu, Zn, and Cd in surface waters, as is the case for the open ocean (BOYLE *et al.*, 1977; BRULAND *et al.*, 1978a, 1978b). This can be interpreted as due to a low rate of removal of these elements by settling biogenic particles in Mediterranean surface waters, but, it is also possible that intense and fast mixing of surface waters with deep waters, which is known to occur in this part of the Mediterranean Sea (LACOMBE & TCHERNIA, 1971), could explain the observed profiles of dissolved trace metal concentrations. Water mixing should thus be considered here as a potentially important transfer process for dissolved and particulate trace metals from the surface waters to the deep waters of the Mediterranean Sea.

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