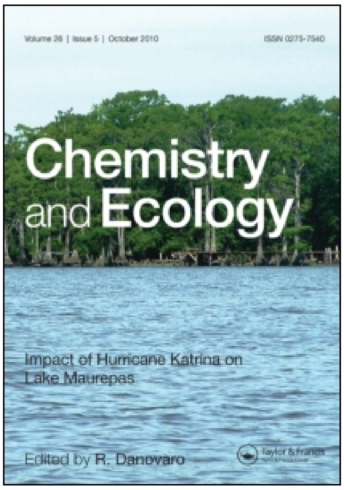

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The Determination of Heavy Metals in the Ligurian Sea. III. Distribution of Copper, Iron, and Nickel in the 0–200 Metre Layer in Open Sea[†]

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Dissolved Cu, Fe and Ni were determined in sea water samples from 9 stations in the Ligurian Sea located along the two traverses Imperia–Capo Corso and Nice–Calvi and at depths between 0 and 200 m. The samples were preconcentrated from small volumes of sea water by complexation with ammonium pyrrolidine-dithiocarbammate (APDC), extraction with CCl_4 and determination by AAS with electrothermal atomisation. The geographical distribution shows that in the central part of the inner traverse there is a maximum of Cu and Fe concentration; the vertical distribution shows no significant depletion of the dissolved elements in the epithalassa.

The results allow for a first approach to the more general problem of the distribution of the trace elements in the Ligurian Sea.

INTRODUCTION

In previous works on the determination of heavy metals in the Ligurian Sea, we studied the distribution of Cu, Co, Ni and Cd in surface waters (Frache *et al.*, 1976) and the geographical and vertical distribution of Cu, Ni and Cd in some off-shore and near-shore stations (Frache *et al.*, 1980).

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After this first approach, in order to obtain further information about the distribution of the heavy metals in this sea, we began a more detailed study of the zone between the French coast and the Corse. Here the Ligurian Sea water mixes with that of the Mediterranean Sea and there is a characteristic divergence with a consequent upwelling (Hela, 1963; Lacombe and Tchernia, 1972; Dagnino and Farneti, 1980).

In this paper we present an examination of the geographical and vertical distribution of soluble Cu, Ni and Fe in samples collected to depths of 200 m along the two traverses Imperia–Capo Corso and Nice–Calvi during the cruise of May–June 1977 (R/V L. F. Marsili). Station locations were chosen in order to check upon differing behaviour in zones more or less internal to the Ligurian Sea and in the divergence and cyclonic eddy of the sea. The sampling down to 200 m assured the examination of the layers related to the thermocline.

EXPERIMENTAL

Sample collection and preservation

The samples were collected at depths of 10, 20, 30, 40, 50, 60, 70, 100, 150, 200 m with polyvinylchloride Niskin bottles, filtered on board after the collection through a 0.45 μm Millipore HA filter and stored in a freezer at −10°C in bottles of low density polyethylene.

In Figure 1 are shown the positions of the sampling stations.

Materials

In the laboratory procedures, vessels of low density polyethylene (LDPE polyethylene, Kartell, Montedison) were shown by our preliminary studies to give no contamination. An Oxford laboratories Micro-set pipette with tips of low density polyethylene (Kartell, Montedison) was used. Before use, all equipment such as the filters, containers, storing bottles and tips were left in 1:1 HCl for some hours, washed with deionized water, dried at 60°C, washed three times with CCl_4 and then dried at 60°C.

Reagents

Nitric acid 65%, hydrochloric acid 30%, carbon tetrachloride, APDC were reagents of suprapure grade (Merck.).

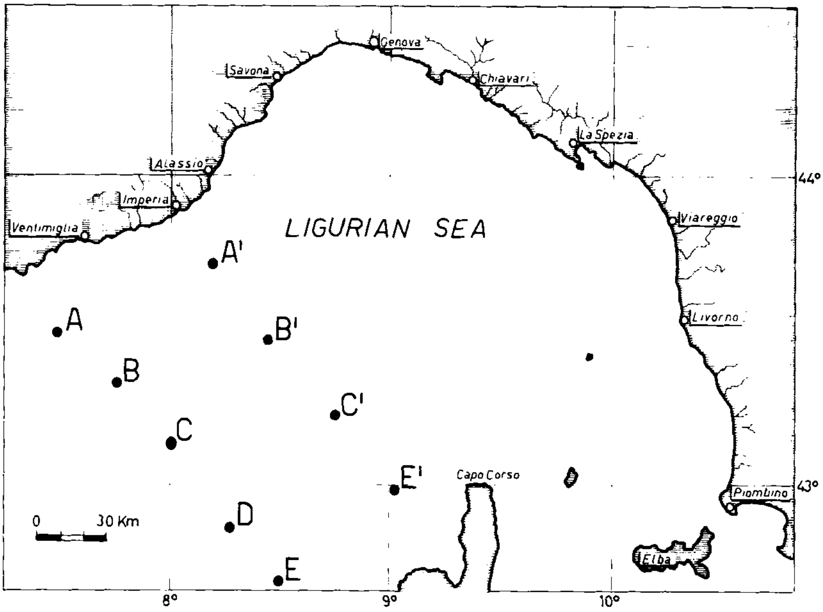

FIGURE 1 Position of the sampling stations.

The solution of APDC, after decantation was washed with an equal volume of CCl_4.

Standard solutions of the ions were obtained by dilution, immediately before the use, of the concentrated solutions prepared from reagent grade salts (Merck).

Instrumentation

A Shandon Southern Model A 3370 flameless atomiser and a Shandon Southern Model A 3400 atomic absorption spectrophotometer were used. Background absorption measurements were carried out by means of a deuterium hollow cathode lamp. We sampled, with the Oxford micropipette, 2 μl of the organic phase for Cu and 4 μl for Ni and Fe, using a Type 2 carbon rod (Ringsdorff-Werke, Bonn) and normalizing the tips five times.

Method

Previously we carried out the determination of the metals using chelating resins and atomic absorption spectrophotometry (Riley and Taylor, 1968; Le Meur and Courtot-Coupez, 1973). To expedite the analyses, determinations by electrothermal atomic absorption spectrophotometry were carried out upon CCl_4 extracts of the complex resulting from concentration of small volumes of sea water with ammonium pyrrolidinedithiocarbammate (APDC).

The sample, at room temperature, was acidified with HNO_3 at pH 2.6 and kept thirty minutes before the analysis to obtain the deabsorption of the ions from the containers. An aliquot (100 ml) of the acidified sample was transferred to an acid-washed 250 ml polythene bottle. 1 ml of 2% APDC aqueous solution and 2 ml of CCl_4 were added and the sample was shaken in a rotating mixer for 30 minutes. After 15 minutes of decantation in a separating funnel, the heavier organic phase was separated.

Because of the stability of the complexes, iron must be measured within 2–3 h after the extraction, whereas the other ions can be measured in the twenty hours following, as found by Brooks *et al.* (1967).

CCl_4 was chosen instead of MIBK because it is practically insoluble in the water and it has a high density which allows for a faster and easier separation of phases.

We obtained a calibration curve by the addition of 0, 10, 20, 40 ng of Cu and Fe and 0, 25, 50, 100 ng of Ni to the samples of seawater and then used the slope of the curve for the determination of the metal concentrations in the original sample.

Reproducibility of the method

The reproducibility of the method was tested by carrying out 10 replicate analyses on a sample of sea water. These gave a coefficient of variation of 15%, 9% and 9% for average content of 0.80, 0.86 and 1.23 $\mu g\ l^{-1}$ for Cu, Fe and Ni respectively. The detection limit of the method was of 0.05, 0.20, 0.16 $\mu g\ l^{-1}$ for Cu, Ni and Fe respectively.

RESULTS AND DISCUSSION

In Table I are shown the concentrations of Cu, Fe and Ni at each station. The hydrological measurements show that the thermocline lay at depths between 50 and 60 m. From a general point of view we can note that mean concentration of the metals fell within the ranges of values more recently published (Table II).

TABLE I

Concentrations of dissolved Cu, Fe and Ni ($\mu g\ l^{-1}$) in water of Ligurian Sea

STATION	LOCATION	SAMPLE depth (m)	CONCENTRATION ($\mu g\ l^{-1}$)		
			Cu	Fe	Ni
A	43°29.8′N	10	0.73	0.54	0.70
		20	0.37	0.41	0.40
	07°29.7′E	30	0.60	0.54	1.10
		40	0.13	0.33	0.70
		50	0.40	0.46	1.70
		60	0.33	0.62	0.90
		70	—	—	1.00
		100	0.40	0.37	0.80
		150	0.20	0.33	0.60
		200	0.27	0.58	0.80
		mean	0.38	0.46	0.87
B	43°18.9′N	10	0.27	0.33	0.80
		20	0.47	0.91	0.80
	07°45.7′E	30	—	—	—
		40	0.33	0.33	1.80
		50	0.37	0.71	0.80
		60	0.40	0.33	0.60
		70	0.36	0.66	1.10
		100	—	—	—
		150	0.27	0.58	1.40
		200	0.24	0.54	1.00
		mean	0.38	0.54	1.05
C	43°08.0′N	10	0.29	0.50	0.80
		20	0.20	0.41	1.00
	08°01.0′E	30	0.24	0.50	1.10
		40	0.47	0.83	0.80
		50	0.27	0.41	1.40
		60	—	—	—
		70	—	—	—
		100	0.27	0.41	1.00
		150	0.37	0.33	1.20
		200	0.33	0.33	1.40
		mean	0.30	0.46	1.08
D	42°57.0′N	10	0.27	0.41	1.00
		20	0.23	0.50	0.96
	08°16.0′E	30	0.67	0.40	1.00
		40	0.47	0.16	1.00
		50	0.27	0.66	1.00
		60	0.40	0.54	1.00
		70	0.40	0.33	0.80
		100	0.33	0.17	0.80
		150	0.80	0.33	1.10
		200	0.53	0.37	0.80
		mean	0.44	0.37	0.94

STATION	LOCATION	SAMPLE	CONCENTRATION ($\mu g\ l^{-1}$)		
		depth (m)	Cu	Fe	Ni
E	42°42.1'N	10	0.40	0.42	0.70
		20	0.27	0.25	0.90
	08°30.0'E	30	0.33	0.58	0.60
		40	0.27	0.62	0.80
		50	0.73	1.00	0.60
		60	0.47	0.41	1.60
		70	0.93	0.54	1.50
		100	0.53	0.75	1.00
		150	0.20	0.75	1.10
		200	0.40	0.66	0.70
		mean	0.45	0.60	0.94
A'	43°43.0'N	10	0.51	0.33	0.60
		20	0.32	0.30	0.30
	08°10.4'E	30	—	—	—
		40	0.37	0.40	0.50
		50	0.22	0.48	0.70
		60	0.26	0.25	0.34
		70	0.30	0.51	0.40
		100	0.66	0.32	0.40
		150	0.37	0.48	0.50
		200	0.80	0.43	0.60
		mean	0.43	0.39	0.48
B'	43°28.7'N	10	1.00	1.66	0.80
		20	0.93	0.54	1.00
	08°27.9'E	30	1.20	1.58	1.20
		40	0.42	1.12	1.40
		50	0.80	1.16	0.90
		60	0.80	0.80	0.90
		70	0.50	0.52	1.00
		100	0.53	0.57	1.40
		150	0.51	0.54	1.00
		200	0.69	0.28	0.70
		mean	0.74	0.88	1.03
C'	43°14.4'N	10	0.43	0.83	1.70
		20	1.27	0.50	1.00
	08°45.0'E	30	1.13	0.96	2.00
		40	—	—	—
		50	0.39	0.96	1.50
		60	0.80	0.96	1.10
		70	0.53	0.54	0.70
		100	0.40	0.16	0.10
		150	0.33	0.58	1.00
		200	0.58	0.41	0.45
		mean	0.65	0.65	1.06

STATION	LOCATION	SAMPLE	CONCENTRATION (μg l^{-1})		
		depth (m)	Cu	Fe	Ni
E′	42°59.8′N	10	0.67	1.21	0.90
		20	0.29	0.41	1.20
	09°02.0′E	30	0.27	1.08	1.10
		40	0.40	0.30	0.90
		50	—	0.30	0.80
		60	0.53	0.83	0.60
		70	0.97	0.71	0.36
		100	0.20	0.47	1.60
		150	0.66	0.20	1.00
		200	0.37	0.28	1.00
		mean	0.48	0.58	0.94

Geographical distribution

For an examination of the metals distribution we used an oneway analysis of variance (ANOVA) in order to test the null hypothesis that the variance related to the geographical position is equal to that related to the depth. All the statistical calculations were made at a confidence limit of 95%. In each case the difference between the mean concentration of metal at the individual station and the overall mean was more significant than the within column differences at a given station. Therefore the geographical variability was more significant than the depth variability. When the values obtained were tested against the precision of the analytical method only the following were significantly different, Cu at Sta. B′ (0.74 μg l^{-1}); Fe at Stas. D, A′ and B′ (0.37, 0.39 and 0.88 μg l^{-1} respectively) and Ni at Sta. B′ (1.03 μg l^{-1}). These results show that, in the outer traverses (Stas. A–E) there was not a significant difference between the mean values of the elements, with the exception of the Sta. D for Fe. In the inner one (Stas. A′–E′) there was a minimum concentration of Ni at Sta. A′ whereas Cu and Fe concentrations were at a maximum in the central zone.

From the data is evident that this maximum was related to the high concentration of these elements in the upper layer. Previously Frache *et al.* (1980) found a maximum concentration for Cu in the station at 43°31.05′N; 08°32.0′E very near to Sta. B′.

Variation of metal concentration with depth

The statistical tests showed that the variability of the concentration of

TABLE II

Data from literature (1975–1980) on the concentration of Cu(II), Fe(III), Ni(II) in filtered sea water

AUTHORS	SEA	ANALYTICAL METHODS	CONCENTRATION ($\mu g\ l^{-1}$)
Gardiner and Stiff, 1975	English coast	ASV	Cu: 0.32–0.51
Zirino and Liebermann, 1975	California coast	ASV	Cu: 0.07
Lund and Salberg, 1975	Oslofjord, Norway	ASV	Cu: 0.22
Boyle and Edmond, 1975	Pacific, New Zealand	AAS	Cu: 0.06–0.20
Lund and Onshus, 1976	Oslofjord, Norway	ASV	Cu: 0.11
Abdullah *et al.*, 1976	Oslofjord, Horway	ASV	Cu: p.04
Batley and Florence, 1976	Australian coast	ASV	Cu: 0.04
Alberts *et al.*, 1976	Atlantic N.W. Ocean	AAS, XRF	Cu: 0.67–1.78 Ni: 0.44–5.02
Sclater *et al.*, 1976	Atlantic, Pacific Oceans	AAS	Ni: 3–12 nmoles kg^{-1}
Fukai and Huynh-Ngoc, 1976	Mediterranean N.W.	ASV	Cu: 0.50
Moore and Burton, 1976	Atlantic N.E. Ocean	AAS	Cu: 0.09–0.23
Bender and Gagner, 1976	Sargasso-Sea	AAS	Cu: 0.12 Ni: 0.10
Guegneniat *et al.*, 1976	English Channel	N.A.A.	Fe: 5–100
Florence and Batley, 1977	Australia	ASV	Cu: 0.4–0.7
Lee *et al.*, 1977	South Korea	N.A.A.	Cu: 1.1 Fe: 0.25
Kremling and Petersen, 1977	Iceland–Faroe Ridge	AAS	Cu: 0.5 Fe: 0.90
Boyle *et al.*, 1977	North Pacific Ocean	AAS	Cu: 0.1–0.4
Moore, 1978	Atlantic Ocean	AAS	Cu: 0.07–0.7
Danielsson *et al.*, 1978	Indian Ocean	AAS	Cu: 0.51 Fe: 0.56 Ni: 0.67
Mart *et al.*, 1978	Ligurian and Tyrrenian coast	ASV	Cu: 0.2–0.5
de Forest *et al.*, 1978	Australia	AAS, ASV	Cu: 0.03–4.5 Fe: 3.1–27.7 Ni: 0.9–11.3
Weiss *et al.*, 1979	Pacific Ocean	AAS, NAA	Cu: 2.20 and 1.98
Bacon *et al.*, 1980	Cariaco Trench	AAS	Cu: 0.007–0.28
Frache *et al.*, 1980	Ligurian Sea	AAS	Cu: 1.19–2.34 Ni: 0.53–0.81

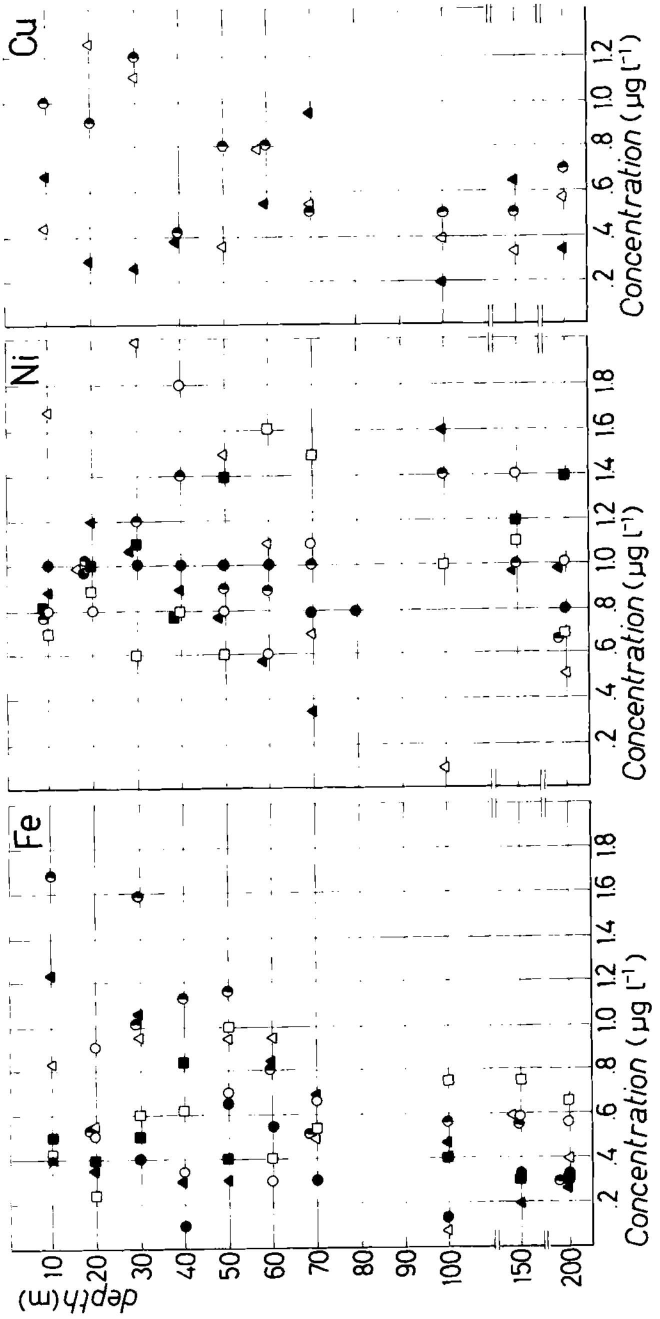

FIGURE 2 Depth versus concentration scatter plot. ◐ Sta. B'; △ Sta. C'; ▲ Sta. E'; ○ Sta. B; ■ Sta. C; ● Sta D; □ Sta. E.

the elements with depth was significantly different from that of analytical methods at Stas. B′, C′, E′ for all metals and at Stas. B, C, D, E, for Ni and Fe only. For these stations a depth-concentration scatter plot is shown in Figure 2.

From these diagrams is evident that while the Ni concentration was independent of depth, for Cu and Fe there was a higher concentration in the epithalassa. It is evident also that this difference was more marked in the Stas. B′ and C′, in the central part of the inner traverse. As pointed out by several authors (Bruland *et al.*, 1978a; Boyle *et al.*, 1976; Boyle and Edmond, 1975; Bruland *et al.*, 1978b; Bishop *et al.*, 1977, Schutz and Turekian, 1965) in the zone where upwelling currents oppose the downward movement, some trace elements can attain a relatively high steady state concentration if no depletion is caused by biological activity. We can ascribe the enrichment of Fe and Cu in the upper layer to this cause, since in the Ligurian Sea the bloom occurs in February, whereas the samples were taken in May–June.

CONCLUSIONS

While these data do not yet yield a clear general pattern of trace element distribution in this area, nevertheless some conclusions may be drawn. Thus, in the outer traverse there was a relatively uniform distribution of Cu, Fe and Ni; possible differences in concentration related to the divergence and cyclonic eddy were, in this zone, so small as to be obscured by analytical variability. On the other hand, the stations of the central zone of the inner traverse, having significantly higher concentrations of Cu and Fe can be considered different from the others. Taken as a whole, there was no significant depletion of dissolved elements from the epithalassa, particularly of the central zone. As this zone is related to the divergence axis and the cyclonic eddy, this description of the trace element distribution in this area can establish a first approach to the more general problem of the distribution of the trace element in the Ligurian Sea.

Much more detailed investigative studies of this region will be necessary in order to measure also the concentration of trace metal in particulate matter that plays an important role in the vertical and geographical distribution of trace elements.

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