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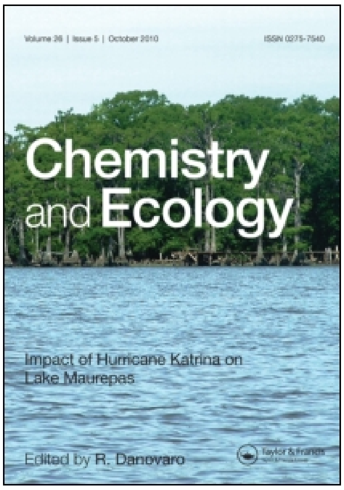

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Heavy Metals in Superficial Sediments from the Ligurian Sea, Italy[†]

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In this paper we are presenting the concentrations and the distributions of trace metals (Fe, Ni, Cr, Cu, Pb and Zn) in the coastal area of the Ligurian Sea between Capo Noli and Capo Mele. Fifty-six samples were subjected to textural, organic carbon and chemical analyses. Three different extraction methods were used: 1N $NH_2OH.HCl$ plus 25% CH_3COOH, nitric acid solution, and total attack with $HClO_4$–HF mixture. The solutions were analysed by atomic absorption spectrophotometry. The results obtained confirm that the extraction methods which are most informative for environmental purposes are the cold or the easily extractable metal techniques. The results also show that for the study area the concentrations of Fe, Ni, Cr, Cu, Pb, and Zn do not indicate traces of anthropogenic inputs.

INTRODUCTION

The determination of trace metals in sediments generally involves several extraction techniques, followed by atomic absorption analysis. Knowledge of the concentrations and distributions of trace metals in sediments is of primary importance when detecting sources of pollution in aquatic systems (Förstner and Wittmann, 1979) and for this reason

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sediments should be monitored in major pollution programmes.

The analysis of trace metals in sediments present a number of complex problems and various methods for measuring inorganic trace materials have been reported in the literature (Agemian and Chau, 1976; Presley *et al.*, 1972; Loring, 1976; Tessier *et al.*, 1979; Malo, 1977; Brannon *et al.*, 1977). Techniques have also been developed for determining the association of metals with various sediment phases (organic, exchangeable, easily reducible, moderately reducible and residual) thus characterizing accumulation sites and the bioavailability of metals in the marine environment (Förstner and Patchineelam, 1980). Regarding the evaluation of trace metal pollution in sediments, it is the available, non-silicate elements which are of fundamental interest. An analysis of the non-silicate fraction, rather than that of the total sediment (which includes the detrital fraction) will often yield more data on the extent of the trace metal pollution; indeed, the latter mask the relationship sought (Agemian and Chau, 1976; Fōrstner and Wittmann, 1979). In our opinion, nevertheless, it is also advisable to determine the total content of metal (Cosma *et al.*, 1979). In fact, the extraction methods that are the most informative for environmental purposes are those for total metal, the cold and the easily extractable metal extraction techniques.

One technique used by us utilizes the attack of samples with a mixture of 1N hydroxylammonium chloride and 25% acetic acid. This technique, not directly applicable to those sediments which contain appreciable quantities of organic carbon, is appropriate in the present case, because the organic carbon content is, on the average, rather low.

Another technique makes use of 8N HNO_3 at 50–60°C in order to extract the non-silicate extractable metal in sediments without materially affecting the silicate matrix.

The present work evaluates 56 samples collected during "Oceanographic Cruises" in the Ligurian Sea by R. V. Bannock sponsored by the "Gruppo Ricerca Oceanologica-Genova." The stations were located on the continental shelf area between Capo Noli and Capo Mele (Figure 1). The samples were analysed to determine the concentration of Cr, Cu, Ni, Fe, Pb, Zn, organic carbon and granulometry.

ANALYSIS

Each sample, suitably homogenized, was divided into two portions. The first was subjected to particle size analysis by wet sieving and aliquots

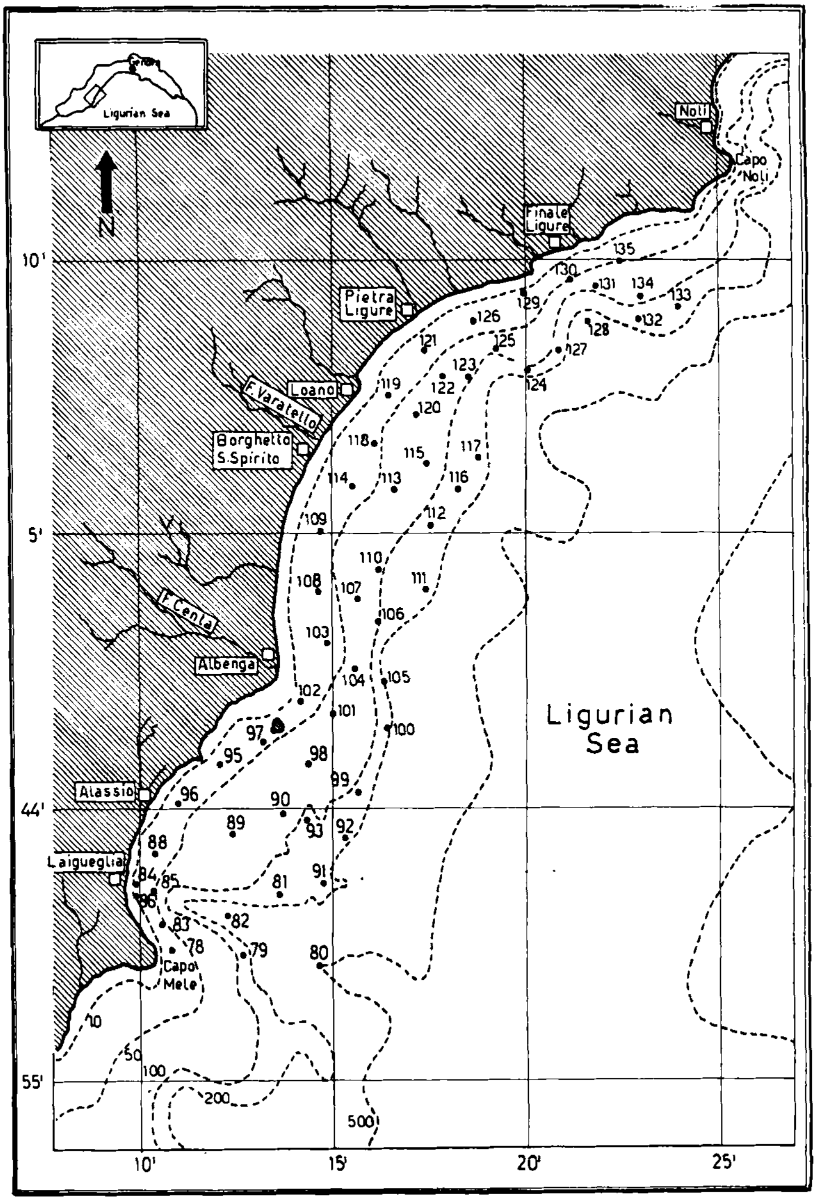

FIGURE 1 Location of the sampling stations.

of the second portion were digested with 1N hydroxylamine hydrochloride plus 25% acetic acid solution (1 : 1) (reagent A), with 8N HNO_3 (reagent B) and with a mixture of 70% $HClO_4$ and 40% HF (1 : 1) (reagent T), according to Cosma *et al.* (1979, 1981). We determine the concentration of Cr, Cu, Fe, Ni, Pb and Zn in the solution, made up to 100 ml with deionized water, by Atomic Absorption Spectrophotometry (Perkin–Elmer model 560) employing an air-acetylene flame.

The determination of metals was carried out by the additions standard method; moreover, the non-specific absorption was determined using a deuterium lamp.

The analytical precision for the extracted solutions and total attacks, determined from five replicate analyses of one sample and expressed as coefficient of variation is as follows: Cu 5.7%, 5.0%, 4.1%; Cr 6.7%, 6.5%, 5.2%; Ni 8.0%, 7.1%, 6.5%; Fe 3.3%, 3.5%, 3.0%; Pb 5.1%, 5.8%, 5.0%; Zn 3.8%, 4.5%, 5.8%; with the reagent A, B and total attack respectively.

Organic carbon (TOC) was determined utilizing the difference between total carbon and inorganic carbon (Shimp *et al.*, 1970).

RESULTS AND DISCUSSION

The location of the superficial sediment sampling stations is reported in Figure 1. The results of the chemical analyses, the textural characteristics and the organic carbon values are presented in Table I and Figures 2 to 9. The figures from 2 to 7 present the concentrations of Fe, Ni, Cr, Cu, Pb and Zn plotted against versus sample location, using the partial extraction methods together with the total attack.†

Generally, the extraction efficiency of the three methods is in an

TABLE I
Depth, textural analyses, organic carbon content (%) of the sediment samples

Sample no.	Depth (m)	% < 74 μm	C org (%)
78	82	77.0	0.30
79	189		0.26
80	497		0.42
81	173		0.26
82	330		0.30

---

† In the figures the data concerning all 56 samples have been included: only a few of them, however, have been represented by dots.

Sample no.	Depth (m)	% < 74 μm	C org (%)
83	39		
84	22		
85	53	68.6	0.20
86	160	90.2	0.50
88	39	76.0	0.78
89	85		0.10
90	115		0.32
91	186	96.0	0.10
92	190	98.2	0.57
93	99	—	0.27
95	30	87.6	0.78
96	44	86.6	0.31
97	41	91.8	0.66
98	83	95.0	0.22
99	173		0.10
100	164		0.10
101	56		0.74
102	33	95.8	0.32
103	39		0.10
104	61	40.2	1.60
105	155	99.0	0.47
106	175	99.4	0.28
107	86		0.23
108	32	84.4	0.10
109	36		0.57
110	89		0.16
111	179		0.25
112	161	98.6	0.43
113	69	83.0	0.50
114	40	74.4	0.61
115	96	98.2	1.02
116	167	96.4	0.14
117	157	97.4	0.55
118	46	92.0	0.63
119	91	82.4	0.64
120	77	92.2	0.18
121	36	80.2	0.44
122	73	92.4	0.10
123	150	98.8	0.34
124	119	96.2	
125	64		0.35
126	32	88.4	0.72
127	103	92.6	0.63
128	60	83.6	0.53
129	38	82.6	0.52
130	39	82.6	0.87
131	64	85.8	0.61
132	109	91.2	0.43
133	117	82.0	0.43
134	83	98.4	0.30
135	41	75.8	0.29

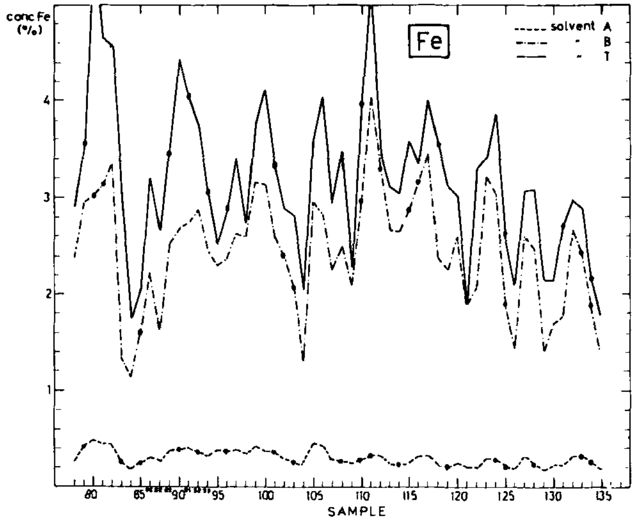

FIGURE 2 Concentration (μg/g) of Fe, Ni, Cr, Cu, Pb and Zn as a function of sample location in sediments extracted by: --------- solvent A = 1N $NH_2OH.HCl + 25\%$ CH_3COOH (v/v); -.-.-.-. solvent B 8N HNO_3; ———— total attack ($HClO_4$ 60% + HF 40% v/v).

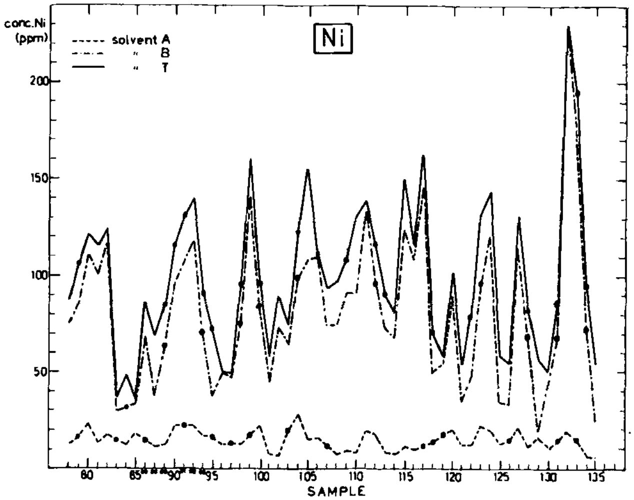

FIGURE 3 Concentration (μg/g) of Fe, Ni, Cr, Cu, Pb and Zn as a function of sample location in sediments extracted by: --------- solvent A = 1N $NH_2OH.HCl + 25\%$ CH_3COOH (v/v); -.-.-.-. solvent B 8N HNO_3; ———— total attack ($HClO_4$ 60% + HF 40% v/v).

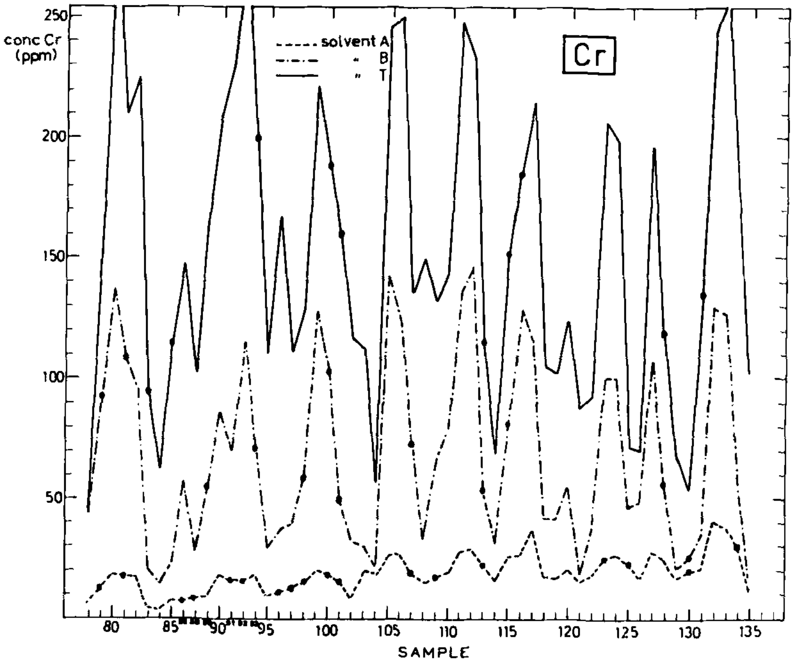

FIGURE 4 Concentration (µg/g) of Fe, Ni, Cr, Cu, Pb and Zn as a function of sample location in sediments extracted by: --------- solvent A = 1N $NH_2OH.HCl + 25\%$ CH_3COOH (v/v); -.-.-.-. solvent B 8N HNO_3; ———————— total attack ($HClO_4$ 60% + HF 40% v/v).

increasing order: 1N hydroxylammonium chloride plus 25% acetic acid (reagent A), 8N HNO_3 (reagent B) and mixture $HClO_4$–HF (reagent T). The extraction efficiency of each depends on the acid strength and on the oxidizing or reducing power of the solutions.

For Fe (Figure 2) the 8N HNO_3 and the total attack reagents extracted the bulk of the Fe, and although the distribution of each is the same the former was notable in showing a lower percentage of the total Fe (15%). This indicates that the cold reagent, probably, attacks only the non-residual part of the sediment; this result is in accordance with that of Agemian and Chau (1977). A linear relationship between the data of the total attack (reagent T) with those of the nitric attack (reagent B) and with those of the cold reagent (reagent A) was noted (correlation coefficient $r_{T/B} = 0.70$ and $r_{T/A} = 0.75$).

The Ni distribution (Figure 3) is approximately similar to that of Fe. In this case a linear relationship between the data of the total attack

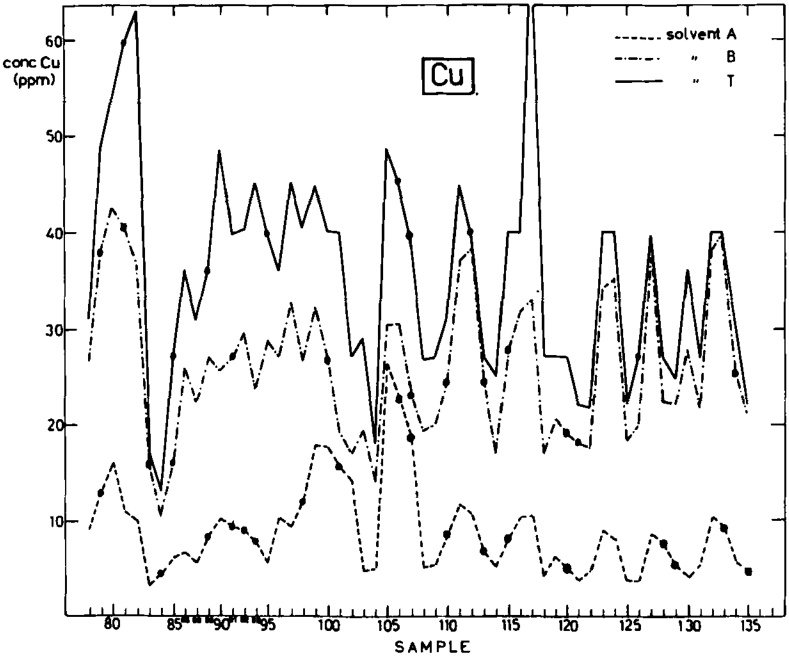

FIGURE 5 Concentration (μg/g) of Fe, Ni, Cr, Cu, Pb and Zn as a function of sample location in sediments extracted by: -------- solvent A = 1N $NH_2OH.HCl + 25\%$ CH_3COOH (v/v); -.-.-.-.-. solvent B 8N HNO_3; ———————— total attack ($HClO_4$ 60% + HF 40% v/v).

versus the two partial attacks was observed ($r_{T/B} = 0.73$ and $r_{T/A} = 0.68$ respectively).

For Cr (Figure 4) the total and the nitric acid attacks give different distributions from the cold reagent. They also show high values of metals at locations where the cold method shows only low ones. This confirms that the weaker extraction methods show a minimal attack on the residual phases in the sediments. In this case $r_{T/B} = 0.87$ and $r_{T/A}$ is not significant.

For Cu (Figure 5) the cold reagent draws out a very small quantity of the metal and this occurs also for Ni and Fe. It is known that Cu is strongly associated with organic carbon (Rashid, 1974). The $NH_2OH \cdot HCl$–CH_3COOH mixture is not sufficiently acid (pH = 1.5) to produce dissociation of the natural complexes, nor is it a sufficiently strong complexing agent to compete in complex equilibria. Nevertheless, this mixture satisfactorily dissolves Zn, Cd, Pb, Cr and other metals from

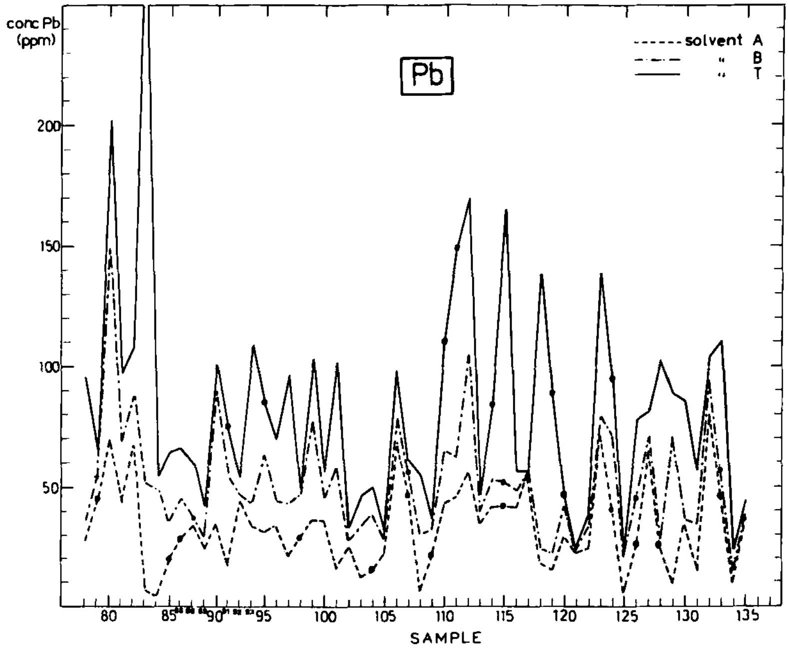

FIGURE 6 Concentration (μg/g) of Fe, Ni, Cr, Cu, Pb and Zn as a function of sample location in sediments extracted by: --------- solvent A = 1N $NH_2OH.HCl + 25\%$ CH_3COOH (v/v); -.-.-.-. solvent B 8N HNO_3; ———————— total attack ($HClO_4$ 60% + HF 40% v/v).

the carbonate and ferromanganese phases and from adsorbed phases of sediment; it is also suitable for other metals that do not form strong complexes with organic matter. Except for the samples from stations 125 to 135 which had similar values, the nitric acid reagent yields lower values than those from the total attack. It is expected, therefore, that in these samples the metal is present in a non-residual matrix. For Cu the linear correlation coefficients are $r_{T/B} = 0.65$ and $r_{T/A} = 0.63$ respectively.

For Pb and Zn (Figures 6 and 7) the absolute amount of metal extracted decreases as the extracting solution becomes weaker. The trend is, on the average, similar for the two metals. The values of the correlation coefficients are not significant for Pb and Zn respectively.

The secondary aim of this investigation is to compare the metal content in the continental shelf area between Capo Noli and Capo Mele

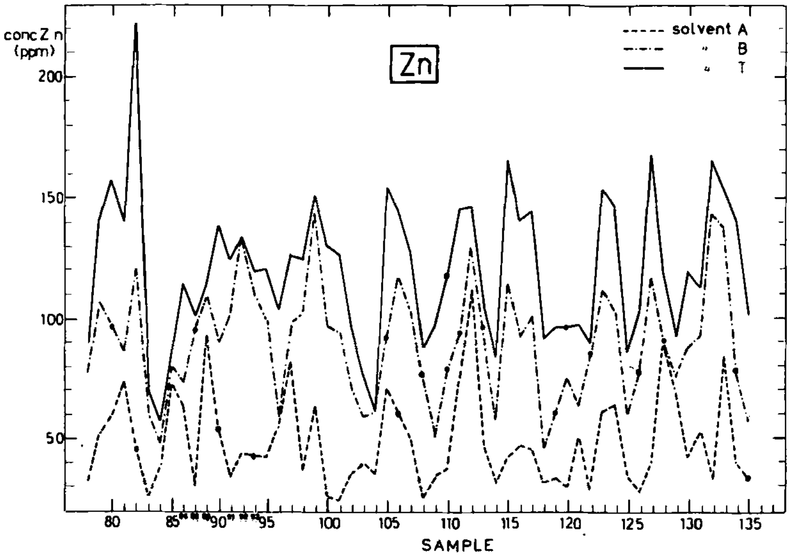

FIGURE 7 Concentration (μg/g) of Fe, Ni, Cr, Cu, Pb and Zn as a function of sample location in sediments extracted by: --------- solvent A = 1N $NH_2OH.HCl + 25\%$ CH_3COOH (v/v); -.-.-.-. solvent B 8N HNO_3; ——————— total attack ($HClO_4$ 60% + HF 40% v/v).

with that of the area between Arenzano and Capo Noli previously examined by Cosma *et al.* (1979).

In the present study area, a general uniform distribution for all metals (Fe, Ni, Cr, Cu, Pb and Zn) with values generally increasing seawards can be noted. This is related to the granulometry distribution (Figure 8) which presents increasing values of fine-fraction content with distance moved seawards. In deeper sediments, only the fine-fraction is present; concentrations of the metals will be affected by sedimentation which takes place closer to the coast. Furthermore, in this area, the local transport and the sedimentation conditions are dominant and affect the distribution of the metals.

Generally, the concentrations of Fe, Ni, Cr, Cu, Pb and Zn, are in agreement with the values reported in literature (Ju Chin Chen, 1976; Chen and Lu, 1974; Bruland *et al.*, 1974; Bower *et al.*, 1978; Campbell and Loring, 1980). Here the organic carbon values are present at natural levels (Figure 9) and confirms that in this coastal area, unlike that which stretches from Arenzano to Capo Noli and Vado Ligure bay (Drago *et al.*, 1982), there are no effects of industrial and domestic inputs.

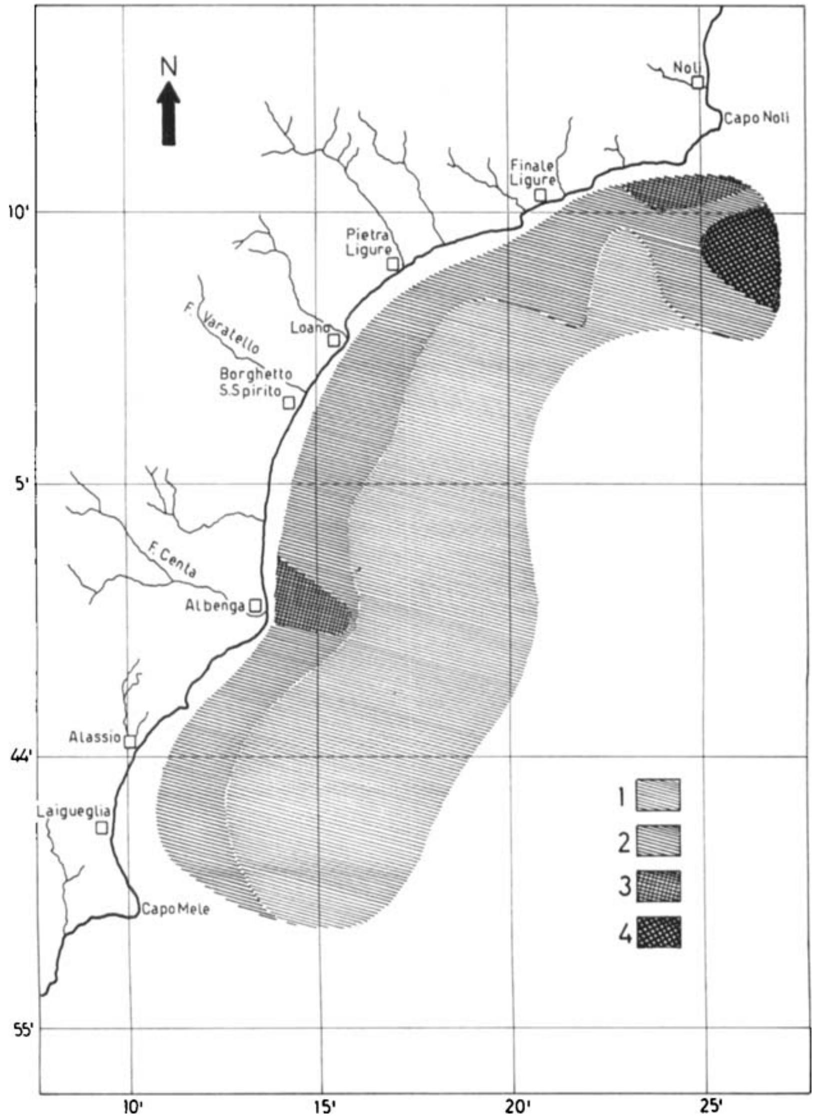

FIGURE 8 Distribution of the grade composition of the sediments: 1) sand <5%; 2) sand 5–30%; 3) sand 30–70%; 4) sand 70–95%.

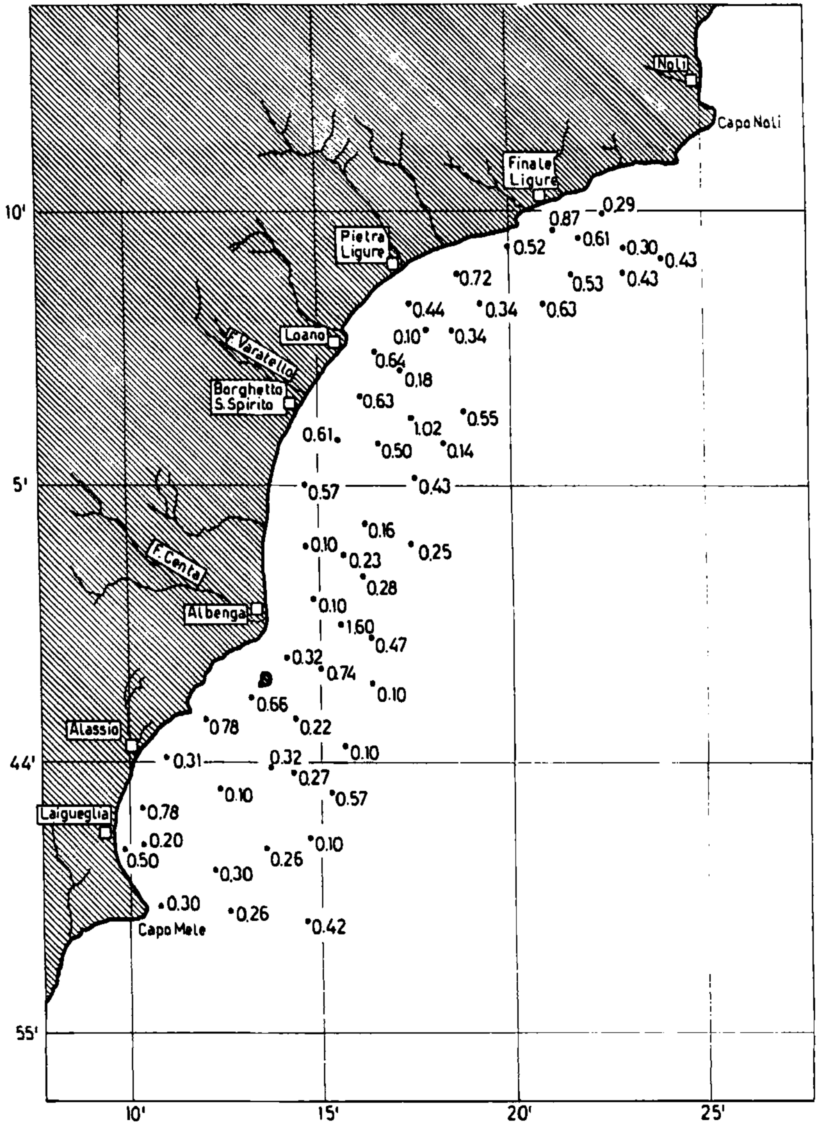

FIGURE 9 Distribution of organic carbon content (%).

CONCLUSIONS

The results of our sediment analyses confirm that the cold reagent 1N $NH_2OH.HCl$ plus 25% CH_3COOH is adequate for the simultaneous extraction of non-detrital heavy metals from a variety of marine sediments. Nevertheless, it does not extract Cu that has been complexed by organic matter.

The comparison of the nitric acid extraction method with the total attack show that the 8N HNO_3 solution supplies a measurement of the available non-silicate metals in sediments. This method provides a high degree of metal extraction and while destroying organic matter, it has little effect on the metal bound in the silicate crystal lattice and removes only precipitated and absorbed metals in sediments.

The results obtained, compared with those of the coastal area of the Ligurian Sea between Arenzano and Capo Noli, confirm that the area studied, Capo Noli and Capo Mele, is not polluted but presents, on the average, a distribution of heavy metals at normal levels.

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