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HEAVY METALS IN HIGH TYRRHENIAN SEA SEDIMENTS: DISTRIBUTION OF Cr, Cu, Ni AND Mn IN SUPERFICIAL SEDIMENTS (***)

Riassunto — *Metalli pesanti nei sedimenti marini dell'Alto Tirreno: distribuzione di Cr, Cu, Ni e Mn nei sedimenti superficiali.* Sono stati esaminati quarantacinque campioni di sedimenti marini superficiali prelevati sulla piattaforma continentale compresa tra La Spezia e Livorno, unitamente a tredici campioni dei sedimenti dei fiumi che influenzano l'area studiata. Il materiale è stato sottoposto ad analisi tessiturali e chimiche con la determinazione del tenore in Cr, Cu, Ni e Mn. Si è inoltre presa in considerazione la geologia e la fisiografia della costa. Con i dati ottenuti sono state redatte carte di distribuzione dei metalli.

E' stato confermato sia il trasporto litoraneo dei sedimenti, indipendentemente dalla corrente generale del Mediterraneo Occidentale, sia la presenza di due zone di convergenza all'altezza di Forte dei Marmi e di Tirrenia.

Abstract — Fourty-five samples of superficial marine sediment collected in the continental shelf area between La Spezia and Livorno were examined, along with thirteen fluvial sediment samples from rivers flowing into the area under examination. The materials were subjected to textural and chemical analyses, the latter to determine the Cr, Cu, Ni and Mn contents.

The geology and physiography of the coastal belt were also studied. From the data thus obtained, maps were drafted showing the distribution of metals. Both the coastal transport of the sediments independent of the general current of the Western Mediterranean and the presence of two zones of convergence in the area of Forte dei Marmi and Tirrenia were confirmed.

Key words — pollution, heavy metals, littoral drift, littoral sedimentation.

INTRODUCTION

During Oceanographic Cruises in the High Tyrrhenian sea sponsored by the « Gruppo Ricerca Oceanologica - Genova » (G.R.O.G.),

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bottom samples of the continental shelf of Tuscany were gathered, in order to provide, through chemical and sedimentological investigation, a contribution to the knowledge of the environment of this area.

A relationship between sedimentation, metal content and coastal transport was also found.

This study evaluates 30 samples collected during the « Bannock » Cruise (1974) in the continental shelf area between La Spezia and Livorno; the investigation includes sediments of the rivers which flow into the study area (Fig. 1).

The samples were analysed to determine the concentration of Cr, Cu, Ni and Mn. These metals were chosen among those having particular characteristics of toxicity and wide diffusion.

The samples were subjected to a textural analysis also. Total solubilisation was done with a mixture of HF and $HClO_4$, following the methodology used for rock analysis (BASSO & MAZZUCCOTELLI, 1975) and also applied to marine sediments (LANGMYHR & PAUS, 1968; JONES, 1972; ERLENKEUSER, SUESS & WILLKOMM, 1974; SLATT, 1974-75).

EXPERIMENTAL

Sampling

A Van Veen grab was utilized to collect and homogenize the superficial part of the sample, up to a thickness of 5 cm.

Apparatus

All analyses were done with a Shandon Southern A 3400 atomic absorption spectrophotometer with an air-acetylene flame, equipped with a Kipp and Zonen mod. 808 recorder. The wavelengths used were 357.9 nm for Cr, 232.0 nm for Ni, 324.7 nm for Cu and 279.5 nm for Mn.

Reagents

All reagents used were analytical reagent (Merck) $HClO_4$, 60%; HF, 40%; HCl, 37%; HNO_3, 65%. Standards were prepared by dilution of 1,000 $mg.l^{-1}$ metal stock solutions.

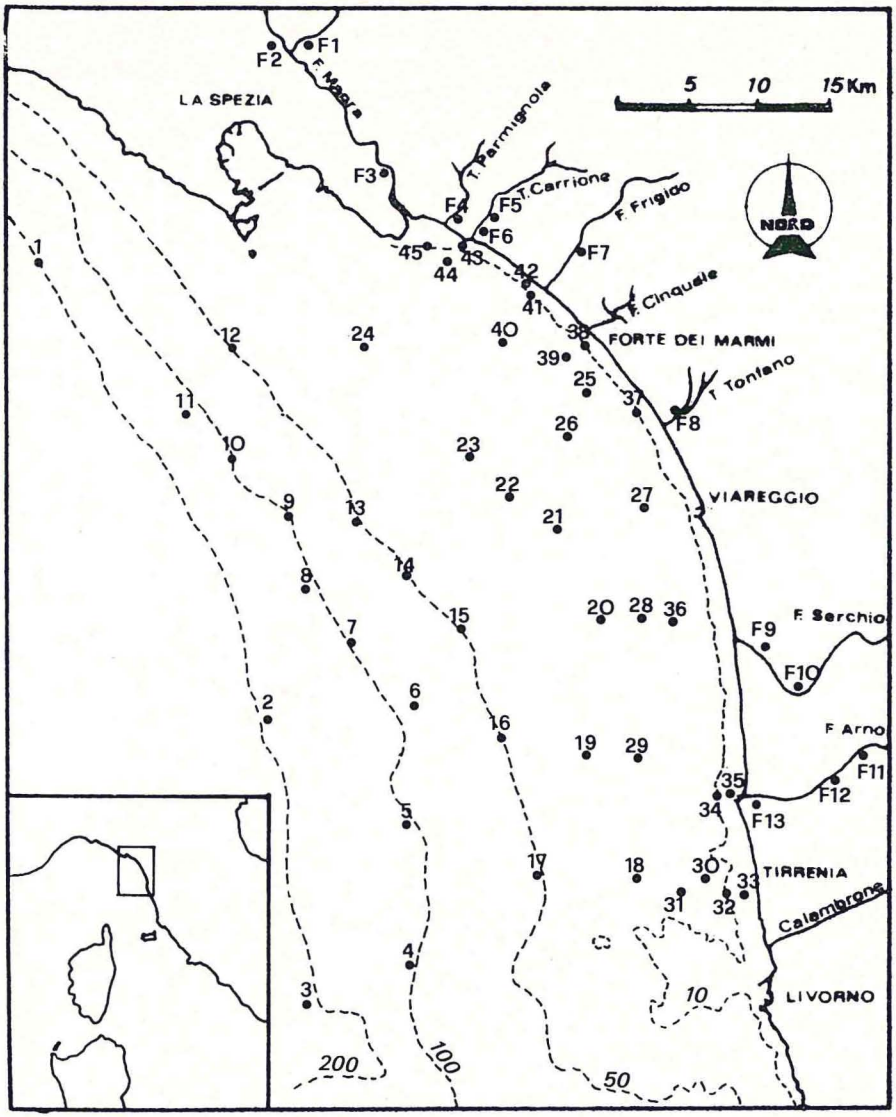

Fig. 1 - Location of the samples.

Procedure

All unsieved samples were dried in an oven at 105°C and then lightly mortared. Sediment (0.5 g) was treated with 10 ml of perchloric acid and 10 ml of hydrofluoric acid, kept for 16 hours at

50-60°C and then dried; the procedure was repeated twice. The residue was dissolved in dilute hydrochloric acid (BASSO & MAZZUCCOTELLI, 1975).

GEOLOGICAL, PHYSIOGRAPHIC AND HYDROLOGICAL CHARACTERISTICS

The littoral in front of the sampling area corresponds to a single physiographic unit and is characterized by a continuous sandy belt, which extends from the Gulf of La Spezia to the Uccellina Mountain, interrupted only by the deltas of the rivers with a greater detrital input which can be identified with the Magra, Serchio and Arno Rivers; beside these, it appears that a fair input can be attributed to the Frigido creek (AIELLO et al., 1975; GANDOLFI & PAGANELLI, 1975).

Geologically the area can be subdivided into two petrographic subprovinces (GANDOLFI & PAGANELLI, 1975): one extending from La Spezia to Marina di Pietrasanta, characterized both by the abundance of ophiolitic rocks and by the presence of sedimentary lithofacies with a predominance of carbonatic rocks, limestone and marble; the second, South of Marina di Pietrasanta, presents outcrops of acid and carbonatic rocks, micaschists and phyllites, besides minor formations.

The inputs of the Magra River are therefore affected by the presence of both ophiolitic rocks and sedimentary lithofacies in the basin, while the Arno and the Serchio shown an almost totally granitic, sandy and carbonatic input.

This situation allows us to predict limited inputs of Cr and Ni on the part of the Magra River, in relation to the ophiolitic rocks and of Mn, due to the carbonatic rocks; for the Arno and Serchio Rivers, instead, inputs of Mn can be predicted, due to the acid and carbonatic rocks. Such inputs, besides being affected by the general transport conditions from South to North because of the effect of the general current of the Mediterranean Sea, are influenced by a transport in the opposite direction along the coast.

It may be recalled that in 1975 the presence of two drifs, distal and proximal, was confirmed along our entire sampling area (AIELLO et al., 1975). The proximal drift involves principally the area near the shore-line and therefore no relation to our samples of marine sediment, taken at a minimum depth of 5 m, can be found.

We can instead look for a relation between transport and concentration of metals in the belt included within the bathymetric of 20 m. From the bibliographical data (SAGGINI, 1967; AIELLO et al., 1975; GANDOLFI & PAGANELLI, 1975) it is evident that the area included between the mouth of the Cinquale River and that of the Tonfano Stream presents the convergence of two distal drifts of opposite directions: one with a NW-SE direction, capable of transporting the sediments of the Magra River and the second with a S-NW direction, which carries out a transport of the inputs of the Arno and Serchio Rivers. A second area of convergence is evidently concentrated in the section of the sea between Tirrenia and the Calambrone Stream: this area therefore feels the effects of both the input of the Arno from the North and of inputs due to the drift which comes from the South.

RESULTS AND DISCUSSION

The results of the textural analyses were utilized to draw up a map of the distribution of the sediments (Fig. 2); for the classification of the lithotypes the Kruit criteria was followed (FANUCCI et al., 1974). This data confirms in a general sense what was discovered in 1973 by FANUCCI et al. (1973) in a section of the Continental shelf area between La Spezia and Forte dei Marmi.

The influence of the Magra River is evident in the whole northern area until Forte dei Marmi; the sedimentation, initially sandy, becomes gradually more lutitic with the increase of the bathymetric, until it becomes completely so for depths greater than 30 m. Two direction of transport of longshore sediments can be pointed out: one following the general current of the High Tyrrhenian with a SE-NW direction and the second, previously mentioned, due to the distal drift in the opposite direction, and which decreases going towards the Frigido River. The lutite field is limited to the South by a lutitic-arenitic field which seems to be related to the contributions of the Arno River. At the mouth of this River no sedimentation of coarse material can be observed; this coarser material is deposited in the immediate vicinity of the coast; the only essentially arenaceous zones is found in front of Tirrenia in connection with the area of convergence of two currents of opposite direction. (AIELLO et al., 1975). The sedimentation North of the Arno is essentially lutitic, and does not show traces of the North-South transport

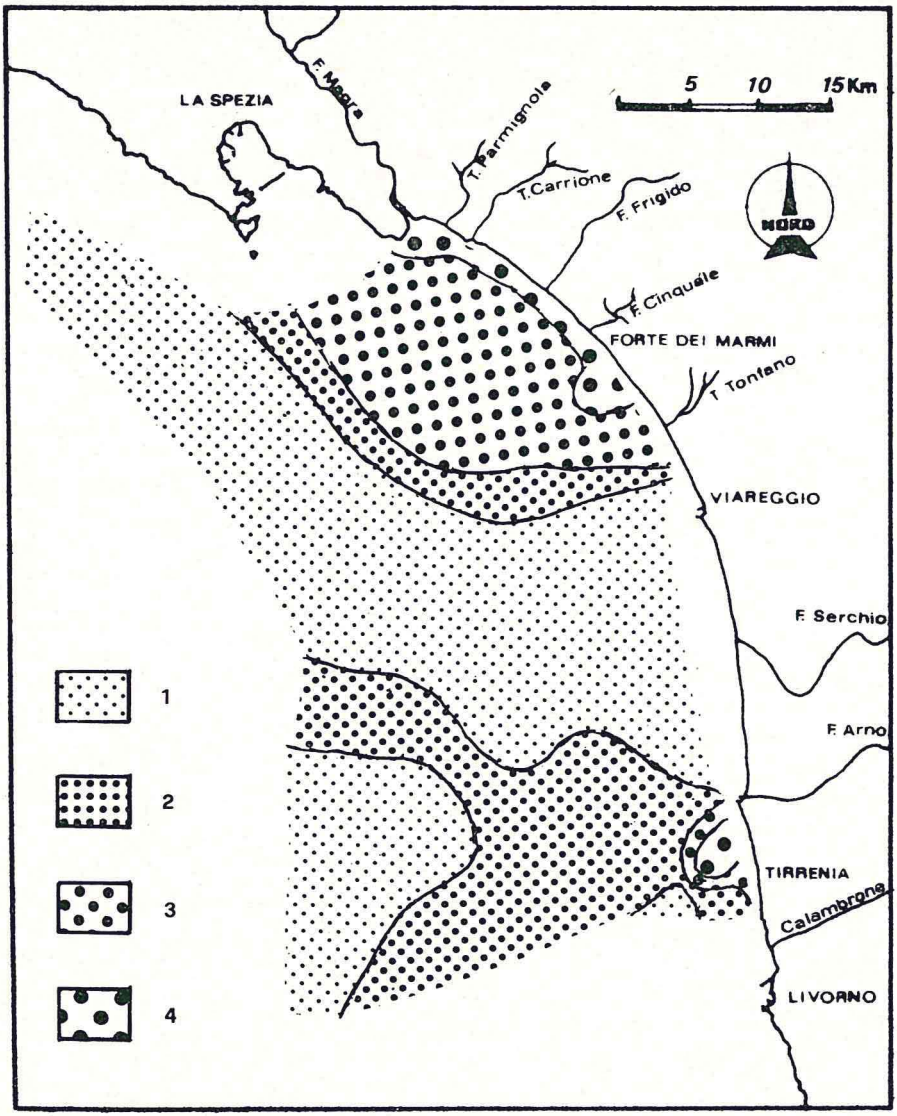

Fig. 2 - Distribution maps of the sediments: 1 - sand < 5%; 2 - sand 5-30%; 3 - sand 30-70%; 4 - sand 70-95%.

already brought to light by GANDOLFI & PAGANELLI in 1975, but we can hypothesize that the transport of the coarser material takes place essentially along the coast in the non-sampled area.

In the area of Forte dei Marmi, there is an increase out to sea

of the coarser area of sedimentation, which seems to be due to the input of the Magra River; this zone is localized in the area of convergence of the two distal drifts of opposite directions and seems to testify to the ceased capacity of transport of the drifts responsible for the long shore movement of the sediments.

The results of the chemical analyses are reported in Tab. 1 and Tab. 2, together with the textural characteristics of the samples analyzed and their location.

The areas of distribution of the single metals were reconstructed and the lines of isoconcentration which are the most adequate to point out the area distribution were reported.

Chromium - The analysis carried out on fluvial sediments demonstrate very high values (1.200-1.700 p.p.m.) for the Serchio and Arno Rivers, values which are not justified by the lithology, of the hydrographic basins which, as was noted, present a predominance of generally acid sedimentary rocks.

The marine samples in correspondence with these two rivers, are noticeably affected by their inputs: in fact, in correspondence with the mouth of the Arno 500-800 p.p.m. are reached: these values are markedly greater than the others of the area studied, which presents, on the average, concentrations of about 300 p.p.m. (Fig. 3). This average value is analogous to that observed by us in Western Ligurian sea sediments (Cosma et al., 1979) with the same extraction method; it is instead higher than values obtained by various Authors with different extraction methods in similar studies (Gross, 1967; Shimp, Leland & White, 1970; Collinson & Shimp, 1972; Slatt, 1974; Bernhard & Zattera, 1975; Slatt & Sasseville, 1976; Armstrong, Hanson & Gaudette, 1977; Griggs et al., 1978). There may also be a possibility that such high values can be related to the intense industrialization along the banks of the two rivers. This possibility seems to be confirmed by the investigations of Taponeco & Giaconi, who in 1969 discovered the presence of high quantities of chromium, due to galvanic and tanning industries.

The chromium content in the fluvial sediments of the other rivers is low; the only value which is slightly higher (242 p.p.m.) was observed in the area above the Magra River and can be related to the erosion of the ophiolitic rocks which constitute the high part of the basin of this river.

In the marine sediments, two areas of accumulation can be

TABLE 1 - Sample locations, textural analyses and concentration of the metals ($\mu g.g^{-1}$) in the marine sediments.

Station n°	Latitude N	Longitude E	Depth (m)	Cr	Cu	Ni	Mn	%<74μ m
1	44°00.9'	10°40.4'	202	350	115	165	1210	99.4
2	43°43.6'	09°52.1'	163	350	65	150	1600	88.1
3	43°32.7'	09°54.4'	266	330	75	116	2000	95.8
4	43°34.4'	09°59.8'	100	250	75	130	1200	90.4
5	43°39.7'	09°59.4'	117	340	75	110	1200	99.6
6	43°44.1'	09°59.7'	85	335	57	143	811	93.5
7	43°46.5'	09°56.3'	98	300	50	160	1148	99.8
8	43°48.7'	09°54.4'	97	300	25	146	1000	99.8
9	43°51.3'	09°52.8'	91	255	50	147	1012	98.7
10	43°53.5'	09°50.2'	106	350	25	170	995	98.9
11	43°55.3'	09°47.0'	117	250	50	160	1095	99.0
12	43°57.6'	09°50.7'	51	400	50	171	1156	99.2
13	43°51.0'	09°56.4'	55	300	50	176	1310	97.4
14	43°48.8'	09°59.4'	51	250	50	144	847	98.7
15	43°47.2'	10°01.3'	48	250	40	165	1200	98.5
16	43°43.1'	10°04.3'	48	330	50	115	710	99.8
17	43°37.6'	10°06.1'	51	200	75	120	850	92.3
18	43°37.5'	10°11.3'	25	250	45	62	700	80.3
19	43°42.3'	10°08.5'	28	260	50	117	825	93.0
20	43°47.5'	10°08.8'	17	180	55	75	1010	99.5
21	43°51.0'	10°07.0'	20	300	35	160	915	99.7
22	43°52.1'	10°04.7'	24	250	40	114	945	81.9
23	43°53.7'	10°02.7'	24	305	20	56	864	55.0
24	43°58.0'	09°56.8'	21	360	25	85	975	56.1
25	43°56.4'	10°07.4'	16	225	25	45	720	21.0
26	43°54.3'	10°07.6'	19	300	25	74	843	41.4
27	43°51.9'	10°11.0'	16	455	75	170	1270	97.5
28	43°47.4'	10°13.0'	14	370	50	120	1110	99.5
29	43°42.1'	10°10.5'	14	190	50	143	907	98.6
30	43°37.0'	10°14.4'	13	100	15	40	850	10.9
31	43°37.0'	10°13.3'	15	250	160	140	860	95.3
32	43°37.0'	10°16.0'	10	200	35	76	710	77.7
33	43°37.0'	10°17.4'	5	300	270	230	800	44.1
34	43°40.7'	10°15.3'	10	840			1874	
35	43°40.8'	10°15.8'	5	500			1316	
36	43°47.6'	10°11.2'	15	375	30	125	1135	98.7
37	43°55.6'	10°11.0'	10	200	75	150	750	37.3
38	43°58.2'	10°08.5'	10	250	100	200	670	58.4
39	43°57.7'	10°07.4'	15	220	280	130	830	40.5
40	43°57.9'	10°03.9'	15	350	25	100	800	62.5
41	44°00.2'	10°05.5'	10	250	35	50	500	32.0
42	44°00.5'	10°05.7'	5	250	200	140	550	24.3
43	44°02.0'	10°01.8'	5	350	25	150	680	10.3
44	44°01.0'	10°01.0'	15	180	30	115	790	44.2
45	44°01.9'	10°00.2'	10	500	25	125	1000	17.5

pointed out: the first, as previously stated, is localized between the Tonfano and Arno Rivers, within the bathymetric of 20 m, and

TABLE 2 - Sample locations and concentration of the metals ($\mu g.g^{-1}$) in the riverine sediments.

Station	River	Cr	Cu	Ni	Mn
F01	Magra	190	35	105	712
F02	Magra	240	50	233	2426
F03	Magra	215	30	160	1805
F04	Parmignola	120	35	155	339
F05	Carrione	110	25	45	200
F06	Carrione	150	80	100	1260
F07	Frigido	60	10	50	140
F08	Tonfano	75	40	50	160
F09	Serchio	200	100	145	1133
F10	Serchio	1450	130	150	1160
F11	Arno	1180	90	150	1200
F12	Arno	1400	70	145	1578
F13	Arno	1700	50	160	1396

is related to the contributions of the Arno and Serchio Rivers; the second is located in the area in front of the Gulf of La Spezia, with concentrations which are on the average higher with respect to those found in the sediments of the Magra River. It would require a detailed study to find out whether sources of input exist.

Nickel - The distribution of nickel (Fig. 4) shows average values of about 140-170 p.p.m. in the clay sediments. At the bathymetric of less than 50 m, on the average, there is instead a marked decrease of the values in correspondence with the mouths of the three main rivers and this takes place in sediments richer in the sandy fraction.

The rivers seem to have a limited input, something which is perfectly in accordance with the geological situation of the hydrographic basins; here the values at the mouths of the Arno and Serchio Rivers are generally inferior to the medium content of the marine sediments (JONES, 1973; CARMODY, PEARCE & YASSO, 1973; CHEN & LU, 1974; BRULAND et al., 1974; SLATT, 1974; BERNHARD & ZATTERA, 1975; SLATT & SASSEVILLE, 1976). The input of the Magra River is slightly higher.

This river flows in serpentinites which generate an enrichment in Ni, especially in sediments at the mouth and along the coast. Two limited areas of accumulation can be noticed, North of Forte dei Marmi and near the Calambrone, respectively: these points coincide with the areas of convergence previously seen.

Copper - The concentrations of copper in the sediments also present values similar to those already found in literature (GROSS, 1967; SHIMP, LELAND & WHITE, 1970; COLLINS & SHIMP, 1972; JONES,

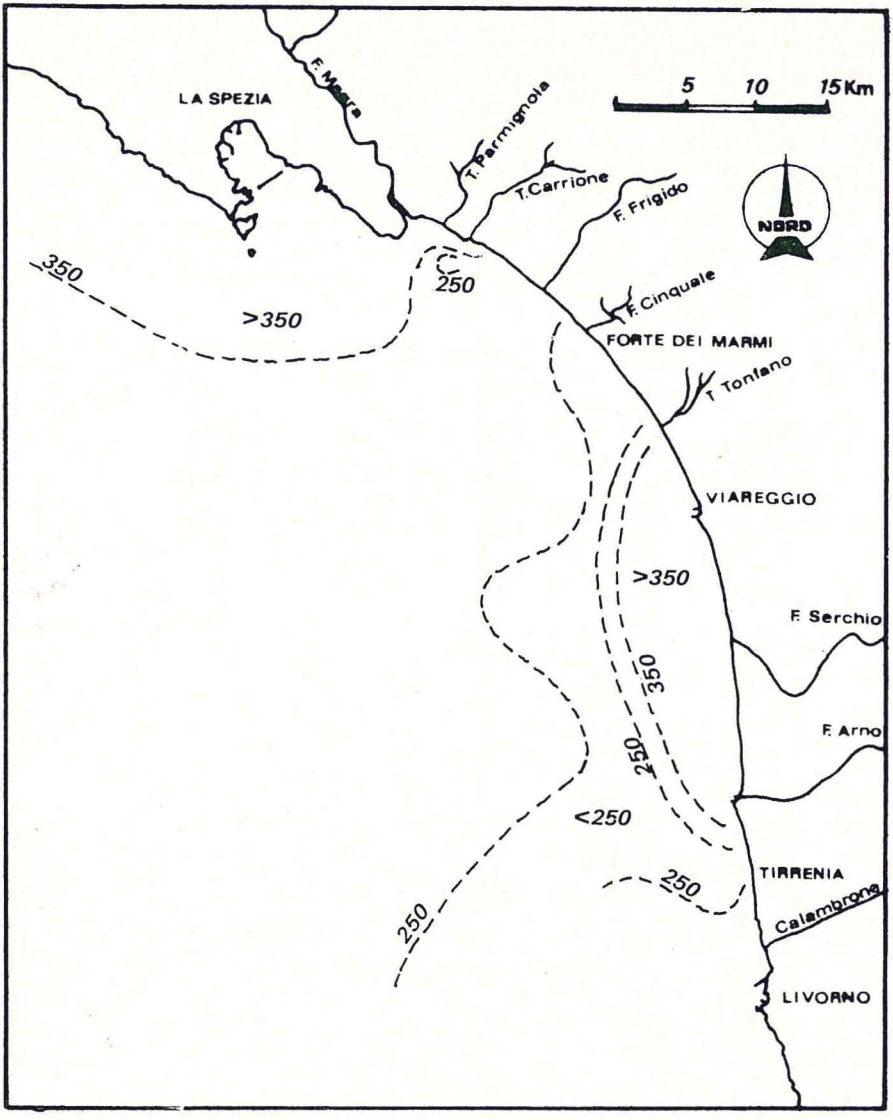

Fig. 3 - Distribution of Cr in sediments.

1973; SLATT, 1974; SLATT & SASSEVILLE, 1976; ARMSTRONG, 1977; GRIGGS et al., 1978). They also confirm the data of an analogous investigation in Western Ligurian sea sediments (COSMA et al., 1979). The rivers North of Viareggio present in their sediments low values, which are compatible with what was found in the marine sediments; to the South instead, the Arno and Serchio Rivers input

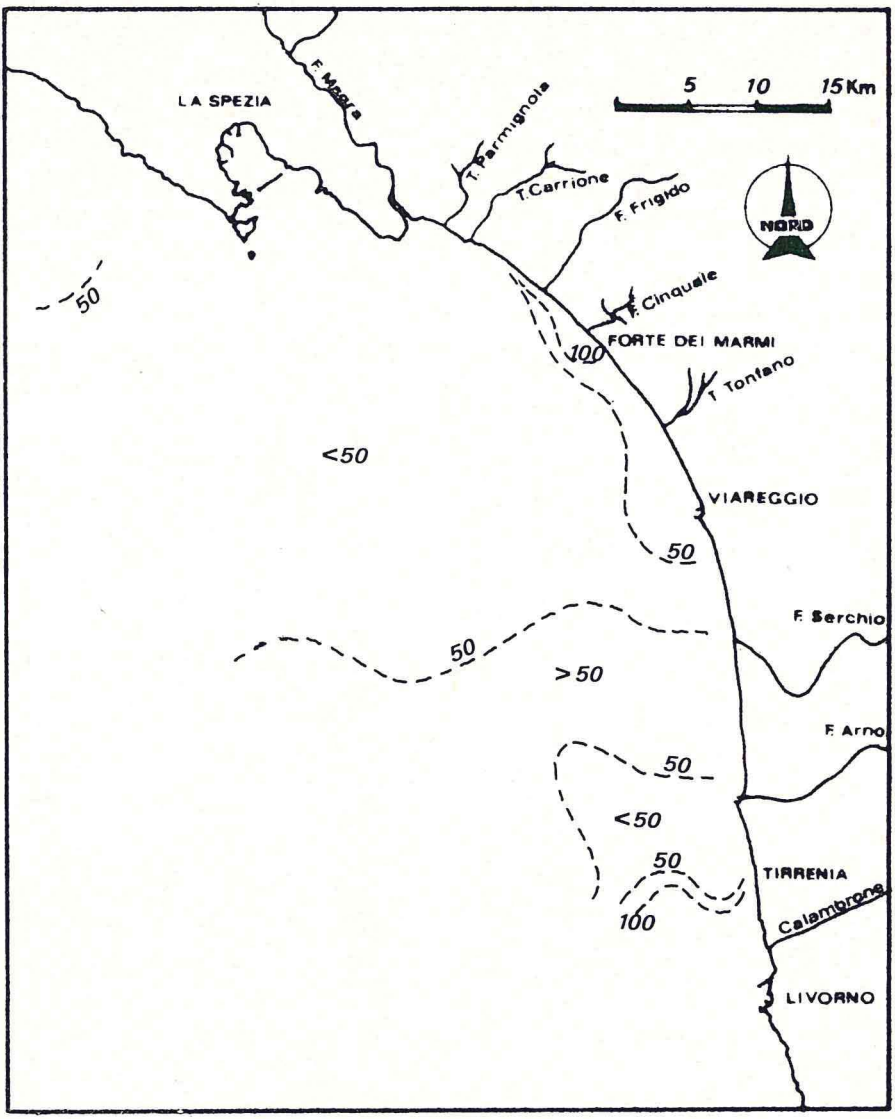

Fig. 4 - Distribution of Ni in sediments.

Cu in greater measure, causing a slight enrichment in marine sediments.

Relationships between Cu content and sediment texture do not seem to exist; in fact, we find similar values both in the clays and in the arenaceous sediments.

Two areas of high concentration are evident (330 p.p.m.: about

three times the average value observed) in correspondence with the two areas of convergence already noted for Ni.

Manganese - The major contributions seem to be due to the three main rivers and to come from the disintegration of the acid rocks present in their hydrographic basin (Fig. 6). A difference in the marine sediments in front of these rivers can also be observed.

At the mouth of the Magra River the percentages in Mn are low and this can be related to the granulometry of the sediment which, we call to mind, is arenaceous: the sediments of the area included between Marina di Carrara and the mouth of the Tonfano River present the minimal values found, and are justified by the coarser granulometry already indicated in Fig. 2. The lutitic marine sediments in front of the Arno and Serchio Rivers are rich in Mn, indicating the relation between granulometry and content in Mn (BITTEL, 1973; COSMA et al., 1979). The map shows an area of high concentration in this metal in the clays located between Viareggio and the mouth of the Arno, whereas the area in front of the mouth, with greater granulometry, presents lower values.

Constant and high values are found parallel to the shore line beyond the bathymetric of 50 m in sediments which are essentially lutitic.

CONCLUSION

The content of the four metals in the sediments was compared in a graph, along with the location for the samples closest to the shoreline (included between 15 and 20 m); a similar trend is illustrated in Fig. 7.

In a primary analysis, it can be noted that the contributions due to the Magra River reach their minimal values at the area of Forte dei Marmi, there is then an increase with maximum values in correspondence with Viareggio; such a trend clearly indicates the limit of the input of the Magra River and the presence of the material due to the Arno and Serchio Rivers; the accumulation registered in the area of the sea in front of Viareggio seems to be due to the effect of the port operations (AIELLO et al., 1975). A part of the material which comes from the Arno is also transported towards the South, forming a point of major concentration in the

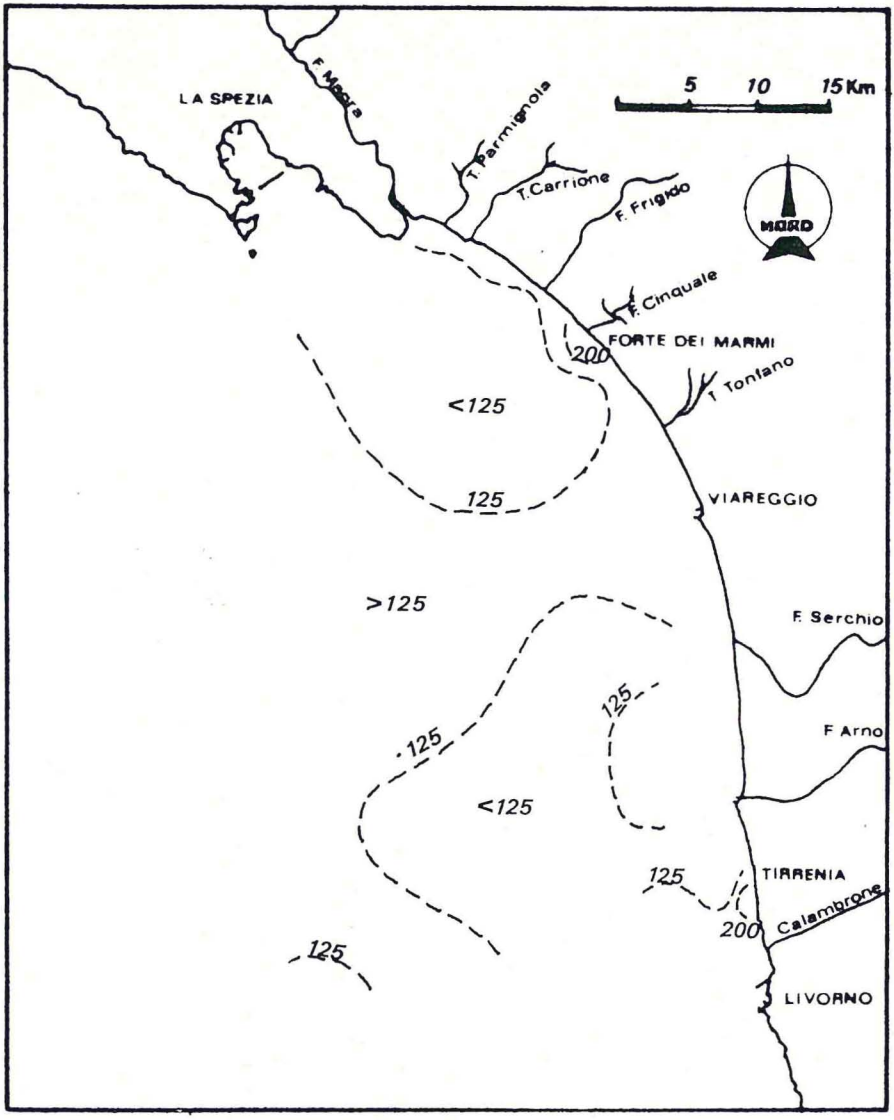

Fig. 5 - Distribution of Cu in sediments.

area of Tirrenia. The high point reached by Cu in the zone in front of the Cinquale River stands out in the graph.

In this situation the metals studied are adequate for use as

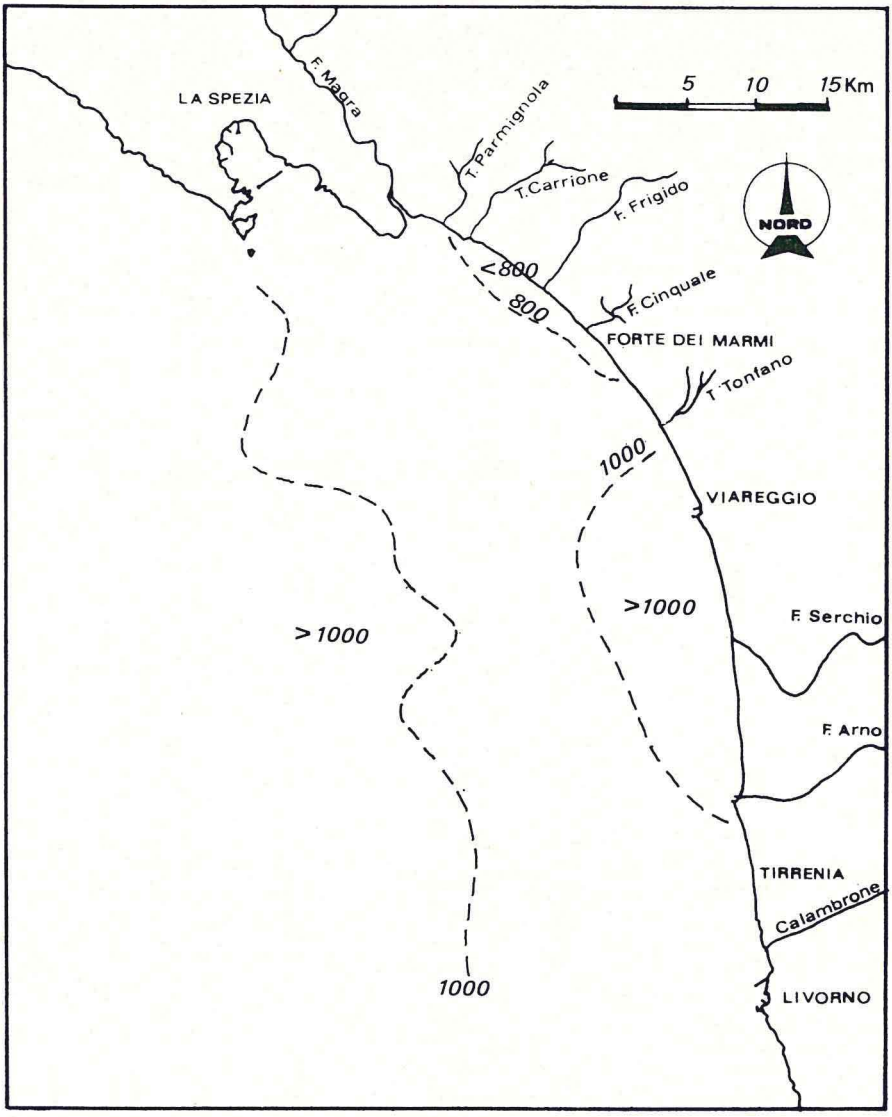

Fig. 6 - Distribution of Mn in sediments.

natural tracers, permitting a comparison with considerations already pointed out in this area, such as the existence of two areas of convergence due to distal drifts and the effect of the port of Viareggio on the transport of the material.

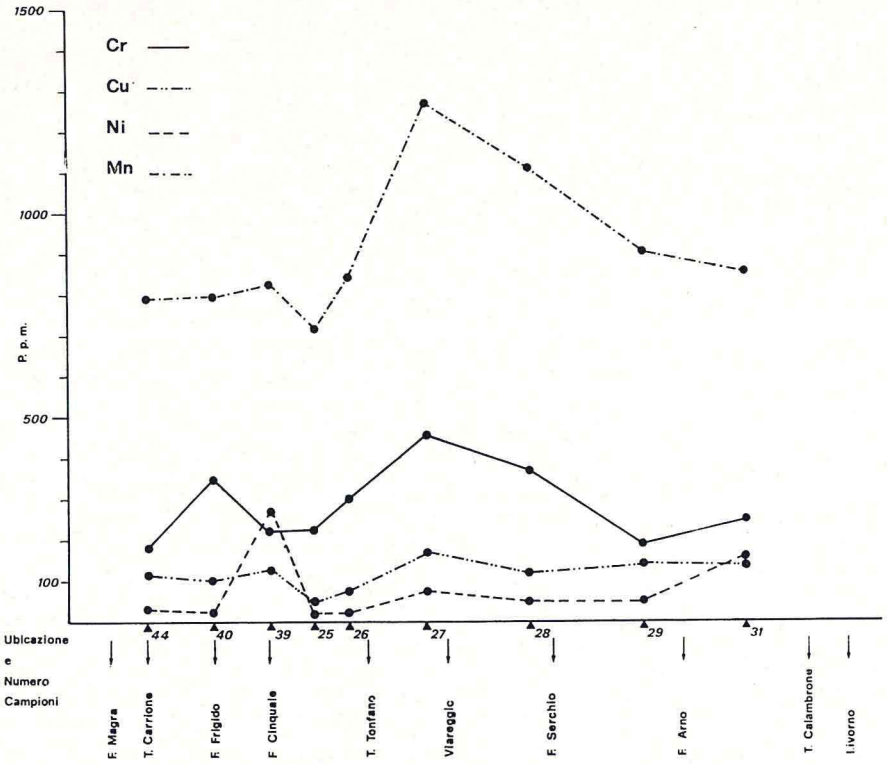

Fig. 7 - Correlation between Cr, Ni, Cu and Mn content and location for the samples included between 15 and 20 m.

The area of sedimentation pertaining to the Magra, Arno and Serchio Rivers has also been clearly pointed out.

From the point of view of the concentrations, an area which is surely influenced by contributions of chromium due to industry has been observed, and a second area with high values is in the Gulf of La Spezia. Although the content in Ni and Cu presents values analogous to those found in literature, it furthermore shows some anomalous values, the origin of which it is not yet possible to establish at this time; lastly the relation between content in Mn and granulometry of the sediments is confirmed with the usual enrichment in the clays.

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