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DISTRIBUTION OF HEAVY METALS IN SUPERFICIAL MARINE  
SEDIMENTS OF SAVONA HARBOR AND VADO LIGURE BAY  
(LIGURIAN SEA) (\*\*)

**Riassunto** — *Distribuzione dei metalli pesanti nei sedimenti marini superficiali del porto di Savona e della baia di Vado Ligure (Mar Ligure)*. Sono state determinate, mediante spettroscopia di assorbimento atomico, le concentrazioni di Cr, Cu, Ni, e Mn nei sedimenti superficiali della Rada di Vado e della zona antistante il porto di Savona. I risultati sono stati messi in relazione con la granulometria e con il contenuto di carbonio organico e di sostanze volatili dei sedimenti. E' stato possibile accertare che le concentrazioni di cromo e rame sono influenzate dalle attività industriali e portuali. La distribuzione di nichel e manganese è invece prevalentemente influenzata dalle caratteristiche geologiche dell'area in studio.

**Abstract** — The concentrations of heavy metals (Cr, Cu, Ni and Mn) in Savona Harbor and Vado Bay sediments have been analysed by atomic absorption spectrophotometry and related to granulometry, organic carbon and volatile substances concentrations in the sediments. The results show that chromium and copper concentrations are influenced by the harbor and industrial activities. Nickel and manganese distributions are largely influenced by the geological characteristics of the study area.

**Key words** — pollution, heavy metals, sea sediments, Savona Harbor and Vado Bay (Ligurian Sea - Italy).

#### INTRODUCTION

A knowledge of the distribution of heavy metals in marine sediments is fundamental to the study of environmental pollution since such elements can be toxic even in traces and can cause harmful effects.

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This study was undertaken to provide information on the abundance and distribution of Cr, Cu, Ni, Mn and their correlations with total organic carbon (TOC) and total volatile substances (TVS) in sediments from Vado Bay and Savona Harbor, which are close to an industrial area.

This study evaluates 27 samples collected during the « Ban-nock » cruise (1974) and 29 samples collected during the « Marsili »

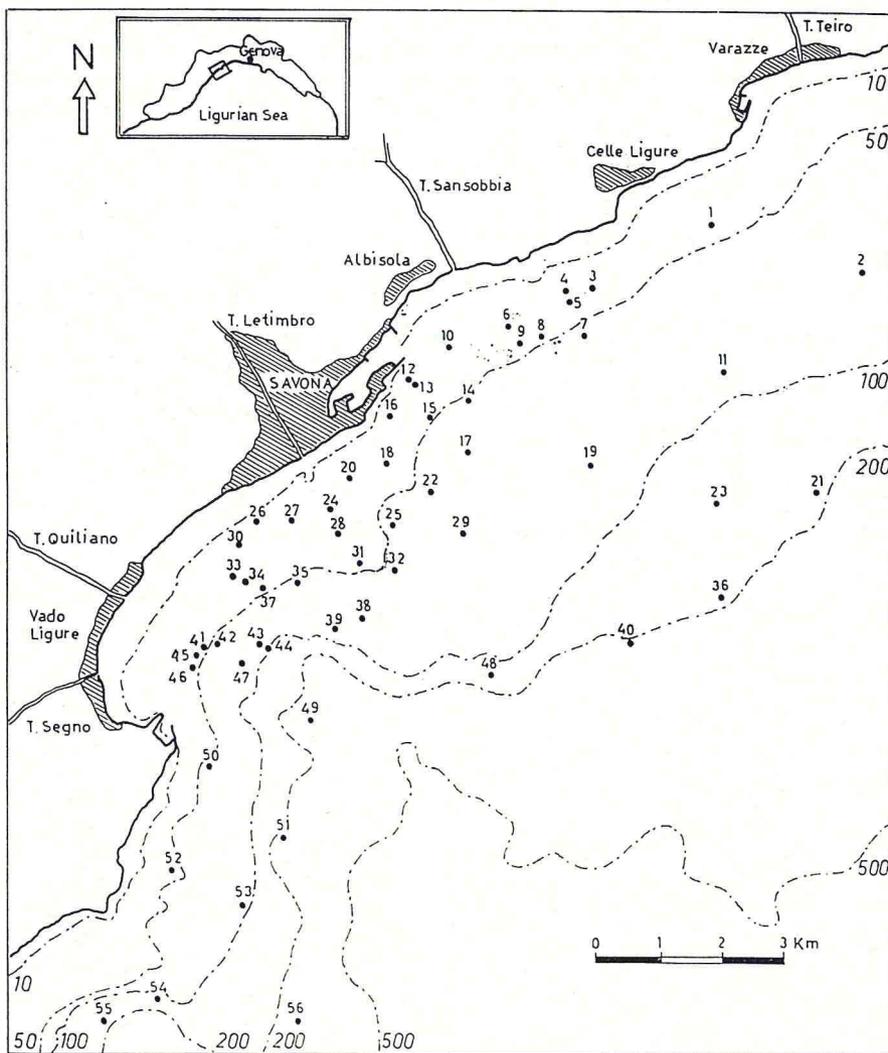


Fig. 1 - Location of the samples.

cruise (1975), in order to assess the extent of the heavy metal pollution in the harbor environment. The samples were analysed to determine the concentration of Cr, Cu, Ni, Mn, organic carbon, total volatile substances and particle size.

The total metal and the easily extractable metal extraction techniques are most informative for environmental purpose. The

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

A) Total attack. B) Nitric attack.

Station n°	Position		Depth (m)	Cr		Cu		Ni		Mn		% 74 $\mu\text{m}$
	Latitude N	Longitude E		A	B	A	B	A	B	A	B	
1	44°20.1'	08°33.7'	53	750	420	105	45	460	140	930	620	97.0
2	44°19.7'	08°35.5'	75	430	130	95	35	260	85	1300	1230	78.8
3	44°19.6'	08°32.5'	36	590	300	30	25	230	75	720	170	59.4
4	44°19.5'	08°32.0'	--	--	120	--	10	--	45	--	220	23.0
5	44°19.4'	08°32.0'	20	280	110	25	20	160	40	590	80	31.0
6	44°19.1'	08°31.3'	20	620	240	35	30	220	75	800	150	74.7
7	44°19.1'	08°32.2'	62	410	610	60	40	360	105	930	630	91.9
8	44°19.1'	08°31.7'	97	730	390	70	40	370	125	960	780	90.8
9	44°19.0'	08°31.4'	46	850	360	65	30	370	125	920	120	94.0
10	44°19.0'	08°30.6'	26	310	180	50	25	200	60	940	500	85.0
11	44°18.8'	08°33.9'	85	650	200	105	40	310	115	1290	1200	98.1
12	44°18.3'	08°30.1'	37	610	180	90	45	280	90	1030	790	75.3
13	44°18.7'	08°30.2'	38	830	220	60	40	220	75	960	630	86.7
14	44°18.5'	08°30.8'	52	690	370	105	50	320	110	950	610	95.1
15	44°18.4'	08°30.3'	47	490	220	100	85	160	60	1150	600	62.9
16	44°18.4'	08°29.9'	--	810	130	90	50	310	80	1130	710	62.1
17	44°18.1'	08°30.8'	66	620	200	70	40	320	125	970	650	97.6
18	44°18.0'	08°29.8'	41	570	220	50	35	180	60	980	640	76.2
19	44°18.0'	08°32.3'	84	740	230	95	40	310	110	1350	910	98.6
20	44°17.9'	08°29.4'	--	510	100	40	30	130	35	1600	1290	38.2
21	44°17.8'	08°35.0'	215	360	170	65	35	170	75	2340	2250	99.7
22	44°17.7'	08°30.4'	59	400	220	40	25	220	85	900	600	90.2
23	44°17.6'	08°38.8'	133	150	140	55	35	230	85	1750	1670	99.3
24	44°17.5'	08°29.2'	27	240	60	25	20	80	30	2390	2110	22.0
25	44°17.5'	08°29.9'	53	410	200	40	25	210	70	920	860	72.6
26	44°17.5'	08°28.3'	--	160	60	40	25	60	20	1590	1260	69.5
27	44°17.5'	08°28.8'	23	330	120	60	40	110	50	1840	1320	81.2
28	44°17.4'	08°29.3'	40	410	190	90	40	250	90	1120	770	69.2
29	44°17.4'	08°30.8'	72	600	100	65	40	350	110	1130	1100	91.1
30	44°17.3'	08°28.1'	--	300	130	70	50	120	45	1070	780	92.5
31	44°17.1'	08°29.6'	46	430	110	30	20	180	50	920	520	70.9
32	44°17.1'	08°30.0'	45	430	170	65	30	240	80	950	660	70.1
33	44°17.0'	08°28.1'	33	440	90	70	50	120	100	920	740	93.0
34	44°17.7'	08°28.3'	40	300	90	100	60	210	75	1140	990	92.4
35	44°17.0'	08°28.5'	50	290	130	75	45	210	70	1200	720	95.1
36	44°16.9'	08°33.9'	187	240	200	75	35	300	75	1100	1100	59.7
37	44°16.9'	08°28.4'	45	530	220	110	75	170	95	1090	820	95.0
38	44°16.7'	08°29.6'	51	220	70	65	25	120	35	1100	1100	11.0
39	44°16.6'	08°29.3'	83	510	150	50	35	290	125	990	700	92.2
40	44°16.5'	08°32.8'	219	300	150	75	35	240	80	1100	890	95.6
41	44°15.4'	08°27.0'	47	350	240	80	40	150	150	820	620	69.0
42	44°16.4'	08°27.9'	51	500	240	65	45	180	75	1090	730	94.7
43	44°16.4'	08°28.4'	129	850	130	75	40	250	105	1270	1000	97.8
44	44°16.4'	08°28.5'	80	340	120	115	40	350	115	1230	890	97.6
45	44°16.3'	08°27.6'	46	440	130	45	35	100	35	640	280	73.2
46	44°16.3'	08°27.6'	71	410	210	90	50	260	100	1100	890	95.6
47	44°16.2'	08°28.2'	80	600	240	70	45	230	110	1050	650	96.5
48	44°16.2'	08°31.2'	100	290	130	75	35	230	90	1160	850	87.2
49	44°15.8'	08°29.0'	313	120	70	80	40	250	110	1070	980	99.5
50	44°15.4'	08°27.8'	67	200	90	60	35	110	50	570	380	92.7
51	44°14.8'	08°28.7'	266	260	180	75	40	250	100	840	770	99.3
52	44°14.5'	08°27.4'	35	330	60	75	15	120	35	900	740	48.6
53	44°14.2'	08°28.2'	90	300	120	40	25	230	75	1130	610	91.4
54	44°13.4'	08°27.2'	75	200	150	45	20	200	65	1260	850	12.1
55	44°13.2'	08°26.6'	30	150	40	55	15	90	25	580	300	93.0
56	44°13.2'	08°28.9'	222	150	110	45	30	230	95	1230	850	99.1

The data of 27 stations are used by permission from MARINE CHEMISTRY

former is well defined and includes both metals from mineral lattices and the non-residual metals. The latter extraction technique gives results only for the weakly held metals.

The dissolution of the sediments was effected with two methods; the first provided the total extraction using a mixture of HF and HClO<sub>4</sub>, the second employed a warm nitric acid solution. Organic carbon was measured by difference between the total carbon and the total carbonate content. The total volatile substances are determined by heating the samples to 550°C.

The study areas are located in the continental shelf between Island of Bergeggi and Varazze; the investigation includes sediments of Vado Bay and Savona Harbor. The geomorphology of the study area appears to be divided in two parts: in the first, the west of Letimbro creek, shows a submarine canyon; in the second the continental shelf extends, with short and regular slopes, to 4000 m from the coast. The rebord follows on average the bathymetric of 100 m (FANUCCI et al. 1974). In the Vado Bay an area of sediment accumulation can be identified and is due to the great input of the creeks and in part to the « bay effect » already pointed out in other areas of Ligurian Sea (FIERRO et al. 1973). The study area is influenced by the general current of the Mediterranean, which flows along the Ligurian coast from E to W thereby in addition to a basic distribution pattern resulting from wave movement (long-shore currents), the transport of the materials are also influenced by sea currents. This trend is confirmed by magnetic susceptibility measurements of the sediments (DAGNINO, 1976).

## 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 determinations were done with a Shandon Southern A 3400 atomic absorption spectrophotometer with air-acetylene flame, equipped with a Kipp and Zonen model 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*

Certified analytical grade reagents were used for all determination: HClO<sub>4</sub>, 60%; HF, 40%; HCl, 37%; HNO<sub>3</sub>, 65%; NaOH 0.1 N. Standards were prepared by serial dilution of 1,000 mg. l<sup>-1</sup> metal stock solutions. All standard solutions were prepared containing the same reagents that were added to the samples.

### *Procedure*

All unsieved samples were dried in an oven at 105°C and then lightly grounded.

### *Total metal content*

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 dried; the procedure was repeated twice. The residue was dissolved in dilute hydrochloric acid (BASSO and MAZZUCOTELLI, 1975).

### *Acid-extractable metal content*

Sediment (1 g) was treated with 25 ml of 8N nitric acid solution for about 30 minutes at 50-60°C. The filtrate was diluted to 100 ml with 2N nitric acid (CARMODY et al., 1973).

### *Total Organic Carbon (TOC)*

Organic carbon was calculated by taking the difference between the percentage of total carbon and that of inorganic carbon (SHIMP et al., 1970).

The determination of total carbon was made by burning a weighed sample (0.2 g) in a closed system tube furnace at 1300°C. Carbon dioxide was absorbed in a tube containing soda-asbestos. Prior to carbon dioxide absorption, sulfur dioxide and moisture were removed from the combustion products. Inorganic carbon was determined by volumetric titration with HCl 0.5N and NaOH 0.1N standard solutions.

### *Total Volatile Substances (TVS)*

The total volatile substances was determined by heating the

sample in a muffle furnace at 550°C for 30 minutes (CHEN and LU, 1974).

## RESULTS AND DISCUSSION

Table 1 shows the results of the chemical analyses, textural characteristics and locations of the samples. Table 2 shows the results of TOC% and TVS%. The values of the nitric attack versus total attack are plotted in Fig. 2. For manganese and nickel a linear relationship between the data of the two attacks can be observed (linear correlation coefficient  $r = 0.91$  and  $0.78$ ). For copper and chromium,  $r$  is respectively  $0.65$  and  $0.56$ . This is probably due to the different ways in which these elements are bonded in the sediment.

Sample n°	C org.	TVS	Sample n°	C org.	TVS
1	1.2	9.2	29	0.5	13.6
2	0.5	10.9	30	1.0	6.7
3	0.1	8.7	31	0.4	11.6
4	0.2	2.4	32	0.5	6.2
5	0.1	4.0	33	0.6	8.1
6	0.1	10.0	34	1.5	9.2
7	0.1	10.3	35	1.3	7.4
8	0.3	10.3	36	0.3	20.8
9	1.3	11.0	37	1.0	8.2
10	0.8	9.9	38	0.0	5.1
11	0.4	17.5	39	1.6	9.3
12	2.4	8.3	40	0.5	14.8
13	1.4	11.1	41	0.9	7.4
14	0.5	9.9	42	0.9	8.8
15	0.7	10.9	43	0.7	7.8
16	0.3	6.3	44	1.4	8.3
17	0.8	10.3	45	0.5	8.5
18	0.4	6.8	46	1.0	9.8
19	0.5	21.8	47	1.0	8.7
20	2.1	6.0	48	0.6	13.4
21	0.4	12.2	49	0.8	11.1
22	0.6	7.9	50	0.5	5.7
23	0.4	23.9	51	0.8	14.3
24	4.7	13.9	52	0.2	6.7
25	2.1	13.6	53	0.2	6.4
26	0.8	3.8	54	0.4	6.0
27	3.2	12.1	55	0.6	6.6
28	1.1	8.6	56	0.5	6.8

TABLE 2 - Total Organic Carbon and Total Volatile Substances in the marine sediments (%).

The distribution chart of the metals was produced on a mini-computer PD11/40 equipped with a CRT Tektronic display and a Calcomp plotter. The mathematical procedure employed consists of three processing steps. First, a triangular grid with vertices at

the given sample points is built up. For all possible triangulations, the procedure generates the most equiangular one. Then, a contour map process is performed directly on the triangular grid (DE FLO-RIANI et al., 1979). Since the contours are polygonal lines obtained by means of a linear interpolation, a smoothing step is performed to produce fair and natural curves passing through the vertices of those lines (DETTORI, 1980). For every metal we have chosen the most significant isoconcentration lines in order to show the distribution.

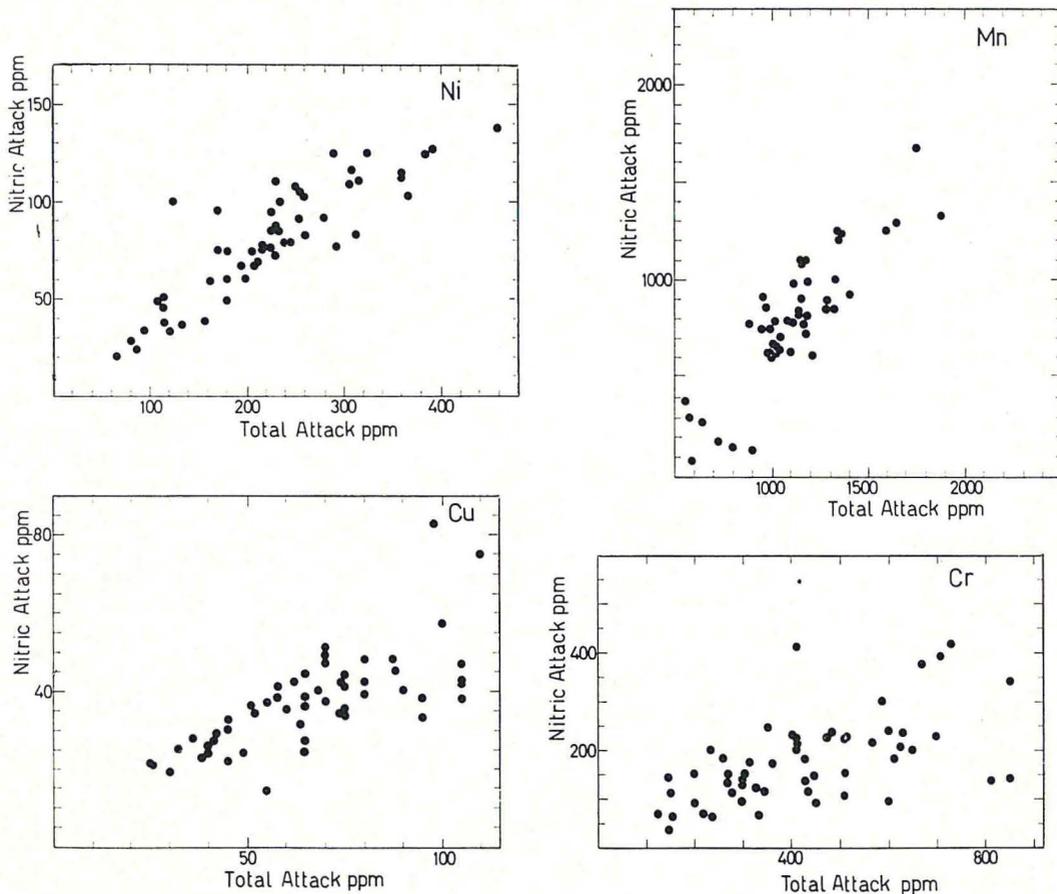


Fig. 2 - Nitric attack results versus total attack results for Cr, Cu, Ni, and Mn concentration in marine sediments.

## CHROMIUM

The results of the chemical analyses for chromium are reported in Figs. 3 and 4. Here we can point out a similar trend for the iso-concentration curves obtained with the total and nitric attack. Two areas of higher concentration in front of the Savona Harbor (800 ppm) and in the Bay of Vado Ligure (600 ppm) are noted. Since

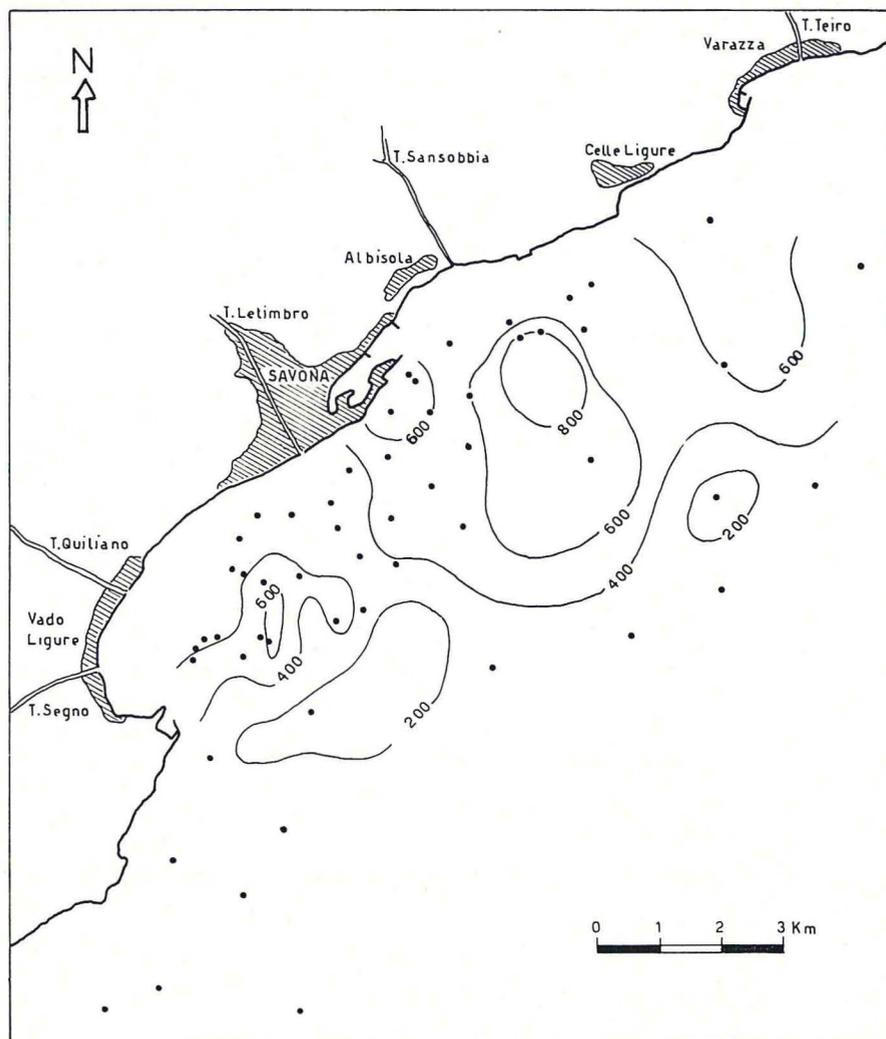


Fig. 3 - Distribution of Cr in sediments. Total attack.

the background of the chromium concentrations varies from 300 to 400 ppm (and this seems to be related to the geological characteristics of the study area) and since the Sansobbia, Letimbro, Quiliano and Segno Creeks have a low concentration of chromium (COSMA et al., 1979), the higher values are considered to be related to the industrial input. No correlation with organic carbon and total volatile substances can be established.

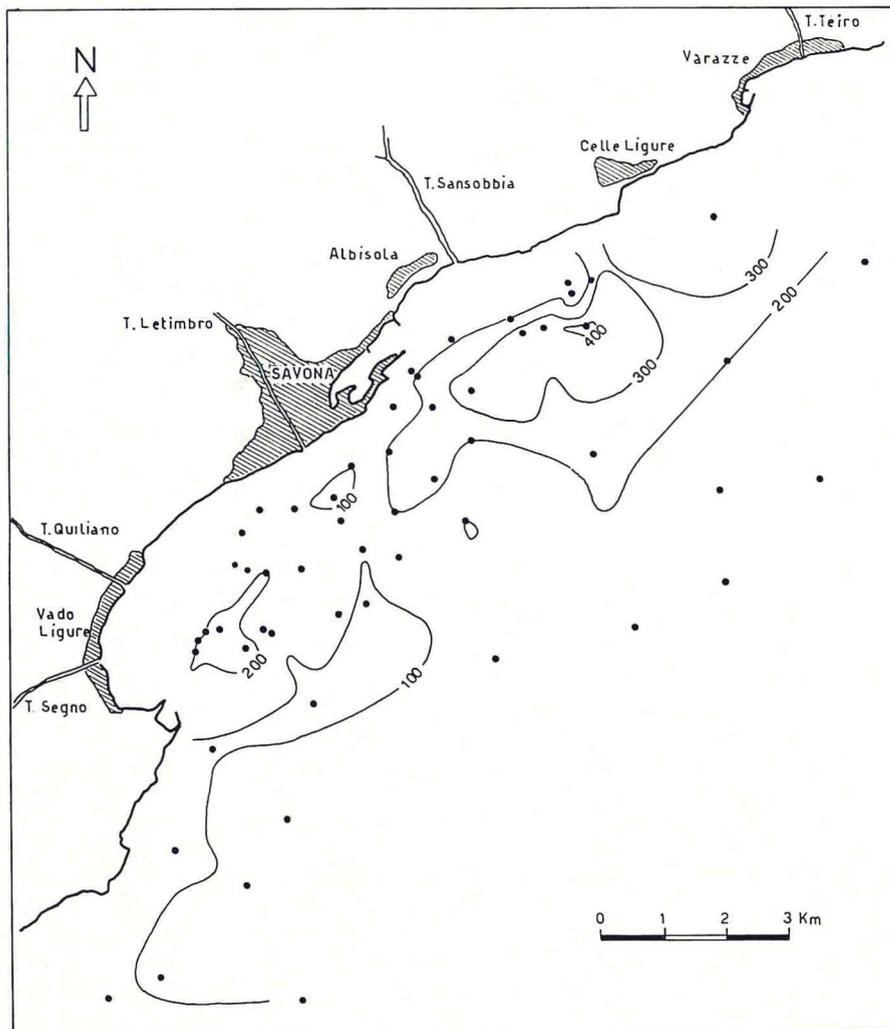


Fig. 4 - Distribution of Cr in sediments. Nitric attack.

## COPPER

For copper a situation similar to chromium can be noted: the concentration trends being similar in both distribution maps (Figs. 5 and 6). Increased concentrations (100 ppm for total attack), occur again in the Savona Harbor and in the Vado Bay. This input is probably due to the industrial activities. In front of the San-

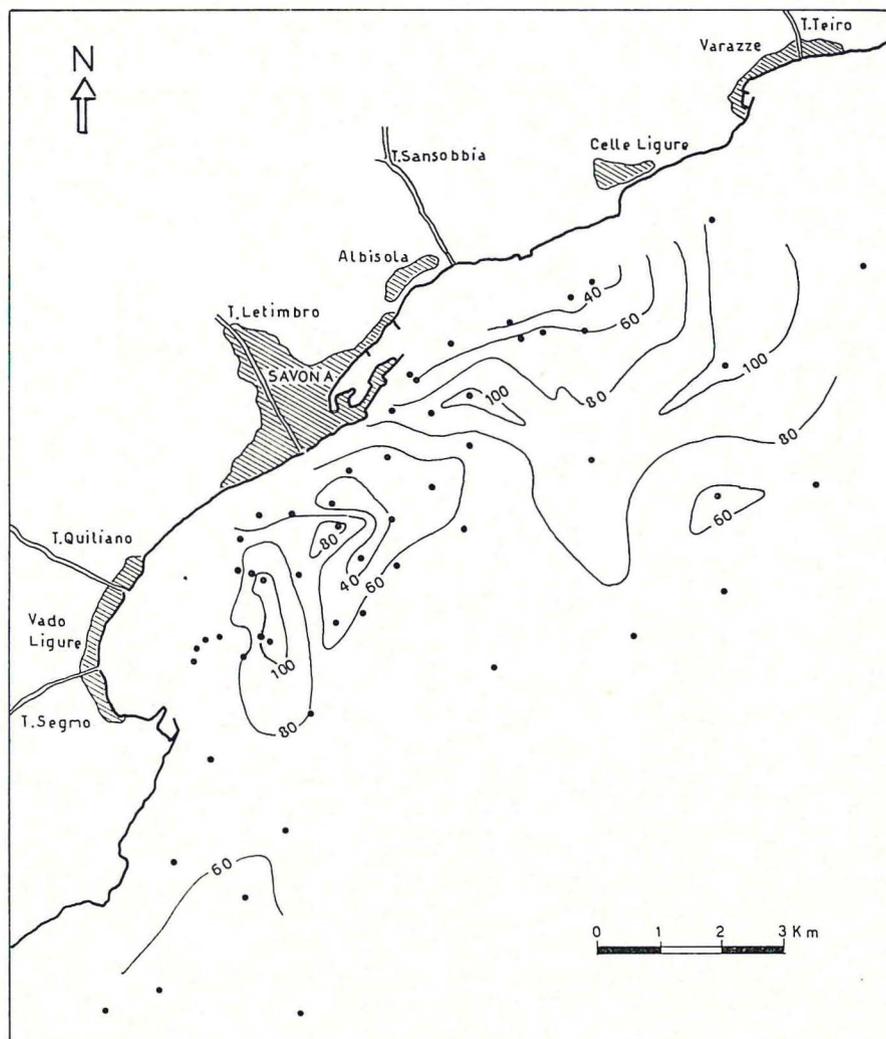


Fig. 5 - Distribution of Cu in sediments. Total attack.

sobbia creek an increase of the concentrations is clearly evident. This is considered to be related to the particle size of the samples.

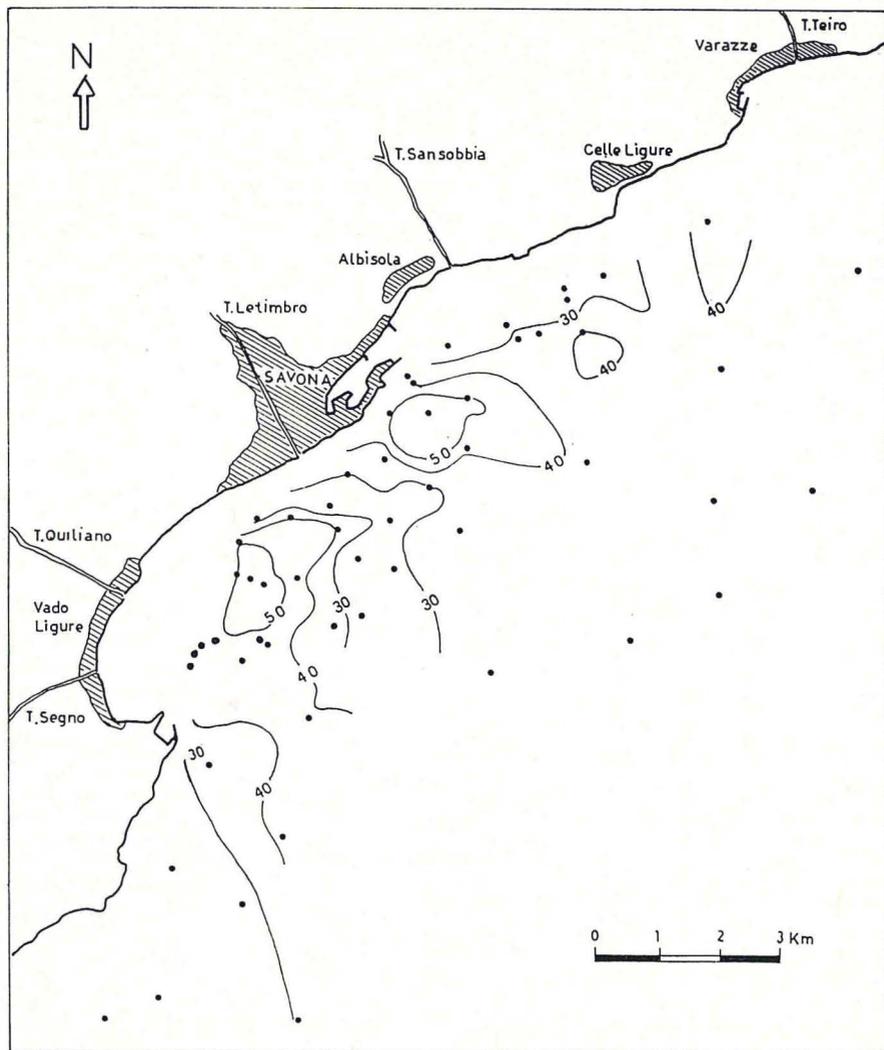


Fig. 6 - Distribution of Cu in sediments. Nitric attack.

## NICKEL

Nickel also (Figs. 7 and 8), presents an area of higher concentration in front of the Vado Ligure Bay. In front of Savona Harbor

the concentration lines confirm the influence of the input from the creeks flowing at NE of the study area. This is in accordance with the current which flows along the Ligurian coast from E to W bringing about a transport trend in that direction. These creeks flow in serpentinites which generate an enrichment of nickel especially in sediments at the mouth and along the coast. No correlation

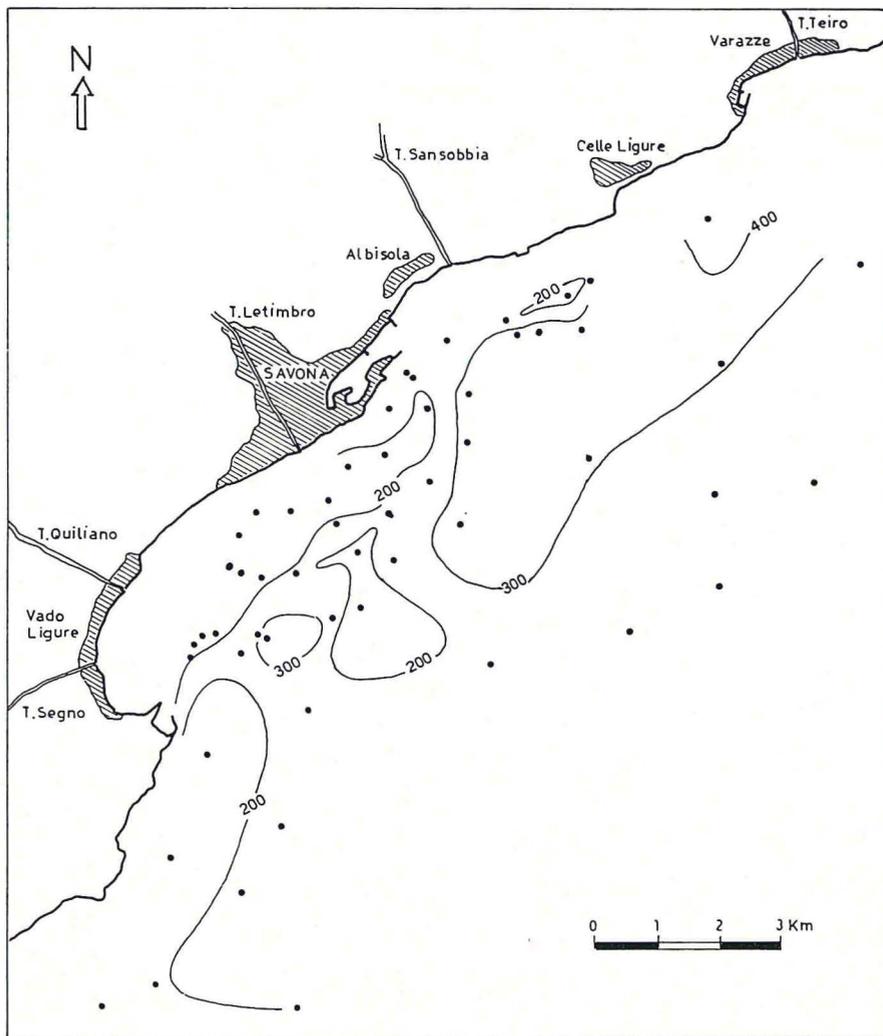


Fig. 7 - Distribution of Ni in sediments. Total attack.

with the organic carbon and the total volatile substances can be noted.

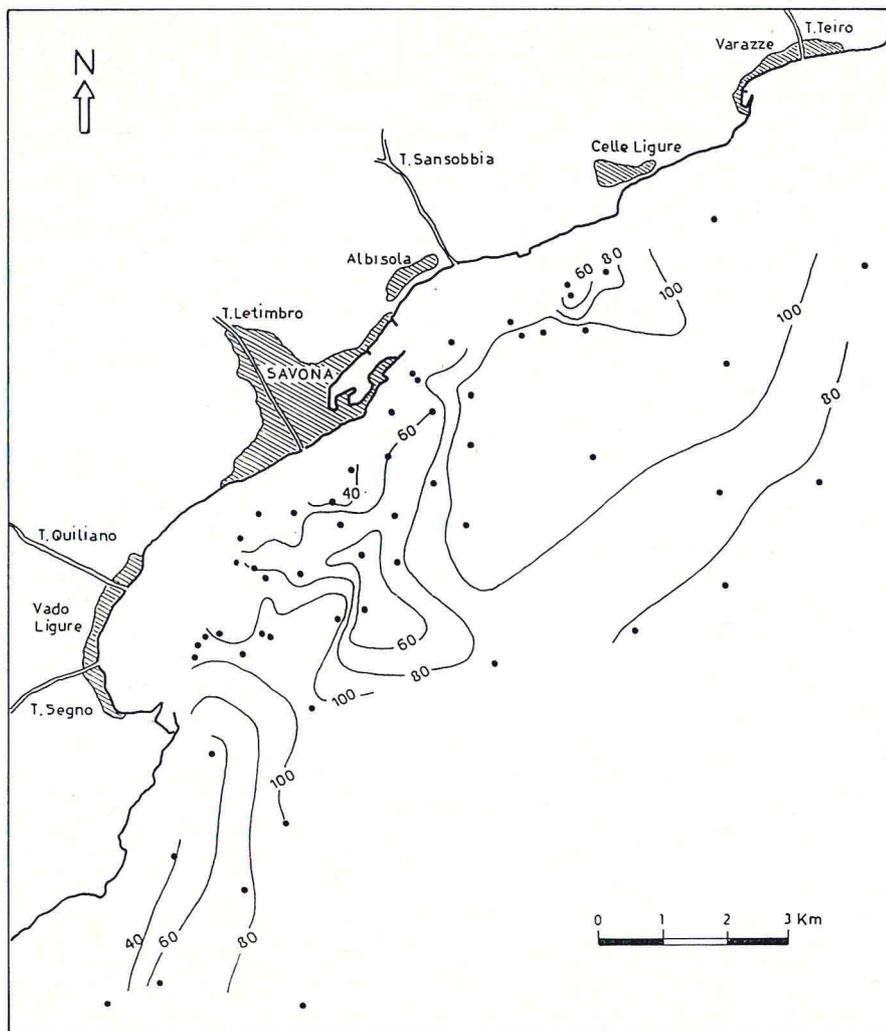


Fig. 8 - Distribution of Ni in sediments. Nitric attack.

### MANGANESE

A study of distribution maps of manganese (Figs. 9 and 10), reveals an anomalous trend for the isoconcentration curves of this metal with respect to the other metals. The highest concentrations

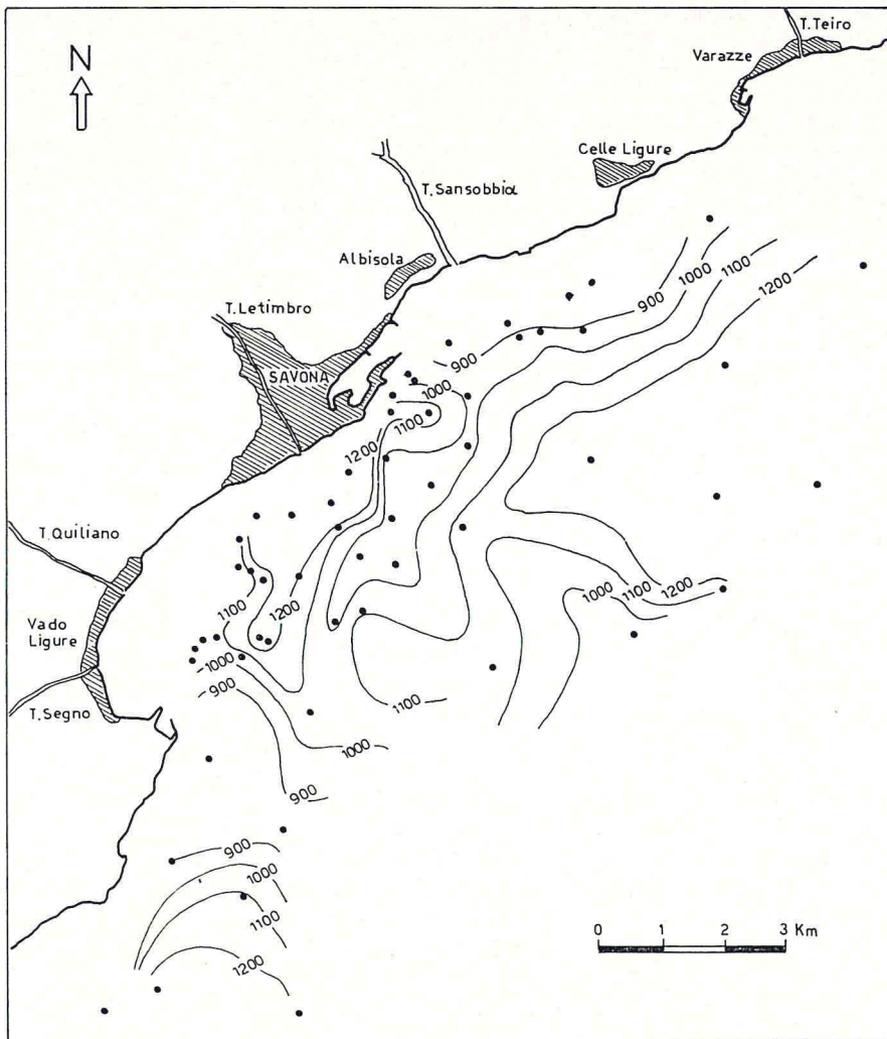


Fig. 9 - Distribution of Mn in sediments. Total attack.

of manganese are mainly found in the open-sea; this is considered to be related to the sediment granulometry. There is, in fact, a positive correlation between manganese content and the increase in the fine fraction. An anomaly in the area in front of the mouth of Letimbro creek is noted; (the creek is near the outlet of the Savona sewer system). Here the concentration of manganese is

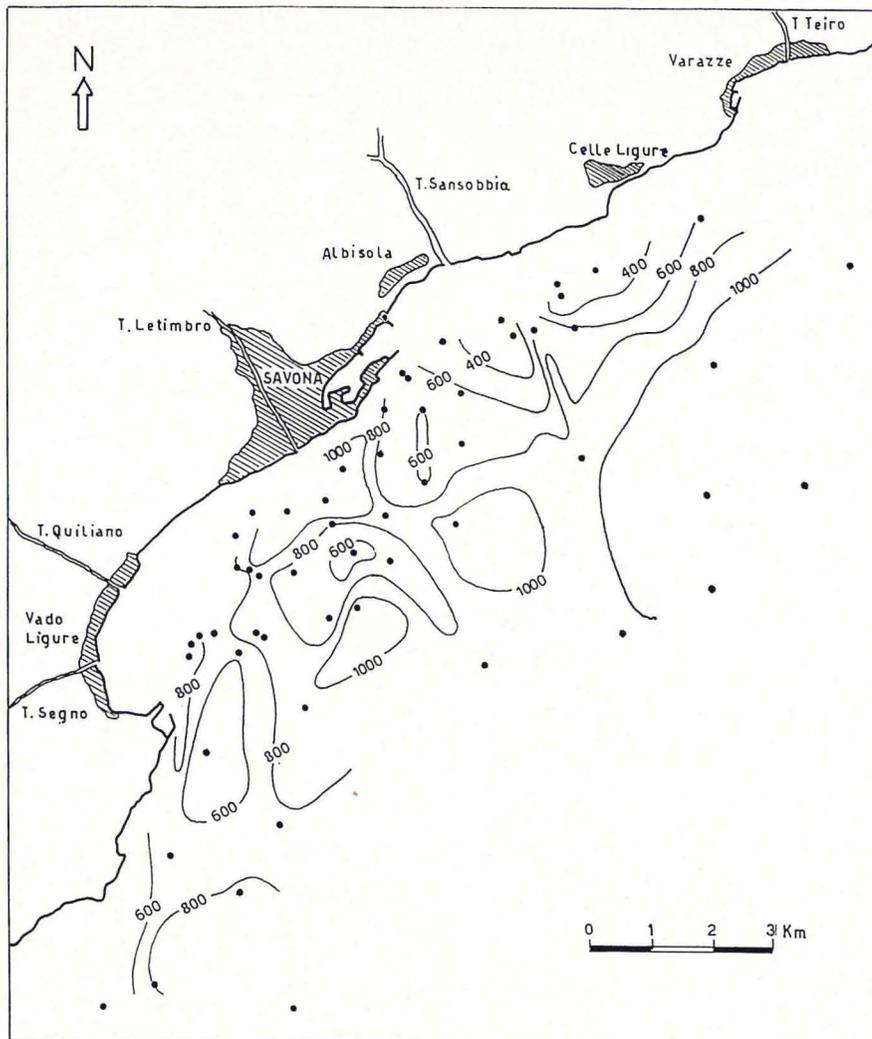


Fig. 10 - Distribution of Mn in sediments. Nitric attack.

higher near the coast; this can be related to higher carbon contents (Fig. 12).

#### GRANULOMETRY

The results of the textural analyses were utilized to draw up a map of the distribution of the sediments (Fig. 11). The influence

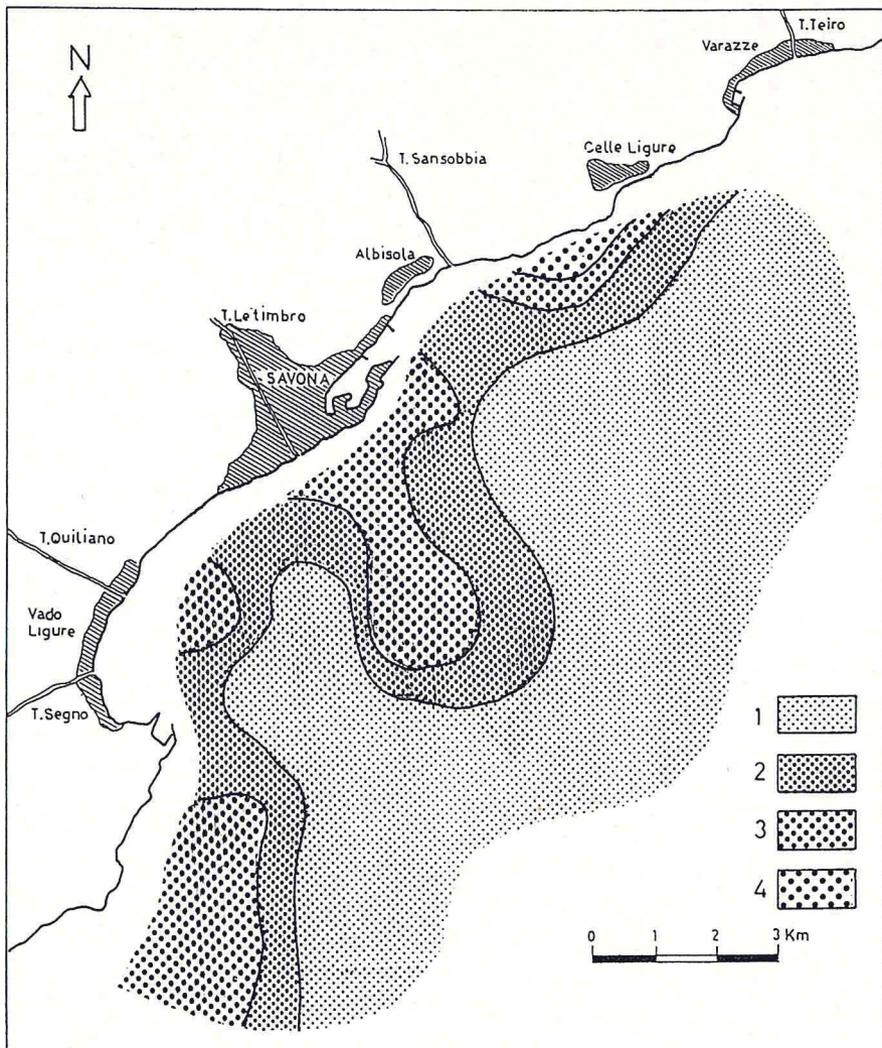


Fig. 11 - Distribution map of the granulometry: 1. sand < 5%; 2. sand 5-30%; 3. sand 30-70%; 4. sand 70-95%.

of the Sansobbia, Letimbro, Quiliano and Segno creeks is evident in the study area; the sedimentation initially sandy, becomes gradually more lutitic with the increase of the bathymetry.

#### TOTAL ORGANIC CARBON

The organic carbon distribution (Fig. 12) is in accordance with

the localization of the urban discharges. There is a higher concentration area in front of the outlet of the Savona sewer system. On the average the trend of the isoconcentration curves is decreasing

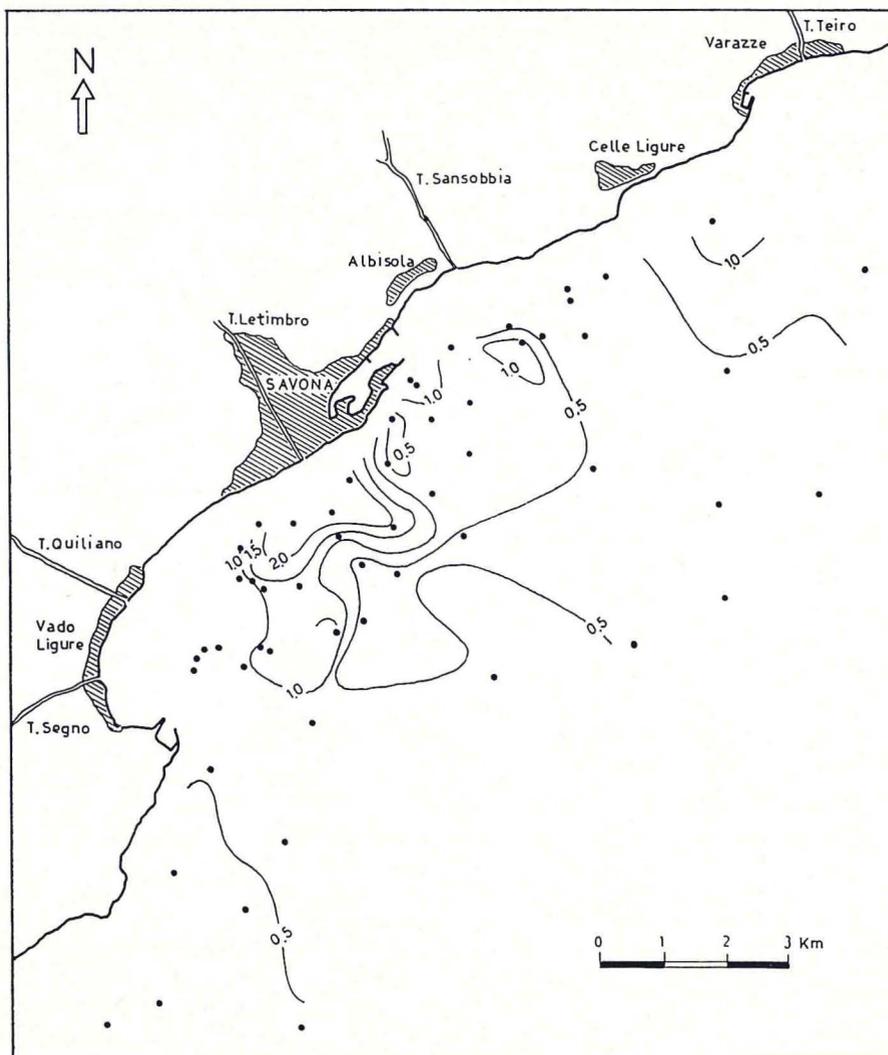


Fig. 12 - Distribution of TOC in sediments.

in the open sea. An area with an organic carbon content higher than average is observed in the vicinity of Celle Ligure.

## TOTAL VOLATILE SUBSTANCES

The distribution map of TVS (Fig. 13) reveals high values in two areas in front of the Letimbro creek and in an area of open sea at depth of 100 m. A high concentration of TVS in the samples at the mouth of the Letimbro is related to high organic matter content.

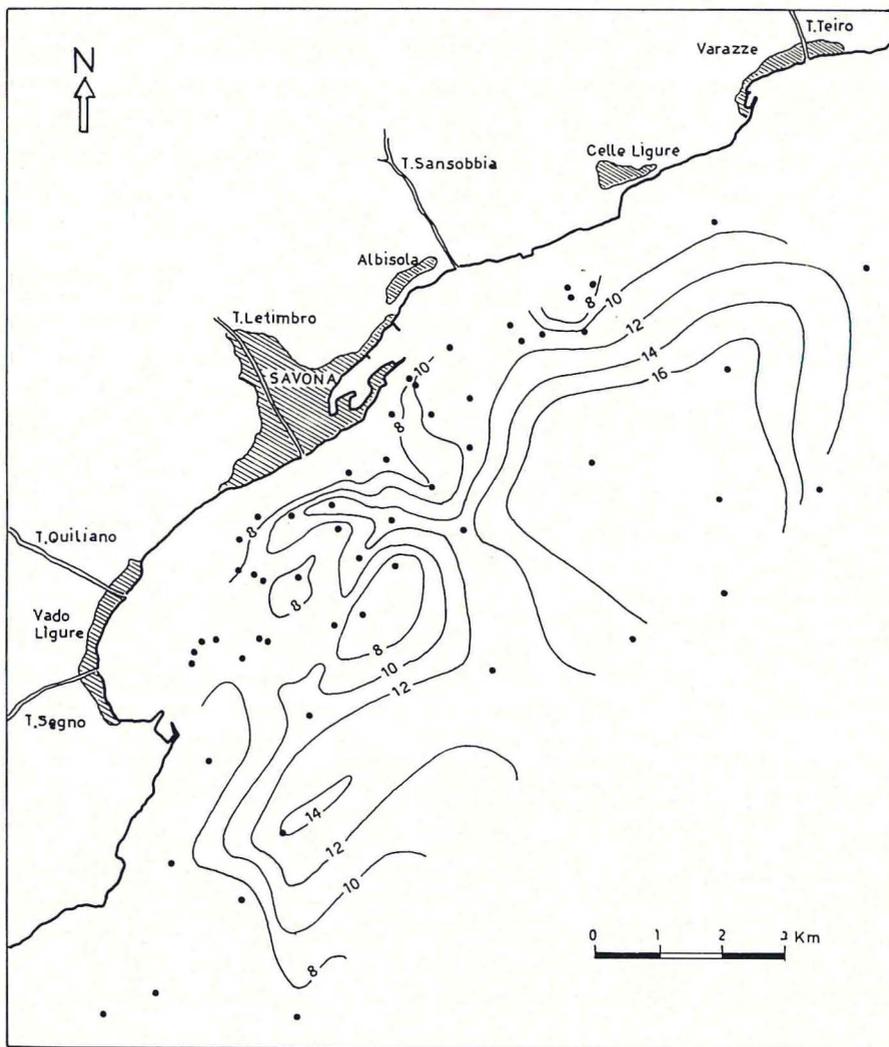


Fig. 13 - Distribution of TVS in sediments.

For the deeper samples the high contents of TVS is considered to be related to the grain size (i.e. increase of the fine fraction).

## CONCLUSIONS

The results of our sediment analyses, when combined with data from earlier studies, indicate that chromium and copper have similar distributions (over several orders of magnitude in concentration), in the sediments of the study area.

The chromium and copper distributions present high values in vicinity of Savona Harbor and in the Vado Bay due to the industrial waste outfall and to the accumulation brought about by the « bay effect ».

For nickel we observe an input from N to W due to the creeks which cross basic and ultrabasic rock formations containing high quantities of nickel. For manganese the distribution is related both to the organic matter in the outlet area of the sewer system and to the granulometry and total volatile substances in the open sea.

On the average for all metals the contamination levels are comparable to or slightly less than other heavily polluted areas where large quantities of domestic and industrial wastes or waste water is discharged (BOWER et al., 1978; CARMODY et al., 1973; CHIN CHEN, 1976; EISLER et al., 1977; GREIG et al., 1977; GRIGGS et al., 1978; HUNG et al., 1975).

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