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DISTRIBUTION AND SPECIATION OF METALS IN SURFACE SEDIMENTS OF TARANTO GULF (IONIAN SEA, SOUTHERN ITALY)

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Summary - Concentrations of metals (Al, Fe, Ti, Ni, Mn, Cr, Zn, Cu, Pb) were determined in surface sediments from Taranto gulf (Ionian Sea, Southern Italy) in order to assess the distribution and the bioavailability of metals. Total metal content and speciation of Fe, Ni, Mn, Zn, Cu and Pb were determined. Sediment cores were also sampled in some stations of particular interest. The analytical results show that metals distribution does not show significant variations in relation to depth. Metal distribution in the Taranto gulf is mainly influenced by industrial wastes from Taranto town, by rivers of the Basilicata region and by prevailing anticlockwise marine currents. These factors cause an accumulation of metals in the sediments near to the coasts of Calabria. The statistical analysis, effected by HCA and PCA methods, can be considered a good starting point in order to classify sediment samples and to locate accumulation areas. Metal speciation shows that Fe, Ni and Zn are present in sediments mainly as sulphides, Mn is present principally in an ion-exchange form or bound to carbonate, while Cu and Pb are mainly present in the fraction bounds to humic acids.

INTRODUCTION

Heavy metals are potentially toxic to human life and the environment. Their effects depend on chemical associations hence determining the chemical form of a metal is important to evaluate its mobility and bioavailability. Marine sediments are a very important accumulation site of heavy metals in the coastal areas; therefore the analysis of metals are important to assess pollution in the marine environment.[1] Sediments, in fact, not only reflect the quality of waters, but also provide

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information on the diffusion and fate of pollutants. Numerous studies have demonstrated that the marine sediments from industrialized coastal areas are heavily contaminated by metals.[2]

Metals are introduced into marine environment by waste water: they are transported by prevailing local current and are removed from water by various biological and physico-chemical processes including their scavenge by sinking particulate or organic matter.

In this work, concentrations of nine metals (Al, Fe, Ti, Ni, Mn, Cr, Zn, Cu, Pb) were determined in nineteen sampling stations of Taranto gulf (FIG. 1) from S. Maria di Leuca (Apulia) to Cirò Marina (Calabria), in order to assess levels and metal distribution in this important area in the Mediterranean Sea. The objectives of the study included: developing a baseline for levels of metal contamination, relating sediment metals levels to sources and examining spatial gradients. The gulf of Taranto represents, in fact, an example of marine ecosystem whose biological balances have been modified related to the anthropic development and, in particular, to the big industry settlement over to urban wastes. Around the examined area, there are located important industrial, urban and agricultural installations, but there are few publications about the contamination phenomena of marine sediments.

Sampling stations were selected by considering the contamination sources: the iron and steel industry and the oil refinery of Taranto, the rivers of Basilicata region flowing into the Ionian Sea (Bradano, Basento, Cavone, Agri and Sinni) are the main sources of contamination. The contribution of particulate matter from the rivers is a very important factor in order to evaluate the sedimentation phenomena of metals.[3] The study of heavy metals contamination is also important because of the toxic effect that these pollutants can cause, especially in organisms at the top of the marine food-chain; it is known that the mobility of metals is strongly influenced by chemical speciation.[4] Therefore, metal speciation in marine sediments is an important research area in environmental studies.

Metal speciation and chemical reactivity of metals play an important role in controlling their availability and toxicity to biota. While the total trace metal content in sediments provides a convenient measure of pollution, numerous reports have highlighted that such measures are deficient in predicting toxicity of these pollutants. However, while various techniques are available for determination of chemical speciation in aqueous systems, methods for speciation in marine sediments are less well developed and it is indispensable to use extraction schemes. A large number of sequential extraction procedures have been developed many of which are variants of Tessier's method.[5] In this work the speciation analysis was carried out by using the extraction method described by Campanella *et al.*[6] to distinguish the metal fraction bound to the organic matter from that bound to sulphides.

The results were then elaborated by using Geographical Information System (GIS) ArcView to show the accumulation areas of heavy metals and multivariate statistical analysis has been used to evaluate the possibility of differentiating the sampling stations and to show the contamination areas.

MATERIALS AND METHODS

Reagents and standards

All reagents were analytical grade and must contain very low concentrations of trace metals. Nitric acid (70% v/v), hydrochloric acid (37% v/v), hydrofluoric acid (48% v/v) and boric acid were Ultrex (J. T. Baker, Phillipsburg, USA). Ultrapure water with conductivity <0.1 μS was obtained from a MILLI-Q® system (Millipore, Bedford, MA, USA). Working standard solution of metals were prepared by serial dilution of stock standard solutions of each metal containing 1000 mg/L (J. T. Baker, Phillipsburg, USA). Normal precautions for trace analysis were observed throughout. All

glassware were previously soaked overnight with 10% nitric acid solution and then rinsed with ultrapure water. The reaction vessels for microwave oven were cleaned before each digestion by using 4 mL of Instra nitric acid (70% v/v) (J. T. Baker, Phillipsburg, USA), heated for fifteen minutes at 600 W and then rinsed with ultrapure water. For digestion method set-up, a certified reference sediment (IAEA-356) was used.

Instruments

A microwave system Milestone model MLS-1200 MEGA (Milestone, Bergamo, Italy) was used to accomplish sediments digestion. An inductively coupled plasma atomic emission spectrometer VARIAN model ICP-AES Liberty 110 (VARIAN Inc., Palo Alto, USA) was used for metal analysis. The instrument was equipped with a vertical torch and an ultrasonic nebulizer CETAC model U-5000AT (CETAC TECHNOLOGIES Inc., Omaha, Nebraska, USA). A diffractometer PHILIPS model X'Pert-MDP was used to carry out the diffractometric analysis.

Sampling

Surface sediment samples (0-5 cm) were collected in March 1994 with a box corer. Sampling stations were chosen in Taranto gulf to provide a good areas coverage (FIG. 1). The sampling depth ranged from 100 to 2200 metres. Three sediment cores were sampled in three stations (station 2, 37 and 48) by using a gravity corer in order to assess metal distribution in relation to depth of the sediment. Cores were one metre in length and they were subdivided in layers of one cm thickness. After sampling, sediments were stored in a plastic vessel and frozen at -20 °C until analysis. In the laboratory sediment samples were defrosted at room temperature, dried at 40 °C up to a constant weight, ground and homogenized in a mortar to a fine powder.
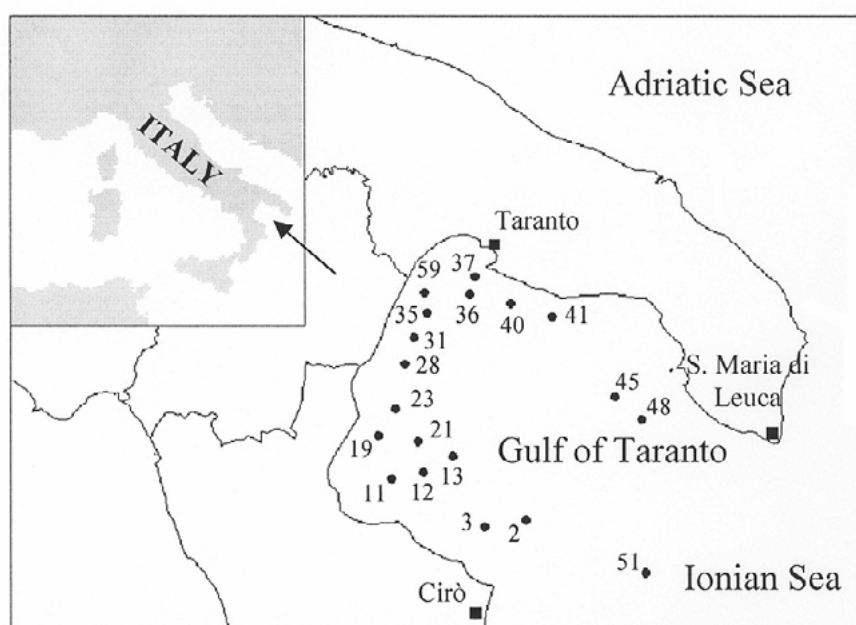

FIG. 1 - Sampling stations in the gulf of Taranto.

Total metal determination and speciation analysis

0.2 g of sample was put into a vessel for digestion with 4 ml of nitric acid, 2 ml of hydrochloric acid and 2 ml of hydrofluoric acid. For each digestion, a blank was prepared with the same amount of acids.[7] The digestion program for microwave oven was: 5 min at 0 W, 3 min at 250 W, 25 min at 450 W and 30 min at 500 W. After digestion, samples were diluted with 20 ml of boric acid, filtered and diluted to 50 ml with ultrapure water. The analysis was performed by ICP-AES technique.[8-9] Accuracy of the method was established by using a standard reference material (sediment IAEA-356). Results were in agreement with certified values, proving a good repeatability of the method (Table 1).

Metal speciation were effected by sequential extraction scheme of Tessier *et al.*[5], modified by Campanella *et al* [6]. The five-step extraction procedure based on successive extractions gives fractions described broadly as: 1) exchangeable (loosely adsorbed to the sediments), 2) bound to manganese and iron oxide, 3) bound to organic matter, 4) bound to humic compounds and 5) bound to sulphides. The content of metals adsorbed into sediments and associated with iron and manganese oxide were utilized as a measure of metal bioavailability. Each extraction fraction was analyzed by using Inductively Coupled Plasma technique.

Difractometric analysis

A diffractometer PHILIPS model X'Pert-MDP was used for diffractometric analysis under the following operating condition: Bragg-Brentano configuration with scanning $\theta/2\theta$, tension 40 kV, current 55 mA, anode Cu-Kα, step size 0.010° and time for step 1 s.

RESULTS AND DISCUSSION

Metal concentration are shown in Table 2. Results were elaborated by Geographical Information System (GIS) ArcView software to show the accumulation areas of metals. In particular, the analysis of metals showed that their distribution in the gulf of Taranto is due to two fundamental factors: sources of pollution (urban and industrial wastes of Taranto area and the rivers of Basilicata region) and prevailing marine currents. Currents into gulf of Taranto have mostly anticlockwise way: this cause accumulation of metals in the sediments near the coasts of the Calabria that is made easy from contribution of particle material carry from rivers. The analysis of cores did not show any interesting differences of metal concentration related to the depth of the sediment. In FIG. 2 is shown, for example, a typical change of Zn concentration along the sediment core taken in the sampling stations n. 37 and 48.

FIG. 3 shows the distribution of some metals (Cr, Fe, Pb and Zn) in the gulf: their concentration increase in the sediments from S. Maria di Leuca (Apulia) to Taranto until to Cirò (Calabria). It has been determined a linear correlation for the pairs Al-Fe ($p < 0.001$) and Pb-Zn ($p < 0.001$).

Multivariate statistical technique has been used to evaluate the possibility of differentiating the sampling stations of the Taranto gulf according to their geographical origin and to show the contamination areas of metals.[10] Principal Component Analysis (PCA) and Hierarchical Clustering Analysis (HCA) have been applied on a data set of eighteen samples and sevent metals (Al, Fe, Ti, Mn, Cr, Zn and Pb) by using statistical software (StatSoft Inc., Tulsa, OK, USA).

The station 51 has been excluded because its geographic position could not be attributed to any cluster, while Ni and Cu have been excluded because they had low weight. The scatter plot of the scores on the first two principal components PC1 and PC2 obtained by Al, Fe, Ti, Mn, Cr, Zn and Pb (FIG. 4) shows a separation among the sampling stations of different geographic position according to their various accumulation of metals. In fact, all stations near Cirò except two (station

19 and 23) have positive scores on the PC1, while the stations near to Taranto and S. Maria di Leuca are characterised by negative scores on the same principal component.

TABLE 1 - Metal concentrations (mg/Kg dry weight) in the certified marine sediment.

Element	Certified value	Range certified	Found value
Al	39000	31800 ÷ 44200	37200 ± 210
Fe	24100	22500 ÷ 25100	23650 ± 930
Ti	2190	1670 ÷ 2560	1935 ± 350
Ni	36.9	35.1 ÷ 40.1	34.1 ± 2.4
Mn	312	288 ÷ 323	312 ± 21
Cr	69.8	62.9 ÷ 74.4	70 ± 3
Zn	977	936 ÷ 1019	861 ± 5
Cu	365	351 ÷ 375	358 ± 13
Pb	347	301 ÷ 365	352 ± 25

TABLE 2 - Metal concentrations in marine sediment samples (mg/Kg dry weight).

Station	Depth (m)	Al	Fe	Ti	Ni	Mn	Cr	Zn	Cu	Pb
2	687	61700	34100	3450	61	2830	98	119	52	55
3	350	72000	35200	3600	52	620	90	129	47	75
11	300	66000	34400	3600	49	650	93	122	47	70
12	420	70600	36100	3900	54	680	95	124	47	71
13	400	65700	35200	3650	61	1230	103	122	50	72
19	150	66000	32700	2950	50	550	82	95	44	55
21	112	70200	34000	3100	53	570	87	99	47	55
23	116	66700	32700	3000	54	560	84	95	46	55
28	225	65700	33600	3050	60	650	88	96	50	50
31	700	58400	30300	2650	48	890	77	88	46	50
35	400	41400	29700	3150	51	730	85	102	43	50
36	544	62700	30700	2600	52	1180	77	91	49	55
37	368	63200	30700	2800	50	590	79	87	49	50
40	350	56600	29200	2350	50	660	75	89	50	55
41	380	43600	27500	2800	53	850	84	98	44	55
45	250	58100	29400	2400	53	890	78	94	50	60
48	180	38800	27600	2950	52	680	83	99	42	60
51	2164	36900	26300	2950	57	1530	81	97	47	60
59	183	48400	30300	3300	52	640	92	99	45	45

The sediments sampled near to Cirò except two (stations 2 and 13) have positive scores on PC2. This demonstrate that the sediments sampled near Cirò are unlike from remainder, but it is not possible to show a significant difference beetween the sediments sampled near Taranto and those sampled near S. Maria di Leuca.

The loading of the variables on the first two principal components (FIG. 5) shows that Zn, Ti, Fe and Cr are the dominant variables on PC1, while Al and Mn are the dominat variables on PC2. HCA was carried out and the dendogram of the sampling stations (FIG. 6) shows the clustering of the stations on the basis of their geographical origin, confirming the results of PCA. Indeed, there are four clusters which can be identified as follows: the first two clusters include the stations near Cirò and two stations near Taranto, the third and the fourth clusters contain the stations near Taranto and S. Maria di Leuca.

The results obtained by HCA, as well as PCA, show that the sediments sampled near Cirò are different from the other samples and the multivariate statistical technique could be used to identify specific areas of accumulation of metals.

Metals speciation showed that for Fe, Ni and Zn are prevalently present as sulphides, Mn is present mainly in an ion-exchange form and/or bound to the carbonate, while Cu and Pb are present as fraction bound to humic acids.
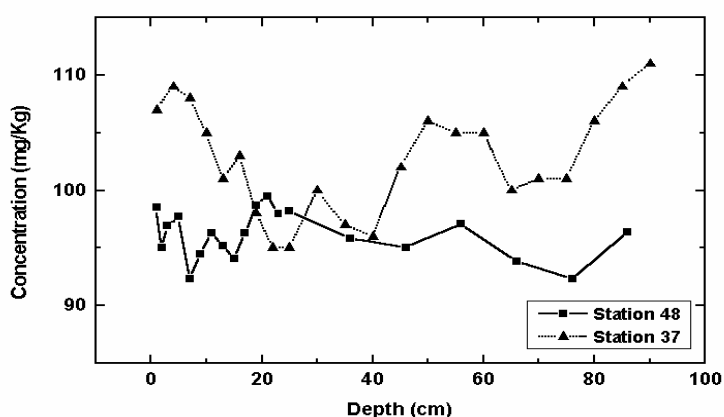

FIG. 2 - Variations of Zn concentrations in sediment cores sampled at stations n. 37 and 48.

FIG. 7 shows the different percentages of metals in the different fractions for stations n. 3, 11, 48 and 59. The stations 3 and 11 are near to accumulation area (Calabria coast), the station 48 is near to industrial area of Taranto, while the station 59 is near S. Maria di Leuca.

Lead is present as fraction bounds to humic acids: 22.6% in station 3, 47.4% in station 11, 26.2% in station 48 and 53.8% in station 59. For copper prevails the fraction bounds to humic acids: 33.0% in station 3, 39.1% in station 11, 37.1% in station 48 and 29.7% in station 59. Nickel, zinc and iron are present principally as fraction bound to sulphides: 45.2%, 51.0% and 92.8 % in station 3, 43.9%, 67.8% and 87.6 % in station 11, 62.0%, 74.0% and 92.6 % in station 48 and 60.7%, 81.0% and 89.3 % in station 59 respectively. Manganese is present mainly as ion-exchange form and bound to the carbonate.

Diffractometric analysis showed that sediment samples are constituted principally of quartz (SiO_2), calcite ($CaCO_3$) and halite (NaCl) with constant ratios in relation to latitude and longitude: however, sediment sample showed a homogeneous composition. In FIG. 8 it is shown, for example,

a typical diffractometric spectrum of a sediment samples taken in station n. 41. The presence of calcite is due to the particular crystallization of $CaCO_3$ at low temperature on the sea bottom.[11]
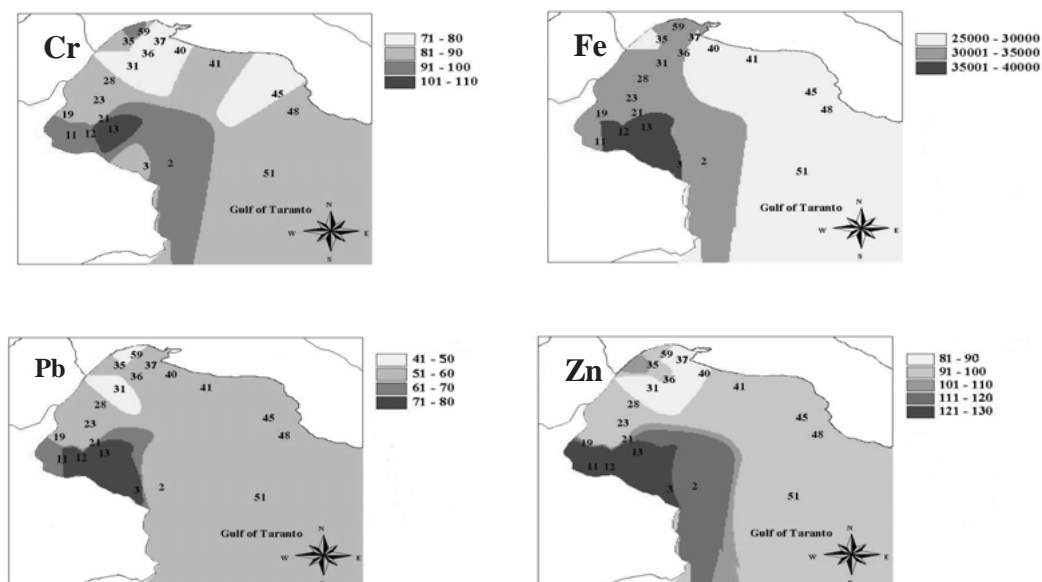

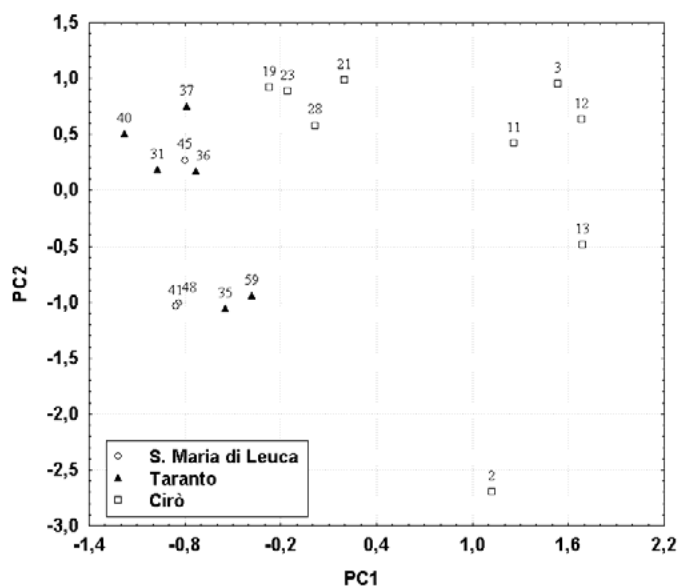FIG. 3 - Typical distribution of some metals (Cr, Fe, Pb, Zn) (mg/Kg d.w.) in the sediments of Taranto gulf.

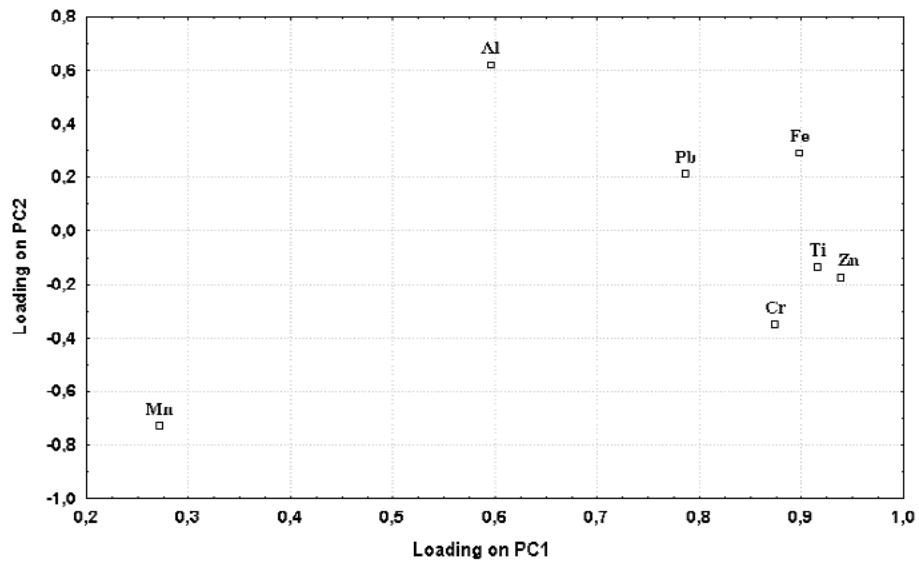FIG. 4 - Scatter plot of the scores on the first two principal components obtained by Al, Fe, Ti, Mn, Cr, Zn and Pb.

FIG. 5 - Loadings of the variables on the first two principal components.
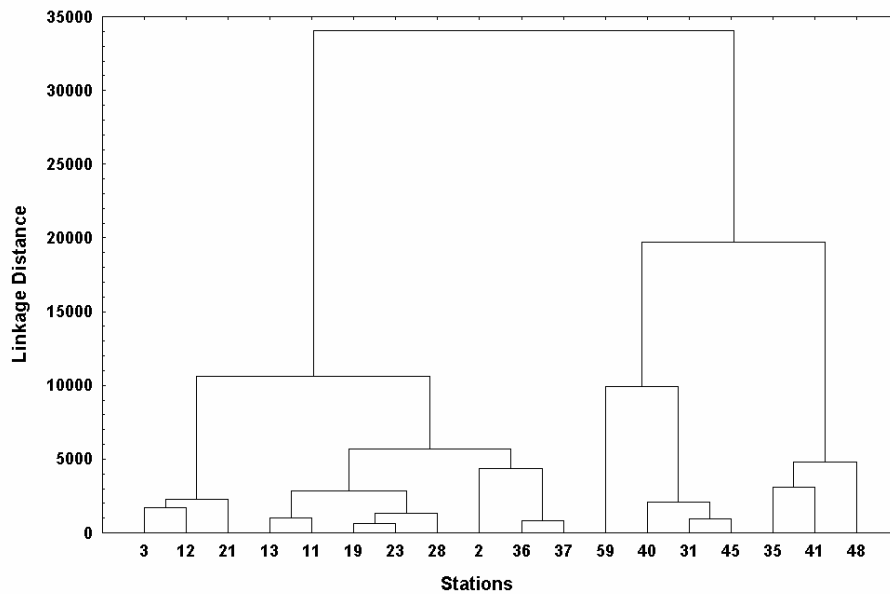

FIG. 6 - Dendrogram of the sampling stations of Taranto gulf: Cirò (station 3, 12, 21, 13, 11, 19, 23, 28 and 2), Taranto (station 36, 37, 59, 40, 31 and 35) and S. Maria di Leuca (station 45, 41 and 48).
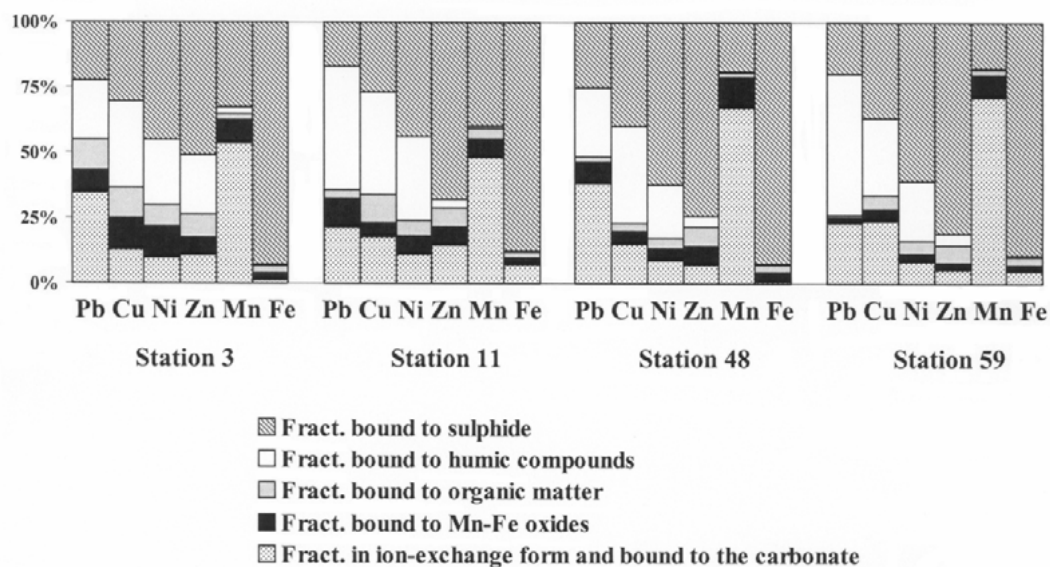
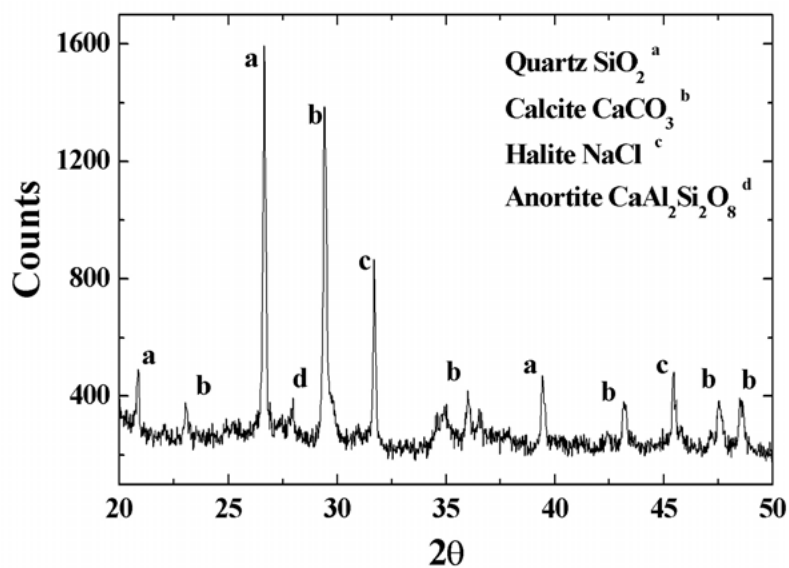FIG. 7 - Comparison of several metal fractions for stations 3, 11, 48 and 59.

FIG. 8 - Typical diffractometric spectrum of a sediment sample (station n. 41).

CONCLUSIONS

Analysis of metals in deep sediments of Taranto gulf has permitted to obtain information about the background level of these contaminants in this important area of the Mediterranean Sea. Moreover, spatial distribution of metals has shown the accumulation areas and the role of currents in the diffusion phenomena. Speciation analysis has demonstrated that, except Mn, metals are mainly present as sulphides in relation to the low oxygen concentration and redox potential on the sea bottom.

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