Ital.J.Geosci. (Boll.Soc.Geol.It.), Vol. 129, No. 3 (2010), pp. 385-394, 6 figs., 4 tabs. (DOI: 10.3301/IJG.2010.23)

Granulometry, mineralogy and trace elements of marine sediments from the Gulf of Milazzo (NE Sicily): evaluation of anthropogenic impact

FABRIZIO PEPE (*), GIOVANNA SCOPELLITI (**), ROSSELLA DI LEONARDO (**) & GAETANO FERRUZZA (*), (***)

ABSTRACT

Granulometry, mineralogy, and trace element concentrations are determined in marine sediments from thirty-six sampling sites in the littoral environment of the Gulf of Milazzo (NE Sicily). Sediment samples were collected in August 2008, along 18 seaward transects, at water depths of –10, –20 and –30 m, by using a Van Veen grab. Grain-size analysis shows predominance of sand (56%) and silt (35%) fractions with respect to clay (7%) and gravel (2%) fractions. Bulk mineralogical analysis documents the presence of quartz, micas, feldspars, calcite, and chlorite, which reflect erosion processes affecting the Kabilian-Calabrian Units. Concentrations of most trace elements in the deeper sediments were notably higher than shallower ones, due to the gradual increase of the fine fraction (<63 μm). Concentrations of Cr, Ni, Pb and, at lesser extent, Zn and Cu in the <63 μm fraction appear to be potentially hazardous, exceeding national and international regulatory guidelines, both close to the Milazzo industrial area and at Capo Rasocolmo. Trace element mean values from the Gulf of Milazzo are comparable with those measured in polluted sediments collected in the Gulf of Palermo and Augusta Bay with a moderate enrichment in Zn. Different sources of trace elements and different geochemical mechanisms are probably responsible of this distribution. Among these sources and mechanisms, local anthropogenic inputs, different contents of organic matter, and surface water circulation may be invoked.

KEY WORDS: *Gulf of Milazzo, North Sicily offshore, Trace elements, Marine pollution.*

RIASSUNTO

Granulometria, mineralogia ed elementi in tracce di sedimenti marini del Golfo di Milazzo (NE Sicilia): valutazione dell'impatto antropico.

Analisi granulometriche, mineralogiche e geochimiche (elementi in tracce) sono state effettuate in 36 campioni di sedimenti marini prelevati nel litorale del Golfo di Milazzo (Sicilia Nord-Orientale). I sedimenti sono stati campionati nell'agosto 2008, lungo 18 transetti, alla profondità di –10, –20 e –30 m, mediante benna tipo Van Veen. L'analisi granulometrica mostra la predominanza delle frazioni sabbiosa e siltosa (rispettivamente 56 e 35%) rispetto alle frazioni argillosa (7%) e ghiaiosa (2%). L'analisi mineralogica documenta la presenza di quarzo, miche, feldspato, calcite e clorite, che riflette processi di erosione delle rocce metamorfiche delle Unità Kabilo-Calabridi. La maggior parte degli elementi in tracce è tendenzialmente arricchita nei sedimenti più profondi. Valori particolarmente elevati, potenzialmente pericolosi se confrontati con i limiti di tossicità nazionali ed internazionali, sono stati registrati per Cr, Ni, Pb e, in misura minore, Zn e Cu, sia in prossimità delle raffinerie di Milazzo che nelle vicinanze di Capo Rasocolmo. Alte concentrazioni di elementi in tracce nei sedimenti in esame dovute ad un apporto fluviale nel Golfo di Milazzo sono state escluse. Infatti, le unità affioranti nell'area ed interessate dall'attività di erosione fluviale non sono caratterizzate da mineralizzazioni. Quest'ultime sono evidenti nell'unità Mandanici affiorante nella porzione più meridionale dei Monti Peloritani. Contrariamente, una sorgente antropica locale potrebbe giustificare le alte concentrazioni di elementi in tracce in prossimità del porto e delle raffinerie. L'aumento del rapporto elemento/% frazione inorganica <63 μm nella zona della raffineria e di Capo Rosocolmo è probabilmente legato da un lato ad una maggiore quantità di materia organica per la quale gli elementi in traccia hanno elevata affinità e dall'altro ad un trasporto verso est dello strato superficiale della colonna d'acqua per effetto della circolazione ciclonica.

TERMINI CHIAVE: *Golfo di Milazzo, Offshore della Sicilia settentrionale, Elementi in tracce, Inquinamento marino.*

INTRODUCTION

Trace elements are constituents of marine ecosystems (water and sediments), resulting mainly from abiotic and biotic processes, although industrial and human activities are also capable of introducing large quantities of trace elements, which, if in excess in marine ecosystems, may determine harmful and toxic effects. Increasing worldwide attention has been paid about the damaging effects of anthropogenic-derived contaminants on the marine ecosystems due to their environmental resistance to biotic degradation that poses a serious threat to marine biota (GONZÁLEZ-MACÍAS, 2006), as they prefer progressively to concentrate in silt-clay particles, organic matter, and/or to accumulate in marine organism tissues (CLARK, 2001). Thus, marine sediments act as both reservoir and as source of many trace contaminants (e.g. LI *et alii*, 2000), the latter being related to several factors, such as resuspension, bioturbation, and diagenesis (BOTHNER *et alii*, 1998; LEE & CUNDY, 2001).

A great affinity between trace elements and the fine-grained fraction (<63 μm) of sediments has been documented (DE GROOT *et alii*, 1982; FÖRSTNER & WITTMAN, 1983; HOROWITZ, 1991; VILLAESCUSA-CELAYA *et alii*, 2000; TRANCHINA *et alii*, 2008). This fraction is the most utilized to compare trace element concentrations in sediments from different areas because: 1) trace elements tend to concentrate in particles of silt-clay size, 2) this fraction is transported almost entirely by suspension, 3) sieving does not affect the trace element concentrations, and 4) it is possible to compare results among samples with different textural characteristics.

(*) Dipartimento di Geologia e Geodesia, Università di Palermo, Italy. Corresponding author: Dr. Fabrizio Pepe, PhD; Dipartimento di Geologia e Geodesia; Via Archirafi, 22 - 90123 Palermo, Italy; Tel. +39 091 23864667; Fax +39 091 6169908; Email: fapepe@unipa.it.

(**) Dipartimento di Chimica e Fisica della Terra ed Applicazioni (CFTA), Università di Palermo, Italy.

(***) Deceduto - Ottobre 2009.

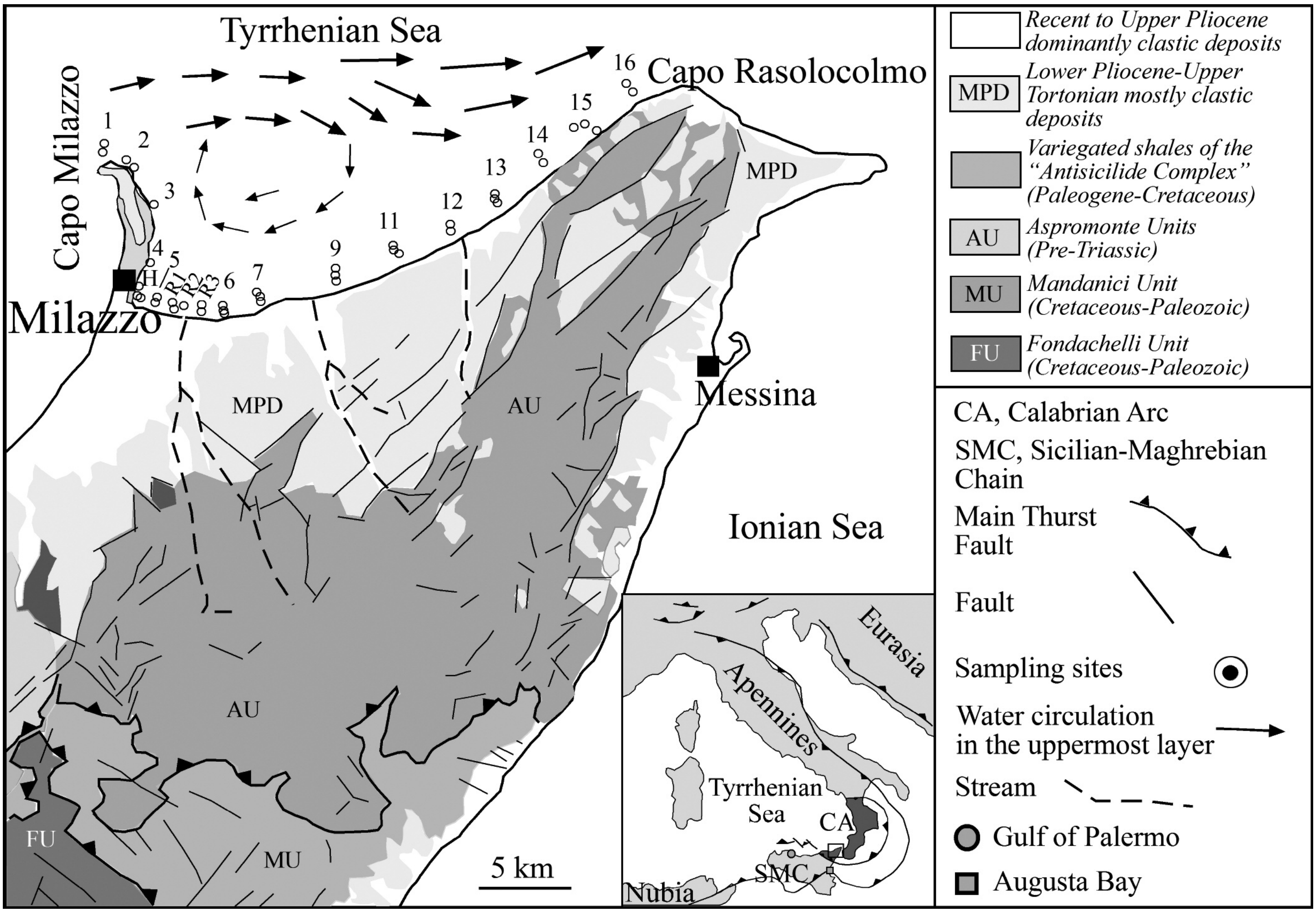

Fig. 1 - Geological sketch map of the eastern sector of the Peloritani Mountains simplified from MESSINA *et alii*, 2004, and location of sampling sites.
– *Carta geologica schematica del settore orientale dei Monti Peloritani semplificato da* MESSINA et alii*, 2004, ed indicazione delle stazioni di campionamento.*

The Gulf of Milazzo is a natural bay located in the eastern sector of Northern Sicily (fig. 1). Since the sixties, the coastal area of the gulf was a preferred site for the development of industries (i.e., crude oil refinery and thermal power plant) as well as the marina and commercial harbour. All these activities coupled with municipal and urban sewages, can be regarded as potential sources for anthropogenic trace element contamination. Consequently, the Gulf of Milazzo represents a natural laboratory for investigating the relationship between human pollution sources and enrichments and distribution of trace elements in the marine ecosystem of the NE Sicily offshore.

In this paper, results from the analysis of granulometry, mineralogy, and concentration of trace elements (Cr, Ni, Zn, Pb, Co, Cu, and As) in the fine-grained fraction (<63 μm) of thirty-six marine sediments collected in the littoral environment of the Gulf of Milazzo are presented. Moreover, to discriminate among natural and anthropogenic sources, patterns of the spatial distribution of the investigated trace elements are discussed and compared with those available in literature for others industrialised Sicilian areas as well as with existing regulatory guidelines.

GEOLOGICAL AND ENVIRONMENTAL SETTINGS

The Gulf of Milazzo was formed along the Tyrrhenian offshore of the Peloritani Belt (NE Sicily), the Sicilian portion of the Calabrian Arc (fig. 1). The bulk of the Peloritani Belt is composed by the Kabilian-Calabrian units that consist of several tectono-stratigraphic units, with Africa-ward vergence, involving both Variscan, or older, crystalline rocks and Mesozoic-Cenozoic deposits (AMODIO-MORELLI *et alii*, 1976; BONARDI *et alii*, 2001; MESSINA *et alii*, 2004). The lowermost nappes (Capo S. Andrea unit, Longi-Taormina Unit and S. Marco d'Alunzio Unit) are made up of a common epimetamorphic basement with distinct Lias-Eocene sedimentary covers. These units underthrust the Fondachelli Unit, which is made up by Paleozoic sequence with a Variscan, low-P, polyphase and monofacial metamorphism with Mesozoic calcareous sedimentary covers. The Mandanici Unit, which consists of a Palaeozoic basement (low-grade metaclastic rocks involving lenses of quartzites and metabasites) and a Jurassic-Oligocene sedimentary cover overthrust the Fondachelli Unit. The uppermost nappe, extensively exposed in the Peloritani range onshore the Gulf of Milazzo, is represented by the Aspromonte Unit, which is characterised by

Variscan medium-high grade metamorphics with Pre-Variscan granulitic relics, intruded by Late-Variscan plutonites. In various localities, the nappe pile is unconformably covered by Middle-Upper Miocene to Pleistocene sedimentary sequences (BONARDI *et alii*, 2001 and references therein), these latter filling a Plio-Quaternary extensional basin in the Milazzo onshore.

Towards the SW, the Kabilian-Calabrian units overthrust the Sicilian-Maghrebian units that consists of a south-east vergent, 12-15 km thick, Neogene-Quaternary tectonic stack formed (from top to bottom) by: 1) Cretaceous-Paleogene pelagic to terrigenous (Neothetyan domain) and Miocene flysch-type (Numidian domain) nappes; 2) nappes of Mesozoic-Paleogene basinal carbonates (African paleomargin), and 3) thick thrust imbricated Meso-Cenozoic Pelagian platform carbonate rocks (CATALANO *et alii*, 1996 and references therein).

The Gulf of Milazzo extends alongshore ~26 km from Capo Milazzo to Capo Rasolocolmo (fig. 1). In this area, the continental shelf is ~200 m wide. Off Capo Milazzo, instead, it increases its size at the centre of the bay where it is ~2 km wide. The most frequent winds are from SE and NW; the latter can be very intense in winter and spring (data for the period 1960-1990; from Eurometeo, http://www.eurometeo.com/, Reggio Calabria station). Hydrodynamics of the superficial water layer is complex: a general cyclonic circulation flowing eastward from Capo Milazzo to Capo Rasolocolmo, whereas an anticyclonic circulation, locally influenced by morphology and winds, characterise the inner sector of the bay (DECEMBRINI *et alii*, 2004, fig. 1).

Three small N-S oriented streams flow from the Peloritani Mountains into the Gulf of Milazzo: the Muto, Corriolo, which in proximity to its mouth flows very close to the crude oil refinery, and Mela streams (fig. 1). During periods of high stream discharge, continental waters carry significant amount of sediments originated by erosion of gneiss and granitoides with subordinate anphybolites and marbles from the Aspromonte Unit and marls, marly clay, sandstones, and conglomerates from the sedimentary sequences (fig. 1). Waters are also mixed with industrial and domestic sewage close to the stream mouths.

TABLE 1

Coordinates of sampling sites.
– *Coordinate dei siti di campionamento.*

Sample	Latitude (°N)	Longitude (°E)
HE 1/30	38.2733100	15.2349517
HE 2/30	38.2603650	15.2489883
HE 3/30	38.2478000	15.2541617
HE 4/30	38.2143467	15.2579817
HE H-out/10	38.2189467	15.2492150
HE H/10	38.2155533	15.2498150
HE H-in/10	38.2159983	15.2482267
HE 5/20	38.2129167	15.2568583
HE 5/30	38.2143800	15.2581367
HE R1/20	38.2108067	15.2665667
HE R1/30	38.2116483	15.2800850
HE R2/30	38.2122750	15.2715150
HE R3/20	38.2101217	15.2802800
HE R3/30	38.2116483	15.2800850
HE 6/10	38.2085300	15.2919133
HE 6/20	38.2093350	15.2916217
HE 6/30	38.2107200	15.2911867
HE 7/10	38.2122117	15.3114750
HE 7/20	38.2138850	15.3110850
HE 7/30	38.2151517	15.3099000
HE 9/10	38.2199417	15.3418367
HE 9/20	38.2216600	15.3409667
HE 9/30	38.2241767	15.3414650
HE 11/10	38.2306450	15.3818550
HE 11/20	38.2331233	15.3794917
HE 11/30	38.2331233	15.3788250
HE 12/10	38.2399733	15.4076550
HE 12/30	38.2425083	15.4076383
HE 13/10	38.2474583	15.4303583
HE 13/30	38.2502133	15.4281467
HE 14/10	38.2614467	15.4546367
HE 14/30	38.2648400	15.4525983
HE 15/20	38.2787867	15.4761683
HE 15/30	38.2776900	15.4704250
HE 16/10	38,2899100	15.5003383
HE 16/20	38.2922683	15.4972800

MATERIAL AND METHODS

Thirty-six surface sediment samples were collected along 18 seaward transects in the submerged littoral zone of the Gulf of Milazzo (NE Sicily), in August 2008. Position, direction, and distance between each transect (~1 nautical mile) were chosen in order to obtain the best area coverage of the studied gulf (see fig. 1). Sediment sampling was carried out at water depths of –10, –20 and –30 m, taking the top 10-cm undisturbed layer of sediment by using a Van Veen grab. Accurate positioning of sampling sites was determined using a Kraun 20 channels Global Positioning System (table 1). The name of sampling transects are reported in detail in fig. 1. Each sampling site was marked by two numbers: the first one indicates the name of the transect and the second one indicates the bathymetry. Samples were immediately sealed in polyethylene flasks, and stored at –20 °C until analysis.

Granulometric analysis was performed on all samples, using the sieving technique for the coarser fractions, which were preventively dried in desiccators. Selected samples were then analysed by using the laser diffraction method (Analysette 22, Fritsch) for the fine fraction (diameters of particles <63 μm). Samples were pre-treated with ~10 ml of 33% H_2O_2 for 72 h to remove the organic matter and then washed with deionised water.

Bulk mineralogy were determined on selected samples powdered manually in an agate mortar and analysed by powder X-ray diffraction (XRD) using a Philips PW14 1373 with Cu-Ka radiation filtered by a mono-chromator crystal and a scanning speed of 2° 2ϑ/min. The relative proportions of minerals were determined according to methods and data of SCHULTZ (1964) and BARAHONA *et alii* (1982).

Pseudo-total trace element concentrations were determined by using an inductively coupled plasma-mass spectrometry (Perkin-Elmer model ELAN-DRC-e) in grain size fractions <63 μm, constituted by inorganic and organic constituents. This fine fraction was obtained by dried sediment samples, which were wet sieved using Milli-Q water on 63 μm nylon sieve, dried at 55°C for 48 h, and then stored in hermetically closed polyethylene bags until analysis. Finally, an aliquot of 0.5 g of this sediment frac-

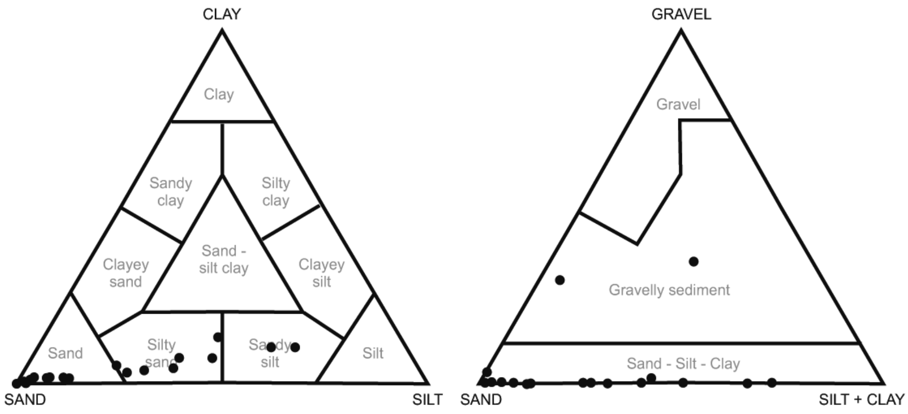

Fig. 2 - Schepard's classification scheme for sediments of the Gulf of Milazzo modified by diagram to account the gravel fraction (Schlee, 1973).
– *Schema classificativo di Schepard per i sedimenti del Golfo di Milazzo modificato da un diagramma che considera la frazione ghiaiosa (Schlee, 1973).*

tion was digested with a mixture of HNO_3-H_2O_2 (2:1) in bombs using a microwave oven (CEM MSD, 2000). Pseudo-total trace element digestion was widely used in environmental geochemical studies to remove non lattice-bound elements, giving an estimate of the maximum amounts of elements that are potentially modifiable with changing environmental conditions (Chatterjee & Banerjee, 1999; Yawar *et alii*, 2010). To remove the polyatomic interferences of As, the ICP-MS was operated in DRC mode with CH_4 as the appropriate reaction gas (with a purity of 99.999%). Precision, reported as percent relative standard deviation (RSD), is better than 5% for Zn, Pb, Co and Cu and 10% for Cr, Ni, and As.

RESULTS

Grain-size analysis shows average value of 56% and 35% for sand and silt fractions, respectively. The clay fraction is an accessory component (7%) and the gravel is only 2%. Thus, according to Shepard (1954), the surface sediments from the Gulf of Milazzo predominantly consist of sand and to a lesser extent of silty sand and sandy silt. This classification is also confirmed by the ternary diagram taking into account the gravel fraction (Schlee, 1973), with the exception of two samples classified as gravely sediments (fig. 2). Grain size distribution in sediments of the Gulf of Milazzo indicates that silt and clay

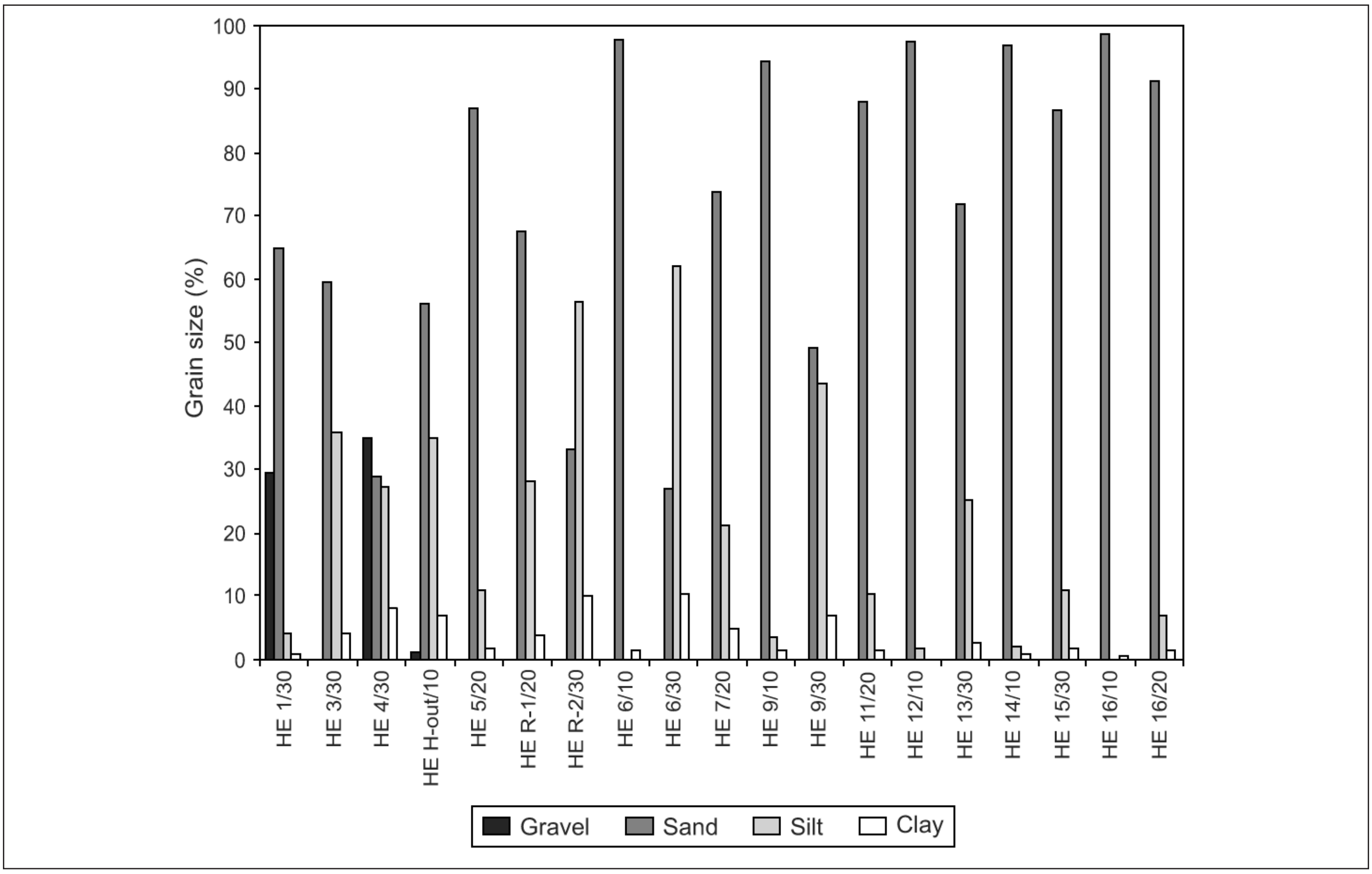

Fig. 3 - Distribution of grain-size in sediments of the Gulf of Milazzo.
– *Distribuzione delle frazioni granulometriche nei sedimenti del Golfo di Milazzo.*

fractions are abundant in more distal and deeper sampling stations. Only samples HE 1/30 and HE 4/30, collected close to the Capo Milazzo and the harbour, respectively, are characterized by high gravel content (29.6 and 35.2% for HE 1/30 and HE 4/30, respectively), whereas sand predominates in samples collected close to the coastline (fig. 3). Fine-fraction (silt and clay) shows a relative increase in the middle part of the Gulf, passing from an average value of 9.1% in Capo Milazzo and Capo Rasocolmo, to 35.2% between transects 3 and 9.

The result of mineralogical analysis is shown in fig. 4. All samples present clear 100 intensity peaks of quartz and mica at 26.67 and 8.8 °2ϑ, respectively. Peaks localized in the range 27.7-28.1 °2ϑ represent feldspars. Diffrattometric effect of carbonate phase, with percentage less then 10%, is sometimes present although the 100-intensity peak appears lightly displaced toward higher angles (~29.8 °2ϑ), testifying a calcite with small content of Mg. One sample (HE 1/30) is also characterized by presence of dolomite. XRD analyses give also evidence of chlorite presence identified in the spectra by basal effects at 7 and 3.5 °2ϑ. Distribution of the mineralogy from west to east in the Gulf of Milazzo is shown in fig. 4. Quartz, micas, and feldspars globally constitute about 90 vol.% of sediments, being generally present in equal proportions. Dolomite and calcite show an increase in correspondence of Capo Milazzo, while chlorite exhibits higher percentage in distal samples.

Concentrations of Cr, Ni, Zn, Pb, Co, Cu, and As, and the percentage of grain-size fraction <63 μm in samples pre-treated with H_2O_2 are listed in table 2. Spatial distribution of trace elements from west to east along the Gulf of Milazzo is shown in fig. 5. Generally, trace element concentrations increase with sampling depth, with the only exception of transects 5, 6, 7, and 16 that seldom show an opposite behaviour. Cr and Ni show average values of 24.8 and 49.4 mg kg^{-1}, respectively, with strong enrichments at Capo Rasocolmo (transect 16). Along this transect, concentrations increase up to 84.5 mg kg^{-1} for Cr and 201.3 mg kg^{-1} for Ni in sediment sampled at water depth of –10 m. Distribution of Zn, Pb, Co, and Cu documents moderate enrichments at the Milazzo harbour (transects 4, H, and 5) with values of 139.0, 36.8, 13.9, 36.0 mg kg^{-1}, respectively against 89.9, 17.5, 9.8, 25.0 mg kg^{-1} in the rest of the Gulf of Milazzo. Arsenic seems to present a uniform distribution along the gulf with an average value of 3.5 mg kg^{-1}.

TABLE 2

Trace element concentrations (mg kg^{-1}) in sediments of the Gulf of Milazzo. Percentages of grain size <63 μm are measured in H_2O_2 pre-treated sediments.

– *Concentrazioni degli elementi in traccia (mg kg^{-1}) nei sedimenti del Golfo di Milazzo. Le percentuali della frazione granulometrica <63 μm sono misurate su sedimenti pre-trattati con H_2O_2.*

Sample	grain size <63μm (%)	Cr	Ni	Zn	Pb	Co	Cu	As
		(mg kg^{-1})						
HE 1/30	5.3	8.2	nd	12.6	4.8	2.2	5.9	nd
HE 2/30	17.3	15.9	8.8	33.8	14.4	4.0	9.2	0.8
HE 3/30	40.3	22.0	10.9	45.1	14.9	4.8	15.9	1.3
HE 4/30	35.9	58.8	36.8	123.2	42.7	14.0	40.6	5.7
HE H-out/10	42.3	76.2	34.1	134.0	49.0	12.9	35.1	4.4
HE H/10	24.7	40.9	24.6	182.0	32.4	10.2	27.8	3.3
HE H-in/10	16.2	50.8	31.8	122.1	29.2	12.6	39.2	4.2
HE 5/20	13.0	86.6	45.6	167.3	49.2	20.6	51.1	5.4
HE 5/30	87.2	78.0	30.4	105.5	18.0	12.8	22.1	2.7
HE R1/20	32.3	54.2	34.9	113.6	20.3	14.1	35.5	6.0
HE R1/30	63.0	77.0	33.0	120.3	18.8	13.9	34.0	3.1
HE R2/30	66.7	88.1	44.2	137.8	21.3	16.5	44.5	3.2
HE R3/20	34.8	22.0	13.7	53.5	9.3	6.4	14.0	2.2
HE R3/30	85.1	76.3	34.8	112.6	18.7	13.7	34.2	2.7
HE 6/10	1.9	45.4	29.8	115.1	23.7	11.8	30.3	5.0
HE 6/20	20.6	37.7	20.9	73.8	17.1	8.8	23.9	3.8
HE 6/30	72.9	54.4	37.5	114.6	20.4	14.9	36.7	6.1
HE 7/10	7.4	45.7	32.3	130.4	29.6	14.0	40.0	5.5
HE 7/20	26.1	26.1	13.7	49.0	10.7	6.5	13.0	2.0
HE 7/30	78.8	61.4	29.6	110.8	19.3	12.8	31.0	3.3
HE 9/10	5.5	23.8	15.1	69.1	11.4	6.3	18.2	2.0
HE 9/20	10.2	62.7	38.2	123.8	21.0	13.2	32.7	5.6
HE 9/30	50.8	63.2	26.9	105.9	15.6	11.7	27.5	2.6
HE 11/10	5.4	12.0	2.5	23.3	4.7	2.9	8.3	nd
HE 11/20	12.1	55.5	18.3	85.6	15.5	8.3	18.1	2.7
HE 11/30	28.6	42.0	22.3	99.6	18.3	10.5	25.2	4.1
HE 12/10	2.2	20.5	5.4	31.9	6.8	3.2	11.5	0.4
HE 12/30	12.3	65.7	24.8	108.2	23.1	11.0	28.2	3.6
HE 13/10	9.5	13.8	3.6	28.6	7.4	3.9	11.1	0.1
HE 13/30	27.9	47.5	28.3	106.4	22.0	11.9	32.4	6.1
HE 14/10	3.1	49.3	21.7	91.6	19.1	9.7	24.6	3.6
HE 14/30	20.4	47.1	23.4	102.3	19.4	10.4	26.1	4.5
HE 15/20	7.0	52.4	22.1	111.1	20.5	8.7	25.7	3.9
HE 15/30	12.9	64.0	34.6	136.4	24.0	14.4	29.2	7.3
HE 16/10	1.1	201.3	84.5	109.8	30.2	12.6	32.1	4.6
HE 16/20	8.8	83.6	34.3	139.8	22.0	12.5	30.8	4.1

DISCUSSION

The mineralogical and granulometric analyses of marine sediments collected in the Gulf of Milazzo give evidence of predominance of quartz, mica and feldspars associated with sand and silt grain size. High content of these minerals indicate that their source area is the north side of the Peloritane Belt, where erosional processes affect granitic and metamorphic rocks of the Aspromonte Unit (see fig. 1). Regarding the abundance of silt and clay fractions associated with chlorite in samples collected between transect 3 and 9; such a concentration can be compatible with the dominant eastward current flow, which, in Capo Milazzo and Capo Rasocolmo, allows accumulation of sand and gravel. Hence, deposition of fine-grain sediments takes place in more internal protected areas of the gulf.

Trace element spatial distribution highlights strong enrichments of Ni and Cr at Capo Rasocolmo, whereas Zn, Pb, Co, and Cu record moderately high concentrations in sediments collected close to the harbour/refinery area (fig. 5). To assess the environmental hazard, levels of trace elements determined for the Gulf of Milazzo are compared with those available in the literature for the toxicity of substances to sediment-dwelling species (LONG *et alii*, 1998). These values offer useful standards in measuring the possible toxicity of polluted sediments and in classifying sediments as contaminated or not (DEL VALLS & CHAPMAN, 1998; MILLER *et alii*, 2000). For this purpose, a set of the eco-toxicological screening values developed for sediment-dwelling species by the North American Sediment Quality Guidelines (SQG; LONG *et alii*, 1995), called Effect Range-Low (ERL) and Effect Range-Median (ERM) values, are here used. ERLs represent the trace element concentrations below which the probability of adverse effects on benthic biota is minimal. Differently, the ERMs correspond to the midrange above which toxic effects are more probable, although not always expected. Among the ERLs and ERMs range, negative ecological

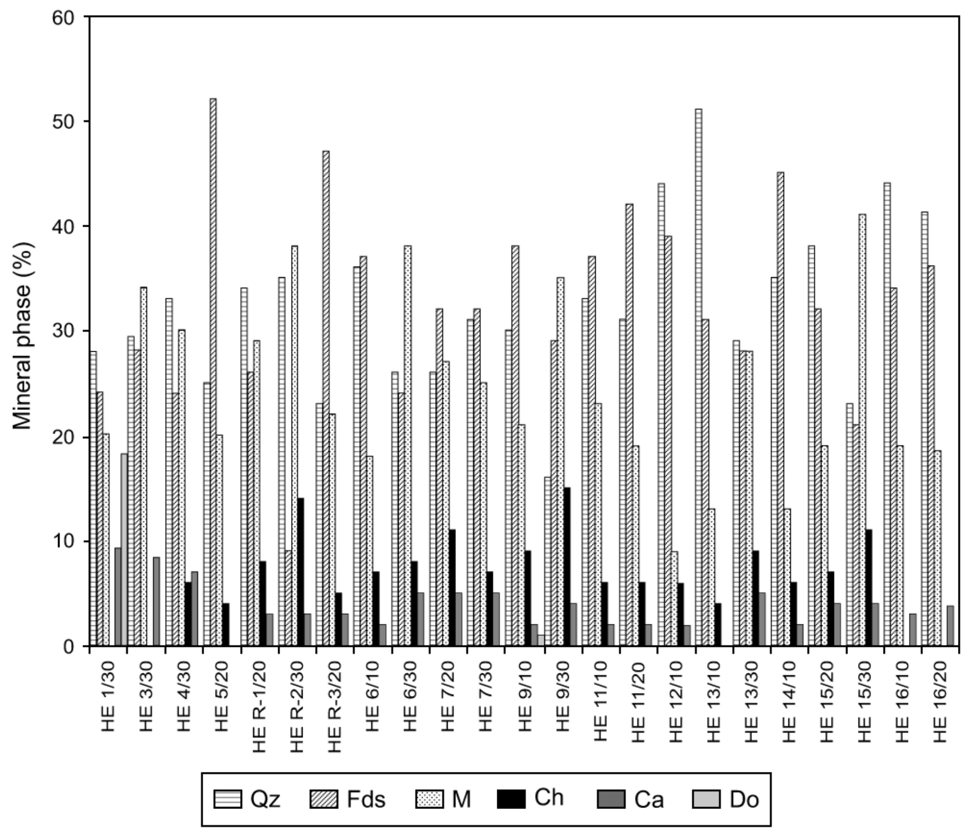

Fig. 4 - Spatial distribution of mineralogy in sediments of the Gulf of Milazzo from West to East. Qz: quartz; Fds: feldspar; M: mica; Ch: chlorite; Ca: calcite; Do: dolomite.
– Distribuzione della composizione mineralogica dei sedimenti del Golfo di Milazzo da ovest verso est. Qz: quarzo; Fds: feldspato; M: mica; Ch: clorite; Ca: calcite; Do: dolomite.

effects would occasionally occur (LONG *et alii*, 1995). Consequently, the observed ecological effects are rare, occasional or frequent when pollutant concentrations are less that the ERLs, between the ERLs and ERMs range or higher that the ERMs, respectively. Only for Co, the ERL and ERM values are not available. For Cr, Ni, Pb, and As are also available the limits indicated by national regulatory guidelines (G.U.R.I., D.M. 367/03, 2004). Enrichments with respect to national sediment quality guidelines have been shown by Cr and Ni, particularly at 30 m-depth samples, and by Pb in the harbour area. Concentrations of As are always below the national limits. With respect to ERL and ERM values, the majority of sediment samples exceed the ERL value for Ni and sample HE 16/10 also exceed the ERM limit. Zinc and Pb are above their respective ERLs in the samples (HE H and HE H-in) collected close to the harbour as well as in the sample HE 5/20, whereas some samples collected between transect 4 and 7 have Cu concentrations exceeding this limit. With respect to the ERL value, Cr is characterized by strong enrichment in sediment sample HE 16/10. Arseniv is below its ERL limit.

To better understand the degree of Milazzo trace element contamination, their concentrations in marine sediments from the industrial areas of Palermo (NW Sicily) and Augusta (SE Sicily) are here considered for comparison (table 3; DI LEONARDO, 2007; DI LEONARDO *et alii*, 2009). Generally, no significant differences are observed between these industrialised areas but, taking into account the mean values, only Zn concentration is enriched in Milazzo sediments with respect to the other considered Sicilian sediments, whereas, considering the maximum values, Cr, Ni, and Zn concentrations exhibit greater values.

To better understand the possible source of the investigated trace elements, natural input is firstly considered. It is here hypothesised that these enrichments are consequent to erosion of mineralised rock cropping out in the Peloritane Mountains, transport by streams and sedimentation in the Gulf of Milazzo. At present, polymetallic mineralised occurrences have been documented in the Peloritane Belt within the Mandanici Unit (FERLA & OMENETTO, 2000; FERLA & MELI, 2007 and reference therein). On the contrary, no evidence of mineralization exists for the Aspromonte Unit and Lower Pliocene-Upper Tortonian deposits, extensively exposed in the Peloritani sector drained by the Muto, Corriolo, and Mela streams (fig. 1). Conversely, the Milazzo area represents a typical sedimentary plane with no evidence of mineralization. Thus, anthropogenic origin of trace elements in sediments from the Gulf of Milazzo can not be excluded. To support this hypothesis, we considered trace pollutants data, available for the investigated area, from the E-PRTR [European Pollutant Release and Transfer Register (http://prtr.ec.europa.eu/Home.aspx)], in which the thresholds are

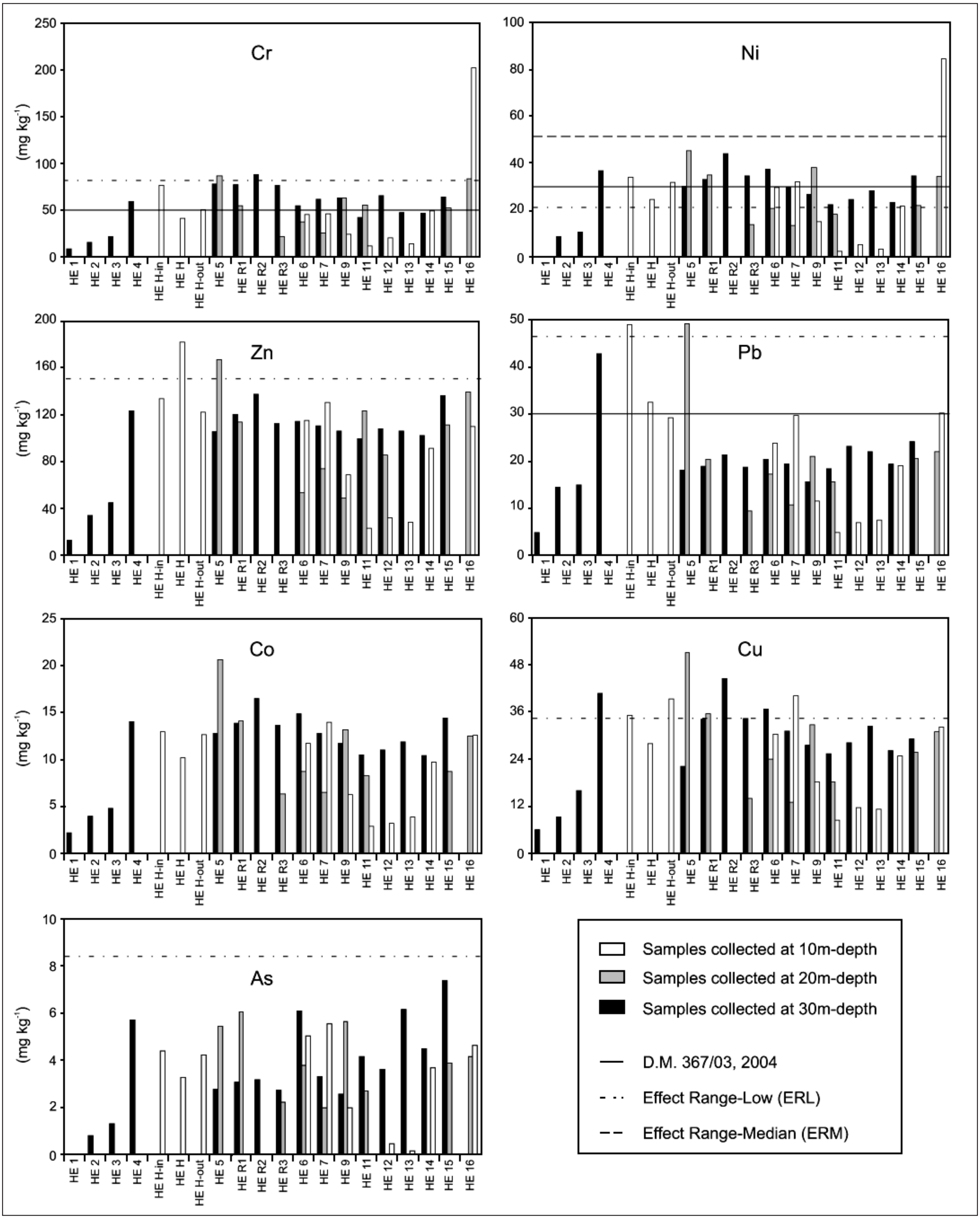

Fig. 5 - Cr, Ni, Zn, Pb, Co, Cu and As concentrations in sediments of the Gulf of Milazzo. ERL and ERM values (LONG & MORGAN, 1990) and concentration limits specified in the Italian regulatory guidelines (G.U.R.I., D.M. 367/03, 2004).
– *Distribuzione lungo la costa delle concentrazioni di Cr, Ni, Zn, Pb, Co, Cu e As nei sedimenti del Golfo di Milazzo. In fig. sono riportati i valori ERL e ERM (LONG & MORGAN, 1990) e i limiti di concentrazione previsti dalla legislazione italiana (G.U.R.I., D.M. 367/03, 2004).*

TABLE 3

Trace element composition range (mg kg^{-1}) with mean and median values and standard deviation; a, this study; b, DI LEONARDO *et alii*, 2006.
– *Intervalli composizionali degli elementi in traccia (mg kg^{-1}) con indicazione dei valori medi, delle mediane e delle deviazioni standard; a, questo studio; b, DI LEONARDO* et alii, *2006.*

Milazzo area [a]	Valid N	Mean	Median	Minimum	Maximum	Std.dev
Cr	36	53.6	51.6	8.2	201.3	33.8
Ni	35	27.2	28.3	2.5	84.5	14.9
Zn	36	98.1	109.0	12.6	182.0	40.8
Pb	36	20.7	19.3	4.8	49.2	10.5
Co	36	10.5	11.8	2.2	20.6	4.3
Cu	36	26.8	28.0	5.9	51.1	10.9
As	34	3.7	3.7	0.01	7.3	1.7
Augusta area [b]	**Valid N**	**Mean**	**Median**	**Minimum**	**Maximum**	**Std.dev**
Cr	80	77.4	83.2	30.7	98.7	17.9
Ni	80	38.0	40.1	18.7	46.7	7.3
Zn	80	76.1	77.5	18.3	112.8	24.9
Pb	80	20.2	17.4	12.9	33.7	5.8
Co	80	14.2	14.6	6.9	21.3	3.1
Cu	80	28.9	27.2	13.4	84.9	10.7
As	--	--	--	--	--	--
Palermo area [b]	**Valid N**	**Mean**	**Median**	**Minimum**	**Maximum**	**Std.dev**
Cr	34	68.3	67.3	49.4	89.6	9.2
Ni	42	30.6	30.6	21.5	45.8	5.0
Zn	41	77.4	77.7	38.0	125.6	19.7
Pb	42	35.1	31.2	11.6	60.2	17.4
Co	42	9.6	9.2	6.6	15.4	1.8
Cu	42	25.4	26.2	12.3	38.6	7.8
As	--	--	--	--	--	--

TABLE 4

Amounts of trace pollutants released to air and water in 2007 from the Milazzo refinery with indication of thresholds (E-PRTR data; http://prtr.ec.europa.eu/Home.aspx).
– *Quantità di inquinanti in tracce rilasciati in aria ed acqua nel 2007 dalla raffineria di Milazzo con l'indicazione dei livelli soglia (E-PRTR data; http://prtr.ec.europa.eu/Home.aspx).*

Trace element	Air	Threshold (air)	Water	Threshold (water)
Cr (kg y^{-1})	109	100	n.a.	n.a.
Ni (kg y^{-1})	1650	50	41.9	20
Zn (kg y^{-1})	200	200	272	100
Pb (kg y^{-1})	n.a.	n.a.	40.1	20
Co (kg y^{-1})	n.a.	n.a.	n.a.	n.a.
Cu (kg y^{-1})	n.a.	n.a.	73.9	50
As (kg y^{-1})	22	20	n.a.	n.a.

also reported. The amounts of trace pollutants, released into the air and water during 2007 from the Milazzo refinery, are shown in table 4. With respect to the flux of pollutants to atmosphere, the most impressive data are related to Ni, being 33 times greater than its threshold. Other reported trace elements are not particularly enriched. Releases of Ni, Pb, Cu, and Zn to water are twice as much with respect to correspondent thresholds. Moreover, wet and dry deposition of anthropogenic particulate may be supported by measurements of trace element concentrations in the thalli of a saxicolous lichen species, biogeochemical indicators of air quality (DONGARRÀ *et alii*, 1995). These authors collected lichens in north-eastern Sicily, near the industrial zone of Milazzo and along a belt crossing areas of known ores mainly constituted by sulfides, demonstrating that the trace element source for lichens in the Milazzo area was ascribed to industrial activities. As far as the emission sources are concerned, Ni and Cr may be related to oil and coal combustion. Lead likely derives from urban traffic and petrol stations located close to marina and commercial harbour; whereas Cu comes possibly from thermoelectric central waterwheels. With respect to other trace elements, it can be speculated that the observed enrichments are due to unloaded during continuous portage at dock of crude or refined oil in proximity of the harbour and the refinery area.

To evaluate the possibility that, in the Gulf of Milazzo, the organic matter can be a controlling factor of element abundance, element concentrations was normalized to the percentage of the grain size <63 μm in samples pre-treated with H_2O_2 (table 3). Results of this normalization and west-east distribution in the Gulf of Milazzo are reported in fig. 6. A significant relationship between higher amount of inorganic fine particles and enrichment in trace elements is documented by the flattening of element profiles for sediment samples collected at depths of –20 and –30 m. An exception is represented by the sediments collected close to the coast at depth of –10 m and, among these, samples HE 6/10 and HE 16/10 are characterized by the highest ratios of trace element concentrations/inorganic grain size <63 μm. In these samples, a higher amount of organic matter, owing to its particular affinity with trace elements, could be responsible for the documented enrichments. Concerning the location of the sampling transects, HE 6/10 is immediately to the east of the harbour/refinery area, whereas HE 16/10 is located in proximity of the Capo Rasocolmo. At least for the latter area, it is presumable an important transport of anthropogenic contaminant strictly related to the dominant eastward current flow, also responsible of the grain size distribution.

CONCLUSIONS

Results from this study can be summarized, as follows:

– mineralogical phases characterizing the sediments are strictly related to the erosional processes affecting granitic and metamorphic rocks (Aspromonte Unit), which are exposed most extensively in the north side of the Peloritane Belt;

– dominant eastward current flow plays a dominant role in the abundance of silt and clay fractions of sediment along the studied gulf;

– trace element concentrations indicate local enrichments for Cr, Ni, Pb and, at lesser extent, for Zn and Cu with respect to regulatory guidelines. Comparison of the gained data from this study with those available in the literature has evidenced that trace element mean values from the Milazzo sediments are comparable with those determined in polluted sediments collected in the Gulf of

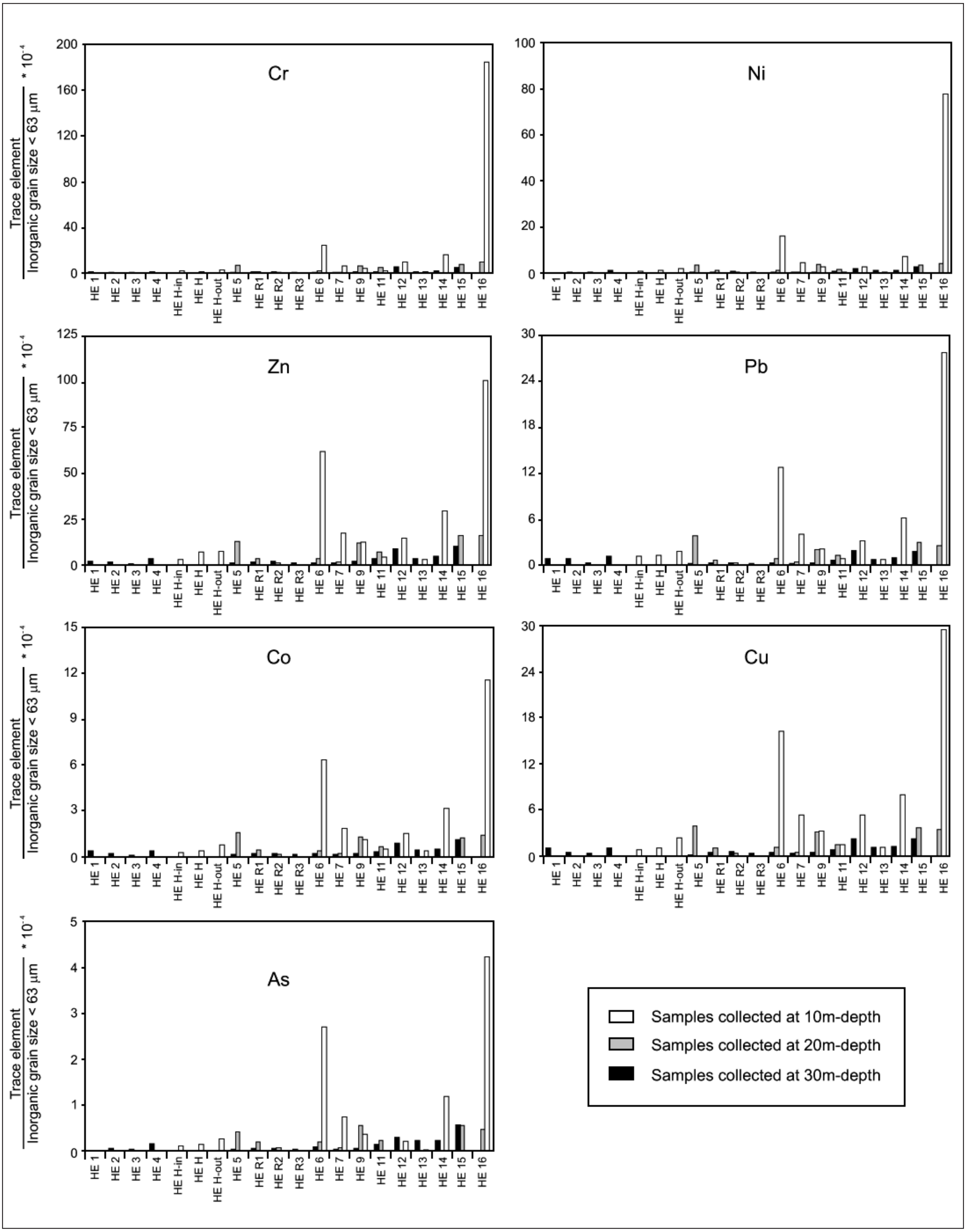

Fig. 6 - Trace elements/inorganic grain size <63 µm ratios in sediments of the Gulf of Milazzo.
– *Rapporti elementi in tracce/porzione granulometrica inorganica <63 µm nei sedimenti del Golfo di Milazzo.*

Palermo and Augusta Bay with a moderate enrichment in Zn. Taking into account the maximum values, Cr, Ni, and Zn concentrations are greater than those measured in the two industrial areas used for comparison;

– an anthropogenic source for trace elements in sediment of the Gulf of Milazzo is invoked as a consequence of pollutant input in air and water from industries as well as from the harbour activities and municipal/urban sewages;

– trace element concentrations normalized to percentage of inorganic grain size <63 μm highlight that the amount of fine fraction is the main responsible of trace element abundances. In sediments with higher values of this ratio, a contribution by organic is lakely.

Results from this study permit, for the first time, the assessment of the influence of the last 50 years of human activities on the Gulf of Milazzo. The same results provide also a baseline data for future monitoring programs of trace element pollution over time.

Acknowledgment

The HEMMAS-08 campaign and, therefore, this study, would not have been possible without the help of support of M. Cardella, M. Calabrò and C. Cucciardi. Great acknowledgment to the Commandant Messina of the Capitaneria di Porto of Milazzo for providing logistic support before and during the campaign, to G. Scotti for his friendship and support. Thanks to G. Borrini for his great patience during data sampling. Dr. C. Cosentino, and Dr. A. Caruso are thanked for their help during laboratory activities. The journal reviewers and the Editor are warmly thanked for the constructive comments that helped to clarify several points.

This research was partly supported by grants «Corso di Laurea Specialistica in Analisi e Gestione Ambientale, Faculty of Science, Palermo University, Italy» and Miur (ex 60%, responsible Prof. A. Sulli).

REFERENCES

Amodio Morelli L. & 14 others (1976) - *L'Arco Calabro-Peloritano nell'orogene Appenninico-Maghrebide*. Mem. Soc. Geol. It., **17**, 1-60.

Barahona E., Huertas F., Pozzuoli A. & Linares J. (1982) - *Mineralogia e genesi dei sedimenti della provincia di Granata (Spagna)*. Miner. Petrogr. Acta, **26**, 61-90.

Bonardi G., Cavazza W., Perrone V. & Rossi S. (2001) - *Calabria-Peloritani terrane and northern Ionian Sea*. In: Vai G.-B. & Martini P.I. (Eds.), Anatomy of an orogen: the Apennines and the adjacent Mediterranean basins, Kluwer Academic Publishers, 287-306.

Bothner M.H., Buchholtz Ten Brink M. & Manheim F.T. (1998) - *Metal concentrations in surface sediments of Boston Harbor-changes with time*. Mar. Environ. Res., **45**, 127-55.

Catalano R., Di Stefano P., Sulli A. & Vitale P.F. (1996) - *Paleogeography and structure of the central Mediterranean: Sicily and its offshore area*. Tectonophysics, **260**, 291-323.

Chatterjee A. & Banerjee R.N. (1999) - *Determination of lead and other metals in a residential area of greater Calcutta*. The Science of the Total Environment, **227**, 175-185.

Clark R.B. (2001) - *Marine pollution (5th ed.)*. Oxford, UK: Oxford University Press.

Decembrini F., Azzaro F., Galletta M. & Raffa F. (2004) - *Short-term changes of hydrobiological features in the Gulf of Milazzo (Tyrrhenian Sicily)*. Rapp. 511 Comm. int. Mer Médit., **37**, 511.

De Groot A.J., Zschuppe K.H. & Salomons W. (1982) - *Standardization of methods of analysis for heavy metals in sediments*. Hydrobiologia, **92**, 689-695.

Del Valls T.A. & Chapman P.M. (1998) - *Site-specific sediment quality values for the Gulf of Cádiz (Spain) and San Francisco Bay (USA), using the sediment quality triad and the multivariate analysis*. Cienc. Mar., **24**, 313-336.

Di Leonardo R. (2007) - *Geochemical and eco-toxicological evaluations in box-core sediments from the Sicilian coast, Central Mediterranean*. Ph.D. Thesis, University of Palermo. Palermo, 113 pp.

Di Leonardo R., Vizzini S., Bellanca A. & Mazzola A. (2009) - *Sedimentary record of anthropogenic contaminants (trace metals and PAHs) and organic matter in a Mediterranean coastal area (Gulf of Palermo, Italy)*. J. Mar. Systems, **78**, 136-145.

Dongarrà G., Ottonello D., Sabatino G. & Triscari M. (1995) - *Use of lichens in detecting environmental risk and in geochemical prospecting*. Environm. Geol., **26**, 139-146.

Ferla P. & Omenetto P. (2000) - *Metallogenic evolution of Peloritani Mountains (NE Sicily): a summary*. Mem. Soc. Geol. It., **55**, 293-297.

Ferla P. & Meli C. (2007) - *Petrogenesis of tourmaline rocks associated with Fe-carbonate-graphite metapelite, metabasite and strata-bound polymetallic sulphide mineralization, Peloritani Mountains, Sicily, Southern Italy*. Lithos, **99**, 266-288.

Gazzetta Ufficiale Della Repubblica Italiana (G.U.R.I.). - Decreto Ministeriale 6 novembre 2003, no 367. Regolamento concernente la fissazione di standard di qualità nell'ambiente acquatico per le sostanze pericolose, ai sensi dell'articolo 3, comma 4, del decreto legislativo 11 maggio 1999, n. 152, vol. 5. Ministero dell'Ambiente e della Tutela del Territorio, Roma, 08 Gennaio 2004, pp. 17-29.

González-Macías C., Schifter I., Lluch-Cota D.B., Mendez-Rodriguez L. & Hernandez-Vazquez S. (2006) - *Distribution, enrichment and accumulation of heavy metals in coastal sediments of Salina Cruz Bay, Mexico*. Environ. Monit. Assess., **118**, 211-230.

Horowitz A.J. (1991) - *A Primer on Sediments-trace Element Chemistry*, 2nd Edition. Lewis Publishers, Chelsea, MI.

Lee S.V. & Cundy A.B. (2001) - *Heavy metal contamination and mixing processes in sediments from the Humber estuary, eastern England. Estuar*. Coast Shelf Sci., **53**, 619-636.

Li X., Wai O.W.H., Li Y.S., Coles B.J., Ramsey M.H. & Thornton I. (2000) - *Heavy metal distribution in sediment profiles of the Pearl River estuary, South China*. Applied Geochemistry, **15**, 567-581.

Long E.R. & Morgan L.G. (1990) - *The potential for biological effects of sediment-sorbed contaminants tested in the National Status and Trends Program*. NOAA Tech. Memo. NOS OMA 62. National Oceanic and Atmospheric Administration, Seattle, WA.

Long E.R., MacDonald D.D., Smith S.L. & Calder F.D. (1995) - *Incidence of adverse biological effects within ranges of chemical concentrations in marine and estuarine sediments*. Environ. Manage., **19**, 81-97.

Long E.R., Field L.J. & MacDonald D.D. (1998) - *Predicting toxicity in marine sediments with numerical sediment quality guidelines*. Environ. Toxicol. Chem., **17**, 714-727.

Messina A., Somma R., Macaione E., Carbone G. & Careri G. (2004) - *Peloritani Continental Crust composition (Southern Italy): geological and petrochemical evidence*. Boll. Soc. Geol. It., **123**, 405-441.

Miller B.S., Pirie D.J. & Redshaw C.J. (2000) - *An assessment of the contamination and toxicity of marine sediments in the Holy Loch, Scotland*. Mar. Pollut. Bull., **40**, 22-35.

Schlee J. (1973) - *Atlantic Continental Shelf and Slope of the United States sediment texture of the northeastern part*. U.S. Geol. Surv. Prof. Paper, **529-L**, 64 p.

Schultz L.G. (1964) - *Quantitative interpretation of mineralogic composition from X-ray and chemical data for the Pierre Shale*. U.S. Geol. Surv, Prof. Pap.

Shepard F.P. (1954) - *Nomenclature based on sand-silt-clay ratios*. J. Sedim. Petrol., **24**, 151-158.

Tranchina L., Basile S., Brai M., Caruso A., Cosentino C. & Miccichè S. (2008) - *Distribution of Heavy Metals in Marine Sediments of Palermo Gulf (Sicily, Italy)*. Water Air Soil Pollut, 191:245-256. DOI 10.1007/s11270-008-9621-3.

Villaescusa-Celaya J.A., Gutiérrez-Galindo E.A. & Flores-Muñoz G. (2000) - *Heavy metals in the fine fraction of coastal sediments from Baja California (Mexico) and California (USA)*. Environm. Poll., **108**, 453-462.

Yawar W., Naeem K., Akhter P., Rehana I. & Saeed M. (2010) - *Assessment of three digestion procedures for Zn contents in Pakistani soil by flame atomic absorption spectrometry*. J. Saudi Chem. Soc., **14**, 125-129.

Manuscript received 10 March 2010; accepted 14 September 2010; editorial responsability and handling by S. Conticelli.

All in-text references underlined in blue are linked to publications on ResearchGate, letting you access and read them immediately.