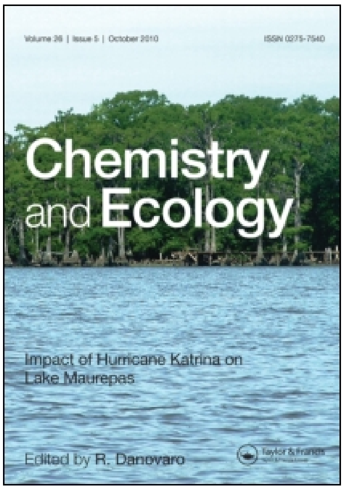

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Determination of Trace Elements in Marine Sediments Collected Between the Volturno River and the Circeo Cape (Tyrrhenian Sea)†

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The determination of Ce, Co, Cr, Cs, Eu, Fe, Gd, Hf, Mn, Rb, Sb, Sc, Ta, Tb, Th, Zn, Zr and Yb by instrumental neutron activation analysis in sediment samples collected from the Gulf of Gaeta (Central Tyrrhenian Sea) is described. The granulometric fractions of the sediments were grouped by cluster analysis into three granulometric facies (sand, clayey silt, and silty clay) which were then assumed to be the main factors controlling the distribution patterns of the elements. This assumption was confirmed by a discriminant analysis carried out on the trace element data.

INTRODUCTION

The study of marine sediments in coastal areas influenced by the inputs of rivers is essential when defining the characteristics of drainage basins and evaluating the effect of man's activities. Thus, if a coastal environ-

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ment is affected by the installation of nuclear or conventional power plants, knowledge of the chemical, mineralogical and granulometric composition of the sediments may be vital in predicting the fate of pollutants discharged during the operation of the plant. As a part of an investigation of the Gulf of Gaeta which has received inputs from a nuclear power plant, through the River Garigliano, for 16 yr, Ce, Co, Cr, Cs, Eu, Fe, Gd, Hf, Mn, Rb, Sb, Sc, Ta, Tb, Th, Zn, Zr and Yb were determined in sediments by instrumental neutron activation analysis (INAA). Twenty-eight samples were collected from the area bounded by the Volturno River and the Sabaudia Lake (Tyrrhenian sea) (Fig. 1).

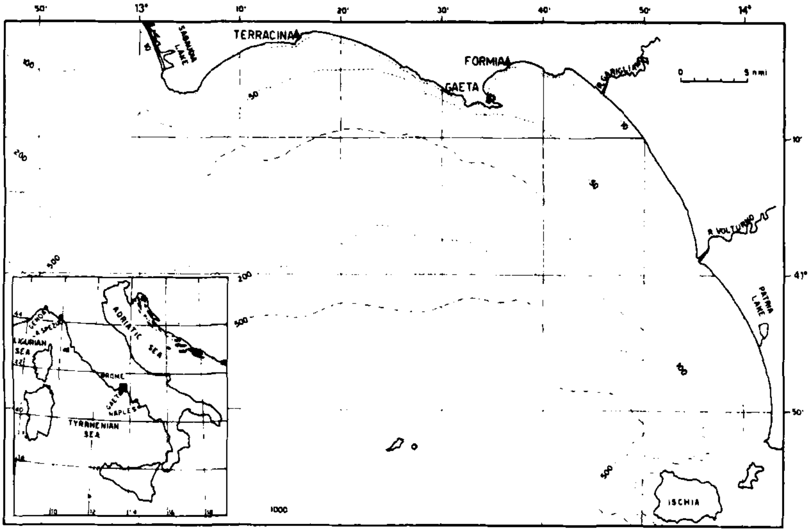

FIGURE 1 Sampling area.

Many elements may occur upon the organic or inorganic surface coatings of particles (Balistrieri *et al.*, 1981; Yuan-Hui Li, 1981). As the importance of this effect is inversely related to the surface area of the particles and therefore to their dimension, 160 additional sediment samples were analyzed for their granulometric composition with the aim of identifying granulometric facies which could be correlated with the observed distribution of the elements. The number of granulometric analyses was sufficient to allow an accurate definition of the sedimentation characteristics of the area, which also plays an important role in the distribution of elements of lithogenic origin.

EXPERIMENTAL

Sample collection and pretreatment

The sediment samples were collected in June 1981 at depths of 10, 20, 40, 70 and 100 m by a free-falling perspex gravity corer (30 cm length; 4 cm diameter). Before chemical analysis, the samples were homogeneized, dried at about 100°C, and then sieved to pass a 250 μm nylon sieve. The sieved samples were ground with an agate mill and subsamples of 500–600 mg were pelletized and placed in polyethylene vials for irradiation. Before granulometric analysis of the fraction <0.063 mm, the samples were dispersed in distilled water containing 0.1% hexametaphosphate.

Neutron activation analysis

The samples were irradiated in the TRIGA MARK II reactor of the Casaccia Center at a flux of 5 × E + 12 n cm^{-2} s^{-1}. The irradiation time varied from 10 s to 30 h according to the elements measured. The gamma-emitting radionuclides were measured after a suitable decay period by using a Ge(Li) detector Canberra (FWHM 1.8 keV at 1332 keV; efficiency 13.6%; peak/Compton ratio 43/1) connected with a multichannel analyzer Canberra 80 (4096 channels). Standardization was carried out using Orchard Leaves (NBS–SRM 1571) and Lake Sediment SL–1 (IAEA–Vienna) standards.

Granulometric analysis

The granulometric fractions between 2 and 0.063 mm were determined by dry sieving, whereas the fractions less than 0.063 mm were analyzed by using a Sedigraph Model 5000 (Micromeritics).

RESULTS AND DISCUSSION

The sampling plan did not allow the distribution patterns of the elements to be clearly related either to the different fluxes of elements transported to the sea upon suspended matter in the Volturno and Garigliano Rivers or to the coastal morphology. Thus, it was argued that the concentration patterns were mainly governed by the granulometric composition of the sediments. In order to check this assumption, a preliminary analysis was performed using the minimum variance clustering method (Orloci, 1978) on the 2 to 0.001 mm granulometric fractions of the sediments. This analysis grouped the 28 stations into 3 granulometric facies (sand, clayey silt, and silty clay) (Damiani *et al.*, 1983). A discriminant analysis (Cooley and Lohnes, 1971) was then carried out upon the trace element data. The analysis showed that the average content of many elements was inversely related with the size of the sedimentary particles. The 28 stations in the plane defined by the first 2 discriminant functions are presented in Fig. 2. The stations grouped into the 3 granulometric facies by means of the discriminant analysis were substantially the same when grouped by means of the cluster analysis. Thus it was confirmed that the granulometric composition of the sediments was primarily responsible for the concentration patterns observed. The elements grouped

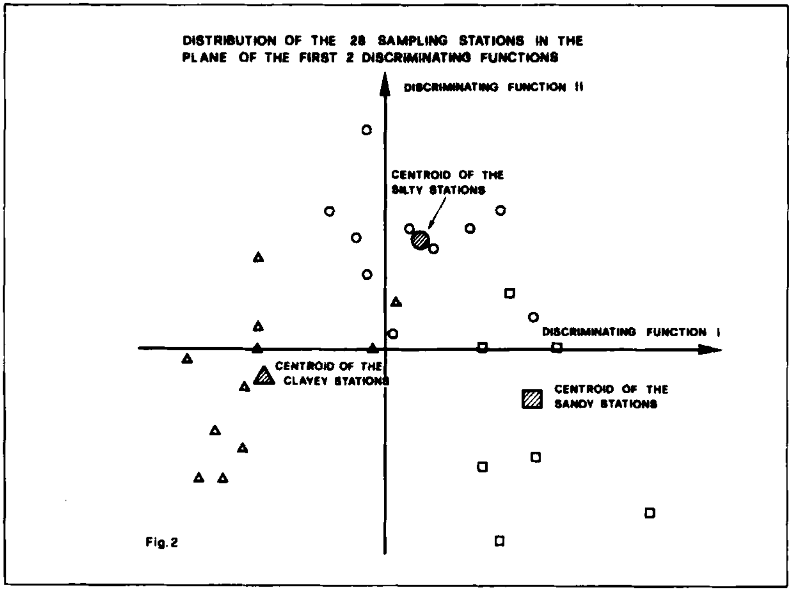

Fig.2

FIGURE 2 Distribution of the sampling stations in the plane defined by the first two discriminating functions.

TABLE I

Analysis of the sediments of the Gulf of Gaeta ($\mu g/g$; *mg/g)

means and standard deviations of the mean for stations belonging to clayey silt facies (n = 7)

Gd	Ce	Th	Hf	Yb	Cr	Zr	Cs	Tb	Sc	Rb	Fe*	Zn	Co	Ta	Eu	Mn	Sb
17	152	21	4	4	89	257	14	1	13	164	41	125	15	1.9	1.3	851	0.17
.8	14	1	.1	.2	2.2	28	.6	.1	.4	18	1	16	.3	.15	.05	67	.02

means and standard deviations of the mean for stations belonging to silty facies (n = 10)

Gd	Ce	Th	Hf	Yb	Cr	Zr	Cs	Tb	Sc	Rb	Fe*	Zn	Co	Ta	Eu	Mn	Sb
15	150	19	5	4	83	323	12	1	13	168	38	111	14	1.8	1.2	770	.16
9	8	1	.2	.2	4.2	25	.7	.1	.6	16	2	11	.6	.1	.04	48	.01

means and standard deviations of the mean for the stations belonging to sandy facies (n = 11)

Gd	Ce	Th	Hf	Yb	Cr	Zr	Cs	Tb	Sc	Rb	Fe*	Zn	Co	Ta	Eu	Mn	Sb
13	137	17	5	3	78	297	10	1	10	131	31	80	12	1.3	1.1	600	.16
.8	10	1	.3	.2	5	17	.7	.04	.4	7	1.6	6	.7	.1	.05	31	.01

according to the granulometric facies are shown in Table I. As this Table shows, the concentration of most, but not all elements, decreases with increasing granulometric size. For example, Hf, Yb, Cr, Tb, Co and Sb were evenly distributed in the 3 facies, whereas the concentration of Ce, Ru and Ta decreased only in the sandy facies. The geochemical interpretation of the discriminant functions was carried out on the basis of their cross-correlations with the original variables (i.e., the trace element contents). The first discriminant function, which yielded 70% of the discriminating power, is an expression of the contents of Sc and of Mn, which were higher in the silty clay facies. Scandium is also representative of Gd, Cs and Fe because of the high statistical correlation between Sc and these elements. The second discriminant function, which yielded 30% of the discriminating power, was an expression of Zr, which was more abundant in the clayey silt fraction. Scandium, Mn and Zr are present in the environment from geochemical sources and not from industrial activities. Because the higher discriminating power is due to these elements, it follows that elements of possible anthropogenic origin (e.g., Zn and Cr) are not so evidently associated with certain granulometric facies as are Sc (Gd, Cs, Fe), Mn and Zr. This suggests that the coastal area surveyed is not polluted by industrial activities.

In order to show the areal distributions of some of the element analyzed, the CalComp's General Purpose Contouring Programme was

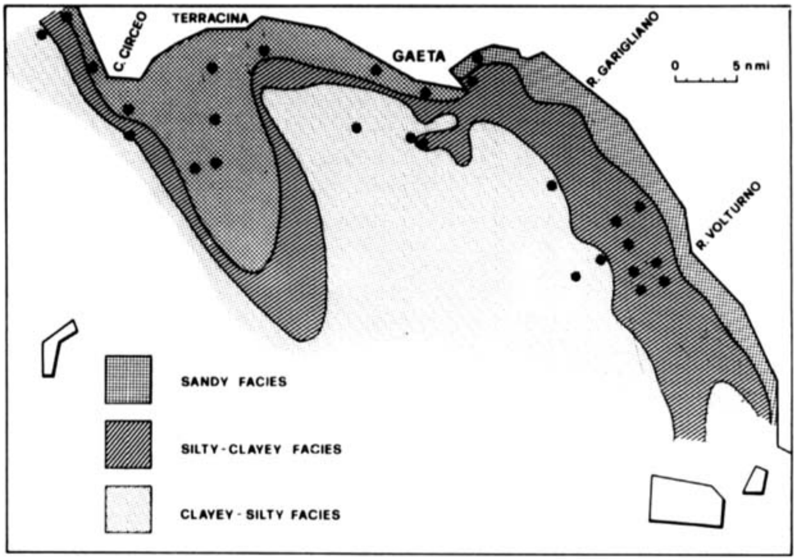

FIGURE 3 Areal distribution of the granulometric facies.

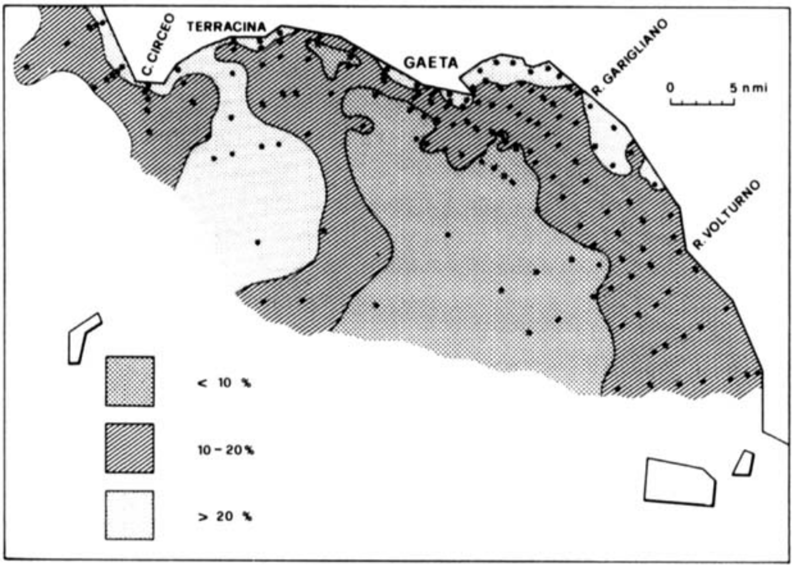

FIGURE 4 Areal distribution of carbonates.

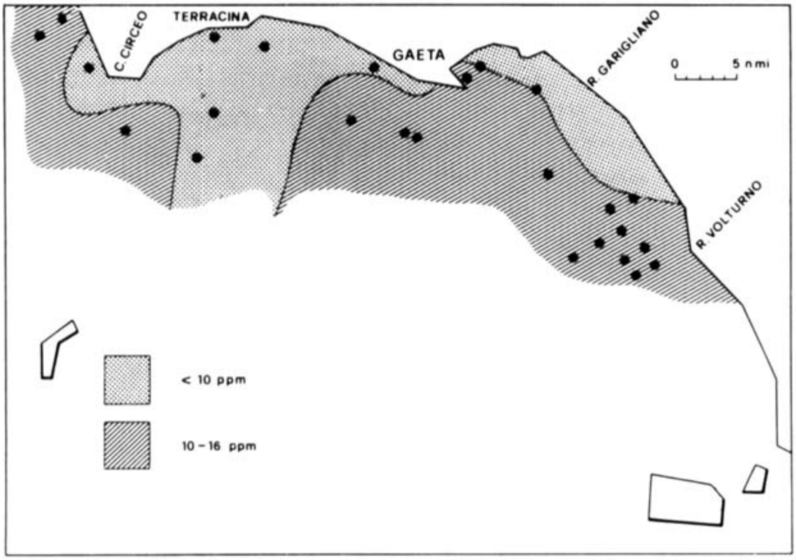

FIGURE 5 Areal distribution of Sc.

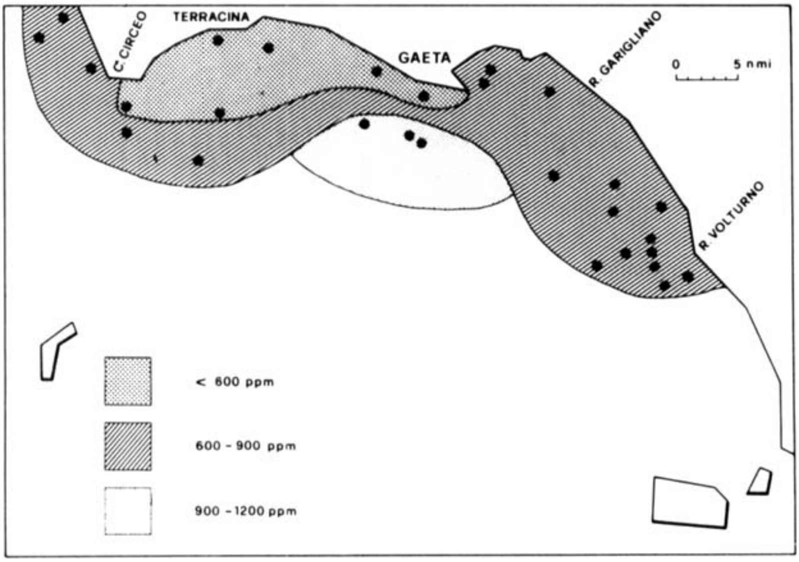

FIGURE 6 Areal distribution of Mn.

used to draw contour diagrams of the element concentrations, carbonates and granulometric facies through the sampling stations.

The areal distributions of the granulometric facies (Fig. 3), carbonates (Fig. 4), Sc (Fig. 5), Mn (Fig. 6), and Zr (Fig. 7) reveal that: (1) the distribution of Sc is inversely related with both the prevailing presence of sands near-shore between the Volturno River and the Gaeta Cape and with the prevailing presence of carbonates in the area delimited by the Gaeta Cape and the Circeo Cape; this agrees with the assumption that Sc is representative of the alumino-silicates; (2) the concentration of Mn is clearly influenced by the diluting effect of carbonates; because of the affinity of 60-Co with Mn (Means *et al.*, 1978), the areal distribution of Mn provides information on the possibility of sediments acting as traps for 60-Co; and (3) the distribution of Zr is influenced by the transport of material of volcanic origin by the Volturno River. The Zr is mainly associated with the silty facies and thus it is transported further out into the sea. This accounts for Zr not being found directly off the mouth of the Volturno River.

The areal distributions of Co (Fig. 8) and Cs (Fig. 9) may provide information on the distribution of 60-Co and 137-Cs released into the marine environment by the operation of the nuclear station. The concentration of Co is lower in the carbonatic near-shore area between Gaeta and Circeo Capes and increases with increasing Mn concentration.

Because Sc and Cs are correlated, the areal distribution of Cs is of course similar to that of Sc. It is also observed that the concentration of Cs tends to increase in sediments collected at greater water depths. The affinity of stable Cs for suspended particulate matter (SPM) in the marine environment is low (oceanic residence time 6 × E + 5 y, Brewer and Spencer, 1975), whereas the residence time of 137–Cs seems to be dependent on both that part of the marine environment investigated (in particular, the chemical composition of the SPM) and the "reactivity" of radiocesium which may be different according to the source (either fallout or operation of nuclear plants). For instance, Noshkin and Bowen (1973) calculated a residence time as low as about 3 × E + 2 y, whereas other authors report that radiocesium remains largely in soluble form in sea water. Thus, the conditions which favour the accumulation of radiocesium discharged by a nuclear station in near-shore sediments may be argued from a knowledge of the concentration pattern of stable Cs on going from shoreline to the open sea.

The areal distributions of Eu (Fig. 10) and Th (Fig. 11) were studied

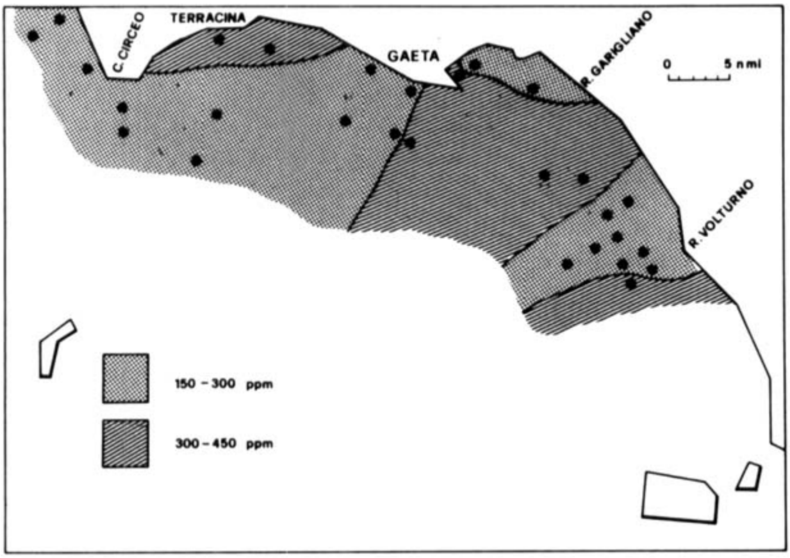

FIGURE 7 Areal distribution of Zr.

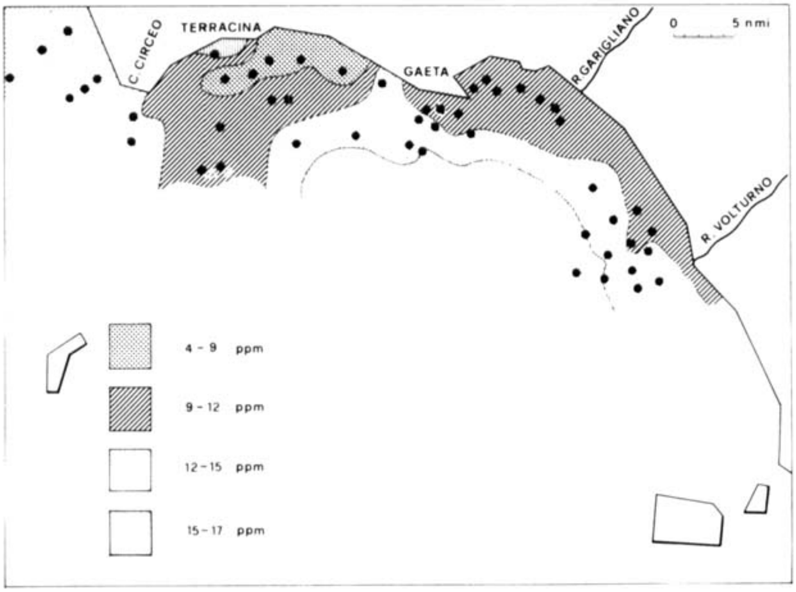

FIGURE 8 Areal distribution of Co.

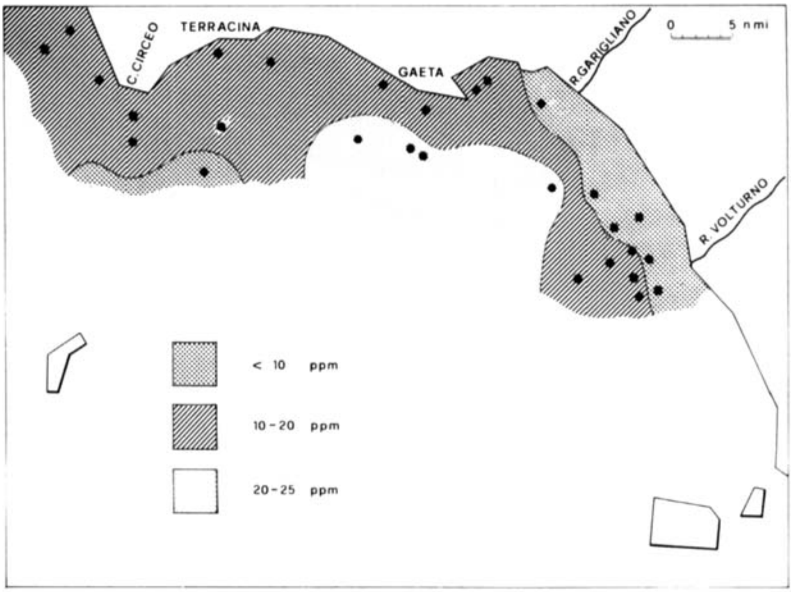

FIGURE 9 Areal distribution of Cs.

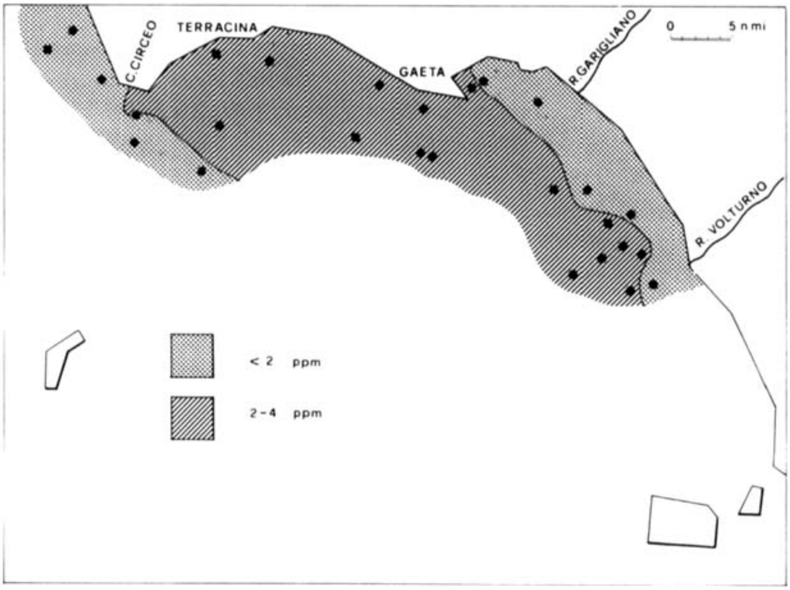

FIGURE 10 Areal distribution of Eu.

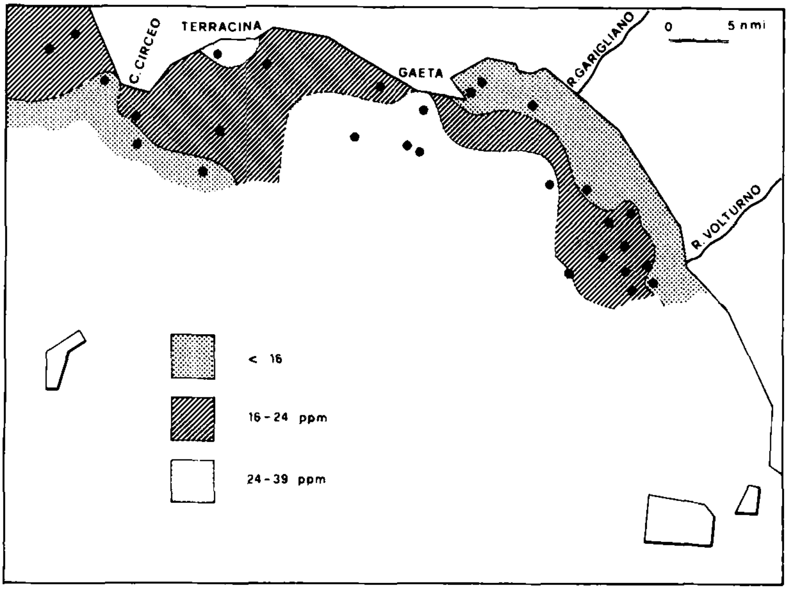

FIGURE 11 Areal distribution of Th.

because these elements may be used as simulators of the behaviour of Am(III) and Pu(IV) in the marine environment (Krishnaswami *et al.*, 1976; Nelson and Lovett, 1978; Weimer *et al.*, 1980; Gueguenjat, 1983). The higher content of Eu was found in sediments with a higher content of carbonates. This agrees with the observation that Eu is more abundant in carbonates and other compounds (e.g., niobates, nitrates, sulfates) with high cation coordination numbers (Kai, 1972). The discriminant analysis above showed that the effect of the granulometric size on the concentration of Eu was negligible.

Thorium is hydrolyzed in the marine environment. In addition, the transport of Th out of surface waters is likely to involve uptake of Th by phytoplankton, ingestion of the phytoplankton by zooplankton, and inclusion of Th in rapidly settling faecal pellets (Feely *et al.*, 1980). Thus, conditions which favour the sedimentation of Th may be reflected by the distribution of Th in the sediments. This might be used tentatively to predict the fate of Pu(IV) in the case of accidental release from the nuclear station.

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