THE RELATION BETWEEN THE GRAIN SIZE COMPOSITION OF THE SEDIMENTS FROM THE NW BLACK SEA AND THEIR TOTAL ORGANIC CARBON (TOC) CONTENT

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Abstract: The relation between the grain size composition TOC (total organic carbon) concentration was examined by linear and non-linear regression analysis of analytical data for more than 500 sediment samples from the NW Black Sea. A significant dependency of the TOC concentration on the percentages of clay and especially the <16 µm fraction (clay plus fine and very fine silt) was identified, the model best fitting the analytical data being exponential. Three groups of sediment samples were identified using the K-means clustering technique, the deep sea sediment samples being clearly singled out.

Key words: NW Black Sea, sediments, grain size, TOC

A positive correlation between the finer grain size fractions (clay and/or silt) and TOC was well established long ago (Buchanan and Longbottom, 1970; Mayer, 1994; Tyson, 1995 etc.). The close association of the two components is probably explained by both the capacity of the finer particles to hinder the diffusion of the oxygen into the sediments, thus favoring the preservation of organic matter and the adsorption of organic particles onto the charged surfaces of the clay minerals. The last process largely depends upon the specific surface of the sediment, so much so that sometimes this parameter is preferred over the percentage of finer fractions as independent variable, determining the TOC concentration in sediments.

Of course there is not a unique, generally valid relation. There are important local variations, determined mainly by the local primary production, sedimentary rates and oxygen regime in the water column and sediments.

The mathematical relation between the percentage of fine fractions and the TOC (organic matter concentration) may be linear (Poppe et al, 2000; Bergamaschi *et al.*, 1997) or exponential (Magni *et al.*, 2008). The percentage of the total TOC concentration explained by its association with the fine fractions of the sediment also varies greatly; sometimes more than 80% of the total TOC concentration may be explained by the percentage of fine fractions.

The present paper tries to establish if such relations are presents in the NW Black Sea and if so, what is the extent of the control exercised by the grain size composition on the TOC concentrations in an area known for its eutrophication problems (Gomoiu, 1992).

MATERIAL AND METHODS

Sediment samples from 67 sampling stations covering all depositional areas in the NW Black Sea (Panin *et al.*, 1999) were collected in the framework of several international cruises: the EROS 2000 1995 and EROS 21 1997 cruises (Secrieru and Secrieru, 2002), the IAEA 1998 Radeux Cruise (Secrieru and Secrieru, 1999) and the 1998 cruise organized by the Max Planck Institute of Marine Microbiology, Germany (Secrieru, D. unpublished data. The primary sediment samples, collected with a 30x30x60 cm Reineck box-corer and/or with a MARK II-400 multicorer were sequentially subsampled up to approximately 50 cm depth into the sediment, a total of 513 samples being collected for laboratory analyses.

Grain size composition of the sediments was determined by the combined method of sieving and pipette (Folk, 1981); besides the main grain size fractions, the <16 µm fraction, including clay and fine and very fine silt, was also determined.

TOC concentrations were determined using a titration method (Gaudette *et al.*, 1974).

RESULTS AND DISCUSSION

The results of the grain size analyses revealed a very high sedimentological diversity, the sediments ranging from pure sands to pure clay. However, the sandy sediments (sand, silty and clayey sand), representing roughly 18% of the analyzed samples) have limited occurrences, appearing as a narrow littoral band (Figure 1) and as isolated bodies, especially in the *Phyllophora* field (Zernov, 1909). Most of the NW Black Sea is dominated by finer sediments, especially silty clays and clayey silts, representing together 58% from the samples.

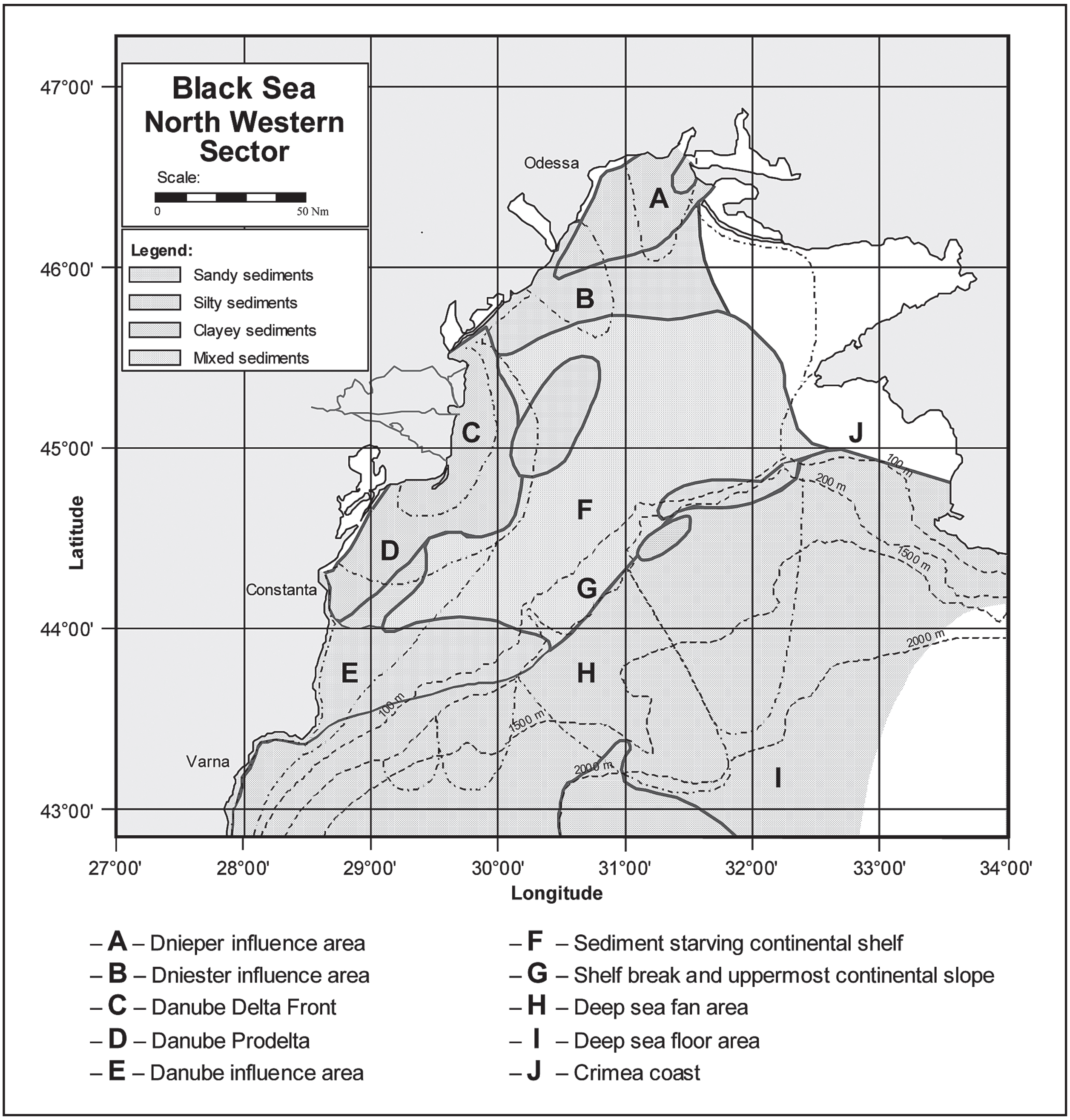


Fig. 1 Depositional zones and sediment types in the NW Black Sea

The TOC distribution pattern in the superficial sediments of the North-Western Black Sea is characterized by a continous offshore increase of the concentrations, the highest being met in the deep sea sediments (Figure 2). Deviations from this pattern are met only in the Odessa bay, in the Dniepr influence area and and the Danube Prodelta and Danube Influence Area. The causes of the deviations are rather similar: high terrestrial TOC inputs from the Odessa human agglomeration and the Danube River and higher local primary productivities due to nutrients inputs from the same sources.

The relation between TOC concentration and the percentage of fine fractions (clay and the fraction <16 μm) was examined by linear and non-linear regression analysis of a statistical sample of more than 500 sediment samples (Figure 3, 4). All sediment types, including the coccolithae mud and the sapropel were represented in the statistical sample.

The results indicated that the exponential model fitted best the analytical results, explaining approximately 30% of the TOC concentration variance versus ≈16% for the linear model if the clay percentage was used as independent variable (Figure 3) and 41% versus 23% of the TOC variance if the percentage of the fraction <16 μm was used as independent variable (Figure 4).

The better correlation recorded between the <16 μm fraction and TOC indicates that the organic matter is associated not only to the clay size; a significant part of TOC is associated to the fine and very fine silt fractions.

Apparently, the percentage of TOC concentration explained by the concentrations of either the clayey fraction or the <16 μm fraction is quite low (16% to 23% for the clay fraction and 30% to 41% for the <16 μm fraction, depending on the chosen model – linear or exponential).

Besides the very high variability of the actual factors controlling the sedimentation and preservation of the organic matter in sediments and determining a high variability of the

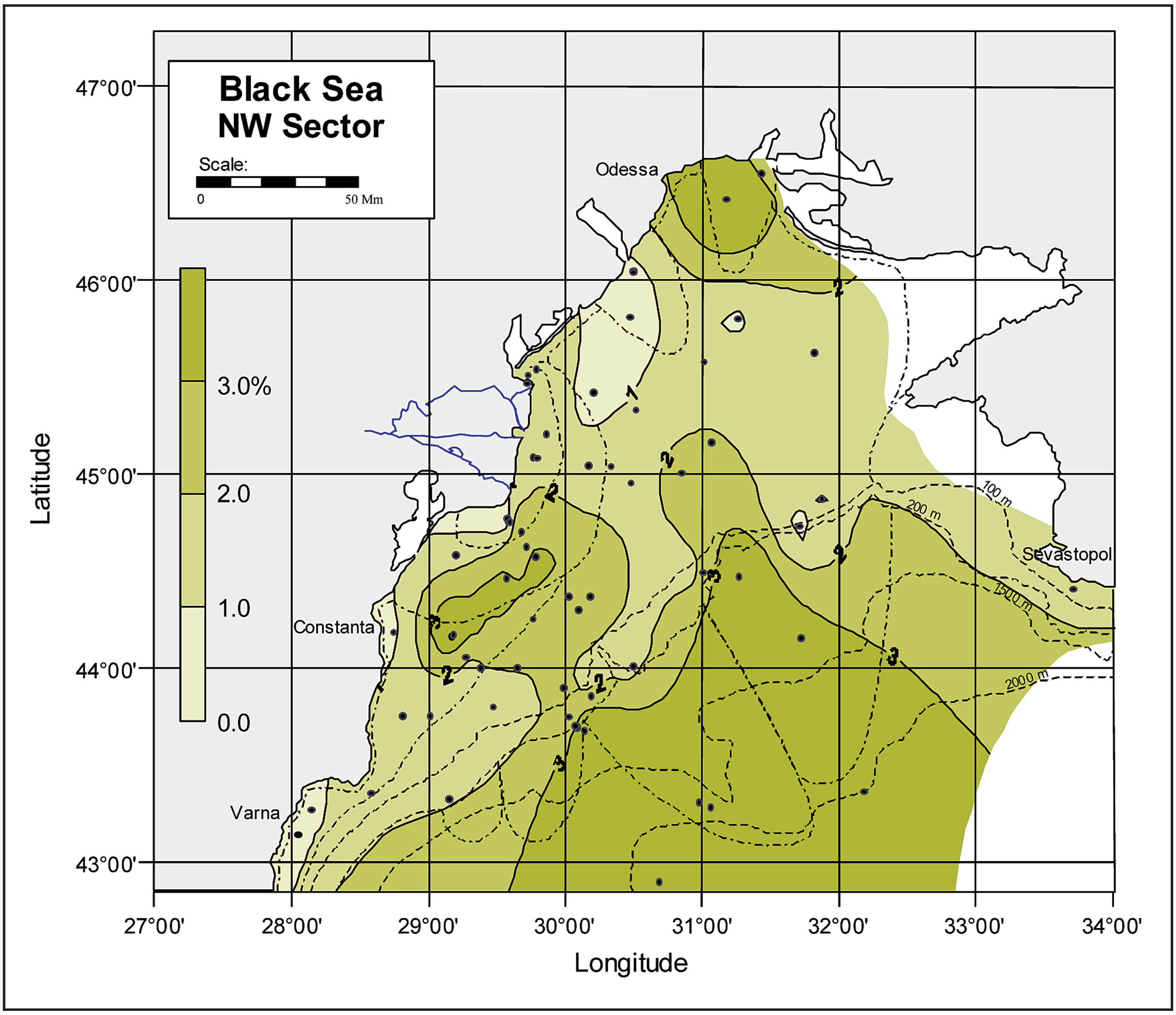


Fig. 2 TOC distribution in superficial sediments from the NW Black Sea

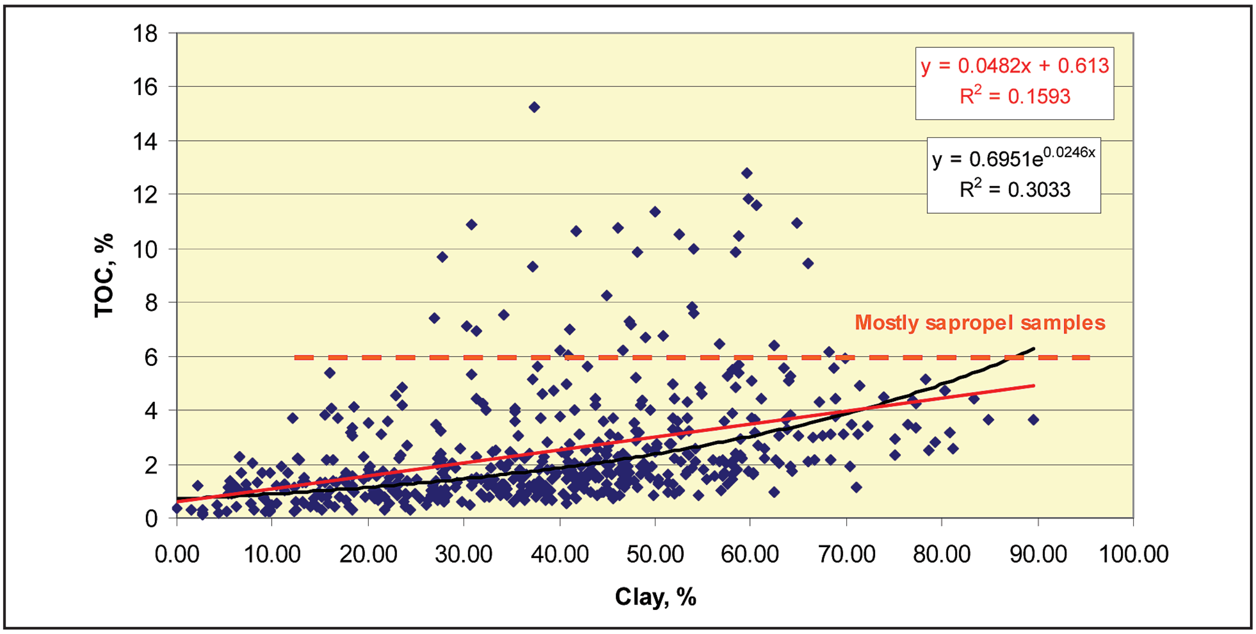


Fig. 3 Relations between the clay fraction and TOC concentrations

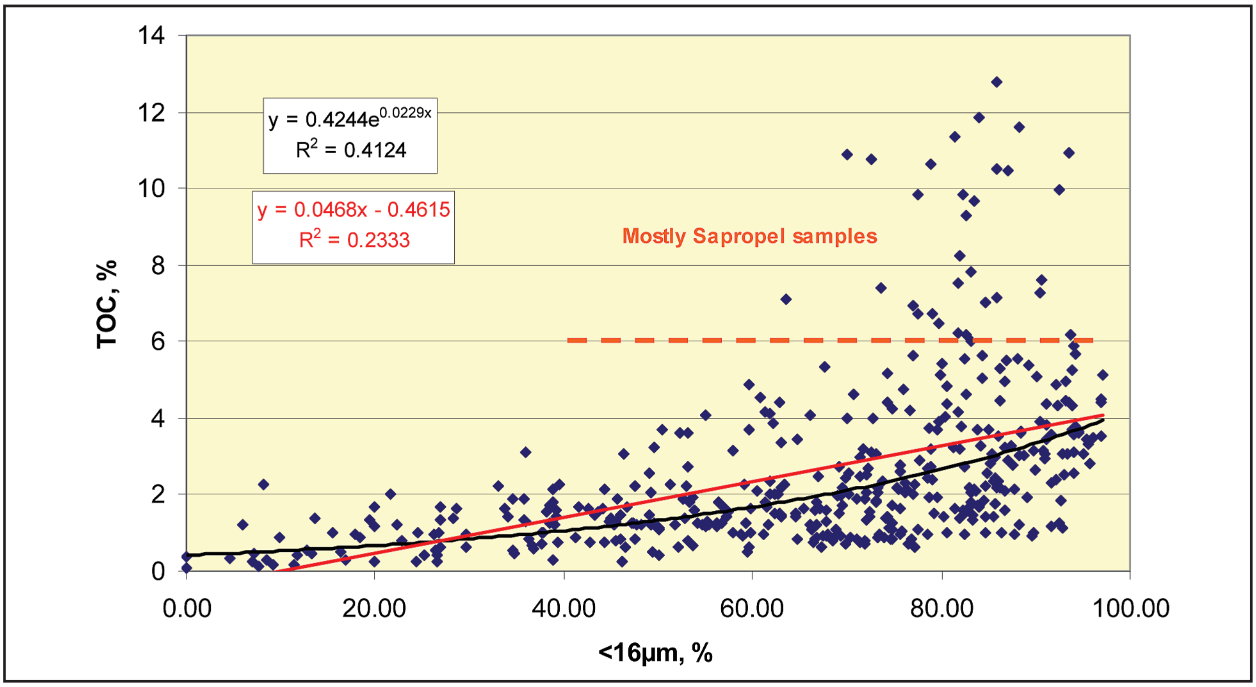


Fig. 4 Relations between the grain size fraction <16 µm and TOC concentrations

TOC concentrations (Cv ≈ 66%) even for the oxic bottoms, characteristic for the NW Black Sea, the relations between the fine fractions and TOC concentrations are substantially altered by the inclusion in the regression analysis of sediment samples with high TOC concentrations (6% TOC was chosen as an arbitrary limit). These samples are coming mostly from the so called sapropel unit (Ross and Degens, 1974), with very few samples from the *fluff* layer, the uppermost layer of sediments consisting mostly in organic flocs. They clearly constitutes a separate group of samples, characterized by a total lack of statistically significant correlation with any major grain size fraction. Moreover, despite the lack of statistical significance, the correlation coefficients indicate a positive correlation between the sandy fraction and the TOC concentration, although the sandy fraction has a minor participation in the constitution of sediments (sand = 0.07 – 4.31%, $r_{TOC\text{-}sand} = 0.114$).

The sediments are fine, silty clays and clayey silts, with the clayey fraction representing 28-68% of the total grain size composition, while the fraction <16 µm varies between 72.5% and 94%.

Considering that the grain size analysis was performed on the integral sediment, without removal of the organic matter, the statistically insignificant correlation of the sandy fraction with the TOC concentrations is most likely explained by the presence of a sizeable part of the organic matter as coarser, even sand sized, fragments of insects, polychaets, fish skeletons etc. (Figure 5).

A well documented grouping of the sediment samples was obtained using the K-means exploratory analysis. The analysis uses a specified number of clusters to compare the between-cluster mean square with the within-cluster mean square and calculates the F-ratios (Table 1). Although the F-ratios cannot be used to test the significance of the clustering, its very high values for TOC and clay or TOC and the <16 µm fraction indicate in both cases the high significance of the variables as differentiating factors.

The analysis identified in both cases three clusters (Figures 6, 7):

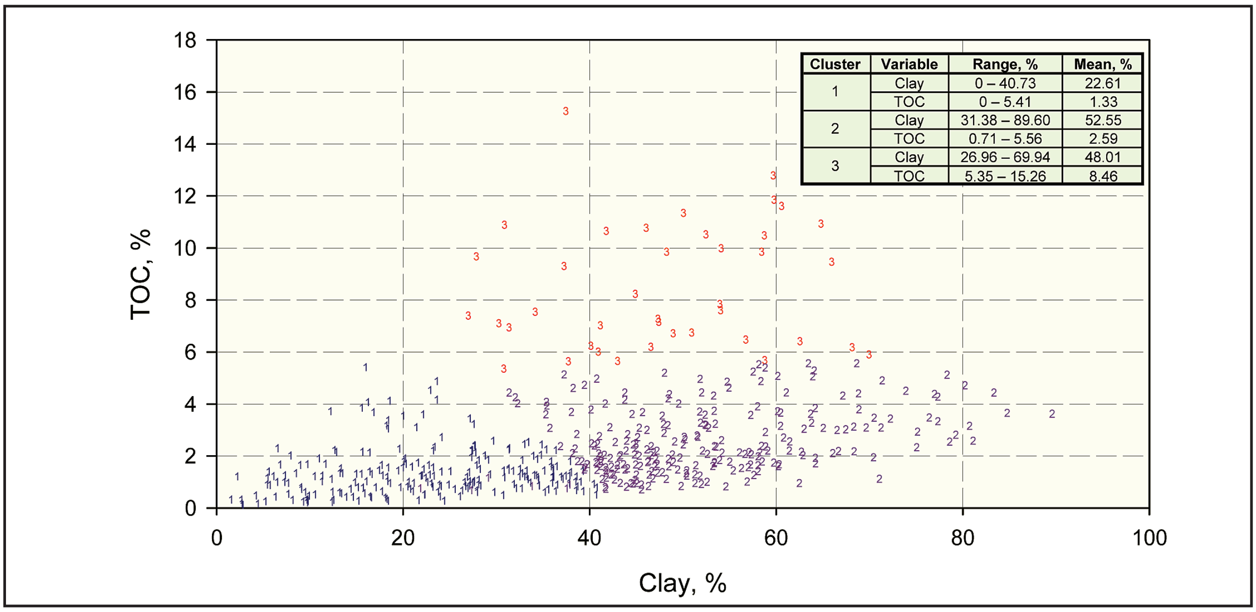
- cluster 1 – coarse to medium grained sediments (clay <app. 40% or <60% clay and fine silt fractions) with low to medium TOC concentrations;
- cluster 2 – medium to fine sediments with medium to medium high TOC concentrations;
- cluster 3 – fine sediments with very high TOC concentrations.

Depending on the pair of variables used for clustering, cluster 3 includes all the sapropel samples with just a few samples from the *fluff* layer of Unit 1 (coccolithae mud) if TOC and clay were used, or all the abyssal sediment samples (sapropel and coccolithae mud) in the second case (TOC and <16 µm fraction used for clustering).

Fig. 5 Insects and polychaets remains (A) and fish skeleton (B) preserved in the Black Sea sapropel

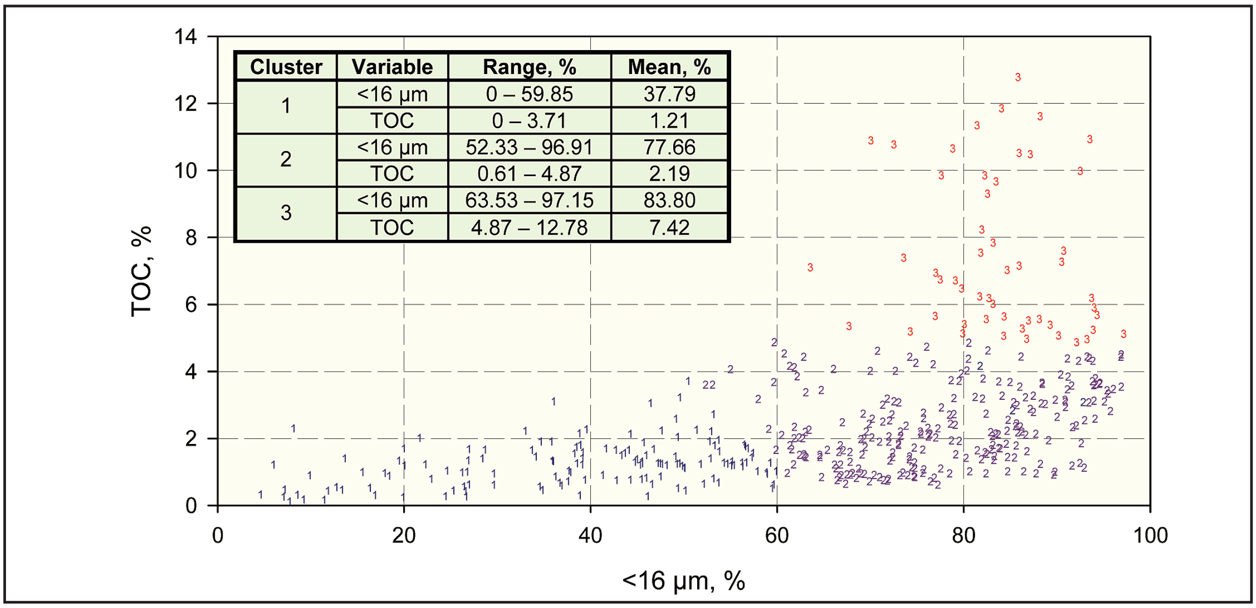
Table 1 Between and within mean squares, F-ratios and probability level for clay-TOC and <16µm fraction-TOC clustering

Relation	Variables	DF1	DF2	Between Mean Square	Within Mean Square	F-Ratio	Prob Level
Clay – TOC	Clay	2	515	55611.82	120.201	462.66	0.000
	TOC	2	549	937.1914	1.496	626.59	0.000
<16µm – TOC	<16 µm	2	430	81191.23	150.03	541.17	0.000
	TOC, %	2	549	963.0012	1.4025	687.03	0.000



Cluster	Variable	Range, %	Mean, %
1	Clay	0 – 40.73	22.61
	TOC	0 – 5.41	1.33
2	Clay	31.38 – 89.60	52.55
	TOC	0.71 – 5.56	2.59
3	Clay	26.96 – 69.94	48.01
	TOC	5.35 – 15.26	8.46

Fig. 6 Clay – TOC clusters



Cluster	Variable	Range, %	Mean, %
1	<16 µm	0 – 59.85	37.79
	TOC	0 – 3.71	1.21
2	<16 µm	52.33 – 96.91	77.66
	TOC	0.61 – 4.87	2.19
3	<16 µm	63.53 – 97.15	83.80
	TOC	4.87 – 12.78	7.42

Fig. 7 <16 µm – TOC clusters

For clusters 1 and 2 the TOC concentrations are rather well correlated with the concentration of the independent variable (clay or <16 µm fraction). Moreover, both clusters are aligned along the same regression line, indicating that they belong to the same population; the percentage of fine material, either clay or <16 µm fraction, largely determines the TOC concentration.

Cluster 3 is characterized by a total lack of correlation between TOC concentrations and the concentrations of the independent variable; TOC concentrations are most likely a function of productivity and do not depend on the grain size composition of the sediments.

CONCLUSIONS

Both the grain size composition and the TOC concentrations of the sediments from the NW Black Sea are highly variable. Statistically significant relations exists between the concentrations of the fine fraction, either clay or <16 µm fraction, in sediments and the TOC concentrations, better described by an exponential model.

Three groups of sediments were identified using the K-means clustering technique: coarse sediments with low TOC concentrations, fine sediments with medium concentrations of TOC and fine sediments (deep sea sediments) with high TOC concentrations.

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