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Surface sediment chemistry in the Olympic Games 2004 Sailing Center (Saronikos Gulf)

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Abstract

Construction of the Olympic Games 2004 Sailing Center is planned in the Saronikos Gulf, in the area of Agios Kosmas. A multi-disciplinary base-line study was carried out to provide background levels of inorganic and organic pollutants before the construction. Two shallow reefs (water depth 2-3 m) are the predominant features in the area's underwater topography. The reef consists of solid rock formations and pebbles, whereas sandy sediments cover predominantly the remaining seabed. Some pockets of fine-grained sand were identified within the existing marina. Sedimentary heavy metal contents were found to be low, showing only slight heavy metal enrichment, attributed mainly to heavy mineral abundance in the area. A small enrichment for lead could be related to anthropogenic sources. Patterns of low concentrations were observed for organic carbon and organic nitrogen. Conversely, the sediment petroleum hydrocarbon content was found to be relatively high, implying anthropogenic pollution related to ship effluents and increased marine traffic.

Keywords: Sediment, Heavy metals, X-ray fluorescence, Polycyclic aromatic hydrocarbons, Agios Kosmas, Saronikos Gulf.

Introduction

Marine sediments are repositories of various organic and inorganic substances introduced into the sea and their study provides valuable information about the quality of the natural system (FÖRSTNER & WITTMAN, 1983; SALOMONS & FÖRSTNER, 1984; CHESTER, 1990; HOROWITZ, 1991). Aliphatic hydrocarbons, polycyclic aromatic compounds (PAH) and trace elements are ubiquitous constituents of coastal sediments and their background concentrations have been increased by human use, causing in many cases adverse effects, especially in coastal areas adjacent to modern megapolis and harbours (STOFFERS *et al.*, 1986; TESSIER & CAMPBELL, 1988; CARLSON & MORRISON, 1992; BUCKLEY *et al.*, 1995; MATTHAI *et al.*, 2002). For this reason, the geochemistry and environmental impact of these compounds have attracted the interest of many researchers worldwide.

The city of Athens (population of 5,000,000) has been elected as the host city for the Olympic Games of 2004. Within this framework, various public works have been planned and/or are underway along the coastal zone of Athens. The Olympic Sailing Center (OSC) of Agios Kosmas is one of the projects exhibiting particular interest, as it is located in a highly populated coastal area of the Saronikos Gulf, with important tourism infrastructure (hotels, marinas, etc.). However, Saronikos coastal zone sediments have not been adequately studied and very limited data exist for the various pollutant substances and especially the organic ones.

The National Centre for Marine Research (NCMR), in collaboration with the Olympic Games Organising Committee, has carried out a detailed environmental survey in the OSC area, in order to: (a) support the future constructions with geological and geotechnical information; (b) to record the present environmental conditions; (c) to assess potential pollution problems and their sources; and (d) to monitor the environmental conditions during and after the construction. The aim of this contribution, which is a part of the detailed environmental survey, was to study sediment texture, organic matter, trace metals and aliphatic and polycyclic aromatic hydrocarbons in the vicinity of the OSC, in order to evaluate the sediment contamination. The knowledge of sediment composition and contamination levels in this area is also essential as dredging operations are expected to be carried out during the marine constructions, and the results of this work could be used as reference for future studies investigating the impact of the constructions and the marinas operation in the coastal environment.

Regional setting

The study area lies in the coastal zone of Athens and is part of the eastern Saronikos Gulf (Fig. 1). The Saronikos Gulf is one of the most heavily polluted regions of Greece, mainly due to the domestic and industrial effluents that were released untreated into the sea until early the 1990s (average flow rate 600,000 m^3 day^{-1}; MAKRA *et al.*, 2001). The sediments of the Saronikos Gulf are particularly enriched in heavy metals and organic compounds, especially around the industrial zone (Elefsis Bay), the Piraeus Port and the old sewage outfall area that was situated about 2 km NW of Piraeus port (PAPAKOSTIDIS *et al.*, 1975; GRIMANIS *et al.*, 1977; VOUTSINOU-TALIADOURI, 1981; ANGELIDIS & GRIMANIS, 1987; KALOGEROPOULOS *et al.*, 1989; VOUTSINOU-TALIADOURI *et al.*, 1989; OCHSENKÜHN & GRIMANIS, 1992). Eutrophication problems have also been documented, as well as major ecological degradation in some areas (FRILIGOS, 1982; FRILIGOS, 1985; FRILIGOS, 1989; FRILIGOS & BARBETSEAS, 1990; THEODOROU, 1995; KARYDIS & TSIRTSIS, 1996; THEODOROU, 1997). For example, zoobenthic studies conducted in the 1970s (ZARKANELLAS & BOGDANOS, 1977) revealed the presence of a 1 km azoic zone close to the outfall. This pattern was also observed in 1992, and a less heavily impacted zone has been identified extending up to 2.5 km south of the outfall (MAKRA *et al.*, 2001). The construction of the Waste Water Treatment Plant (WWTP) on the little island of Psyttaleia (Fig. 1) and its operation since 1994, has helped to significantly improve the environmental conditions (hence, of the marine ecosystem) and further improvement is expected in the future due to the improvement of the WWTP facilities (NCMR, 1999; SIOKOU-FRANGOU *et al.*, 2000).

The area under investigation lies a few kilometres SE of the Piraeus Port; it is about 3 km long parallel to the coast and 1.2 km wide (Fig. 1). At the southeastern part of the area a marina was constructed in the early 1970s, but it remains underdeveloped till today. The Olympic Sailing Center will be hosted in the existing marina after major reconstruction.

The mean depth in the study area does not exceed 10 m and the maximum depth reaches 25 m at the NW edge. Two reefs, in the northern and the central sectors, reach depths of 1 m and 3 m, respectively, and are separated by an open valley. These reefs form the main morphological features on the seabed, which in general is dipping westwards with slope values of 1 % - 4 % (Fig. 1).

Winds predominantly blow from the NW and the NE (ATHANASOULIS & SKARSOULIS, 1992). Although such northerly winds are most

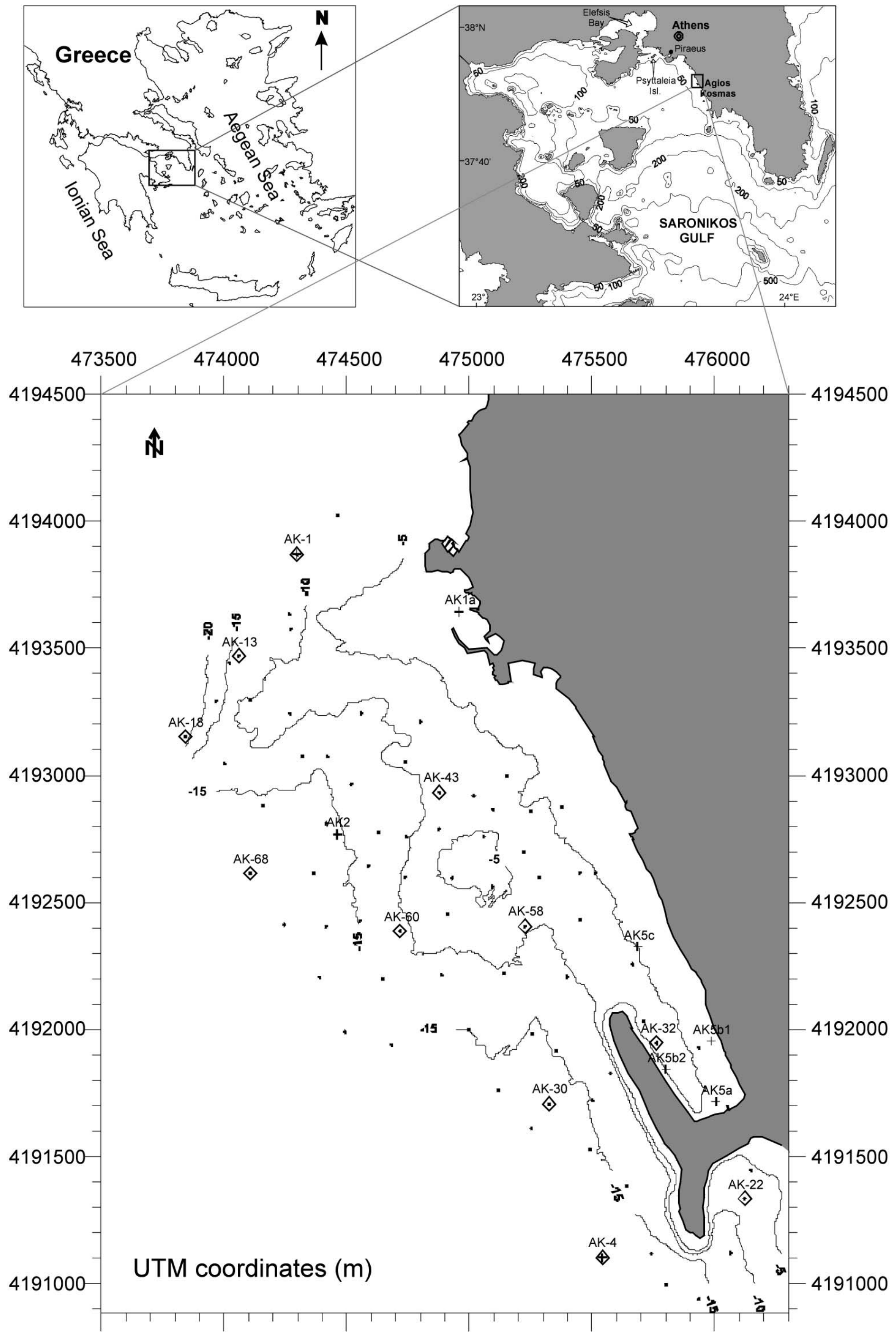

Fig. 1: Location of the study area. Depth contours in metres. Dots: grain-size and carbonate content; rhombs: organic carbon and total nitrogen; crosses: PAH analysis.

frequent, it is the winds blowing from the south that generate the highest waves, because the geometry of the coastline of Saronikos Gulf limits the fetch from all directions except south.

Dissolved oxygen levels were measured in the area in the period April 1999-February 2000 (sampled 8 times) and were found to be relatively elevated throughout the water column, ranging between 4.3 and 6.3 ml/l (NCMR, 2000).

Materials and Methods

Sample collection

Surface sediment samples were collected on board the 14-m long research vessel PLOIGOS of the Public Oil Company of Greece equipped with differential GPS, during a single cruise (April 1999). Seventy-five surface sediments were recovered with a Van-Veen grab. We were careful to collect samples from the inner part of the grab, to avoid any possible contamination. Samples to be analysed for heavy metals were collected with plastic tools, while stainless steel tools were used for the samples dedicated for organic geochemical analyses. All samples were transported to the laboratory within a few hours. Samples for trace elements were air-dried and those for organic analysis were freeze dried.

Grain-size and carbonates

Grain-size analysis was performed in all 75 samples by dry sieving (FOLK, 1974). Sediment mean size Mz was calculated from cumulative curves after FOLK (1974). Carbonate contents in all samples were determined by the carbonate bomb (MÜLLER & GASTNER, 1971).

Trace elements and aluminium

Eleven selected samples were ground to a fine powder in a twin swinging motorised mill with agate mortar and balls and were analysed for their chemical composition in a Philips PW-2400 wavelength X-Ray fluorescence analyser, equipped with Rh-tube, according to the following procedure: 5 g of powdered sample were mixed with 0.5 g of wax and subsequently pressed in a 31 mm aluminium cup. The powder pellets were analysed in the XRF to determine trace element (V, Cr, Mn, Co, Ni, Cu, Zn, As, Rb, Sr, Pb) and aluminium concentrations. Analytical accuracy was checked by parallel analysis of the certified sediment standards MESS-2 and PACS-2 and was found better than 5% for all elements analysed. Analytical precision was checked in sample replicates and was always better than 0.5%, showing the excellent reproducibility of the method (KARAGEORGIS *et al.*, 2000a).

Organic carbon and total nitrogen

Eleven dried sediment samples were thoroughly ground in an agate mortar and very well homogenised to reduce variability between replicates. Splits of 10-20 mg of powdered homogenised sample were weighed accurately (0.01 mg) into specially designed silver containers. Organic carbon was determined after removal of inorganic carbon by acidification of samples with 20 μL of 6N HCl at 60° C (this treatment was conducted five times at 12 hour intervals). After the inorganic carbon removal, the samples were dried at 60°C overnight. After drying, the containers were pinched closed, compacted and formed into a ball. The balls then were placed in the auto-sampler of a Fisons Instruments CHN elemental analyser type EA-1108 to determine C and N concentrations. The operating parameters were very similar to those reported by VERARDO (1990), CUTTER & RADFORD-KNOERY (1991) and NIEUWENHUIZE *et al.* (1994). The precision of the method is within 5 % for both carbon and nitrogen. For the analysis of the sediment samples for total carbon and nitrogen, separate splits (10-15 mg) of the samples were transferred into tin cups that were sealed and analysed without any pre-treatment.

Hydrocarbons

Eight sediment samples were analysed for aliphatic and polycyclic aromatic hydrocarbons (PAHs). The analytical methodology used was based on UNEP suggestions (UNEP/ IOC/ IAEA, 1992). Briefly, the sediment samples, after freeze-drying, were spiked with known amounts of internal standards (androstane and deuterated PAHs) and Soxhlet extracted for 24 hours with a 2:1 mixture of dichloromethane and methanol. The extracts were saponified with methanolic KOH and the unsaponified material was further extracted with n-hexane. The hexane extracts after drying with sodium sulphate and concentration in a rotary evaporator were cleaned-up and fractionated in a glass column loaded with 2 g of activated silica gel. Two fractions were collected: the first one, containing the aliphatic hydrocarbons, with 10 ml of n-hexane and the second containing the PAHs with 10 ml of a 9:1 mixture of hexane and ethyl acetate. The two fractions were analysed in a gas chromatograph – mass spectrometer (HP 6890 GC-MS) operating in full scan mode. A CP-Sil8 MS (30 m X 0.25 mm, 0.25 μm film thickness) analytical column was used and the oven temperature program was the following: 60 ˚C for 1 min and then to 290 ˚C with a rate 15 ˚C/min and final hold for 10 min. The quantitation was based on the internal standards added in the beginning of the procedure. The detection limit of the individual compounds was estimated as 0.05 ng/g dry sediment.

Results and Discussion

Grain-size

The seabed around the northern reef is covered by medium sand (1-2 φ) (Fig. 2a). The central sector of the study area is covered by coarse sand (0-1 φ). The central reef sector contains very coarse sand (0 to -1 φ). In the

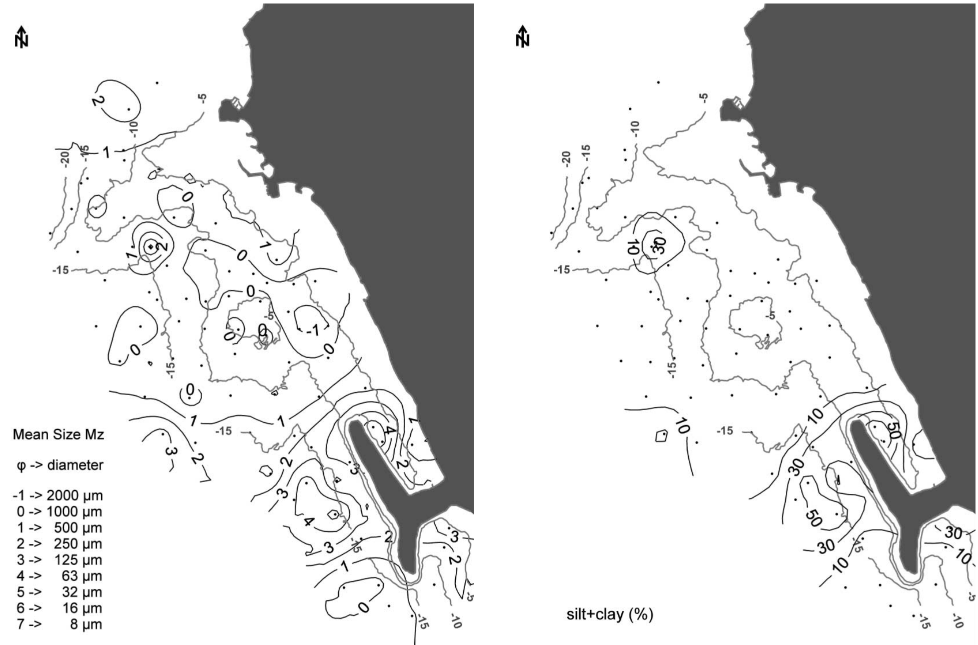

Fig. 2: (a) Surface sediments mean-size spatial distribution (in φ units); (b) Silt+clay (fraction <63 μm) spatial distribution (%). Major depth contours in gray color (m).

immediate vicinity of both reefs, the sea-bottom was rocky without any sediment cover. Most likely, the coastal currents and the waves have frequently reworked these sediments, whereas their finer components have been winnowed toward the deeper waters. Relatively finer sediments (mud) prevail in the inner part of the existing marina, as well as in the outer southwestern part of the marina. This feature is more clearly illustrated in the distribution of the sediment fraction <63 μm (Fig. 2b). Inside the sheltered marina, fine-grained sandy silts have been deposited (see also Table 1). The sediments that cover the sea floor originate from weathering of the Plio-Pleistocene sedimentary deposits that outcrop locally on the adjacent land area and along the coastline of the study area (KARAGEORGIS *et al.*, 2000b). These formations consist of laterally and vertically alternating, terrestrial or lacustrine red clay, marls, sandstones and consolidated conglomerates and breccia.

Carbonates

Sedimentary carbonate concentrations were found to be very high, between 39.9 and 87.9 %, with an average content of 65.2 %. These high carbonate contents reflect both the lithology of the terrestrially exposed formations and the abundant presence of biogenic carbonates (bivalves, echinoderms, etc.). Spatially, the carbonate contents are relatively homogeneous throughout the study area, but

Table 1

Carbonate, organic carbon, total nitrogen, Corg/N ratio and trace metal contents in the Agios Kosmas surface sediments.

Station	**M_z (φ)**	**<63 μm (%)**	**carbonates (%)**	**C_{org} (%)**	**N^{total} (%)**	**C_{org}/N**	**Al (%)**	**V (ppm)**	**Cr (ppm)**	**Mn (ppm)**	**Co (ppm)**	**Ni (ppm)**	**Cu (ppm)**	**Zn (ppm)**	**As (ppm)**	**Rb (ppm)**	**Sr (ppm)**	**Pb (ppm)**
AK-1	2.4	0	56.5	0.26	0.02	11.5	1.25	29	64	204	2	26	3	27	3.8	19	1427	15
AK-4	-0.2	0	84.8	0.41	0.04	9.3	0.46	27	33	104	2	15	1	19	n.d.	7	3653	16
AK-13	0.8	0	57.4	0.18	0.01	13.6	1.25	35	75	191	1	23	0	26	5.8	17	1550	11
AK-18	0.3	0	60.9	0.43	0.05	8.4	0.50	16	24	118	1	15	3	27	n.d.	8	3578	24
AK-22	1.4	0	72.4	0.21	0.02	14.0	2.34	50	87	318	7	51	16	68	16.8	32	443	26
AK-30	4.7	64	41.5	0.81	0.06	12.6	3.07	60	109	343	7	68	20	75	19.8	43	779	38
AK-32	5.5	92	43.2	0.93	0.09	10.9	3.23	63	111	346	8	77	28	87	21.4	48	356	48
AK-43	-0.9	0	44.2	0.52	0.05	10.4	2.16	48	69	212	4	36	3	45	6.7	30	2028	18
AK-58	0.4	0	61.5	0.29	0.02	13.0	1.07	40	58	220	2	26	3	28	4.5	15	1212	13
AK-60	1.0	0	77.5	0.26	0.03	9.1	1.28	37	63	175	2	22	1	28	3.4	17	2229	13
AK-68	0.7	0	74.0	0.56	0.07	8.3	0.30	19	18	102	3	11	2	21	n.d.	7	3831	20
Core sample	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	4.43	77	112	727	15	106	22	78	11	65	1256	46
min	-0.9	0	41.5	0.18	0.01	8.3	0.3	16	18	102	1	11	0	19	3	7	356	11
max	5.5	92	84.8	0.93	0.09	14.0	3.2	63	111	346	8	77	28	87	21	48	3831	48
mean	1.3	16	57.4	0.43	0.04	10.9	1.6	38	63	213	4	34	8	42	10	22	1636	22
median	0.7	0	59.2	0.36	0.04	10.6	1.3	39	66	202	3	25	3	28	6	17	1381	19

n.d.: not determined

Fig. 3: Surface sediments carbonate content spatial distribution (%).

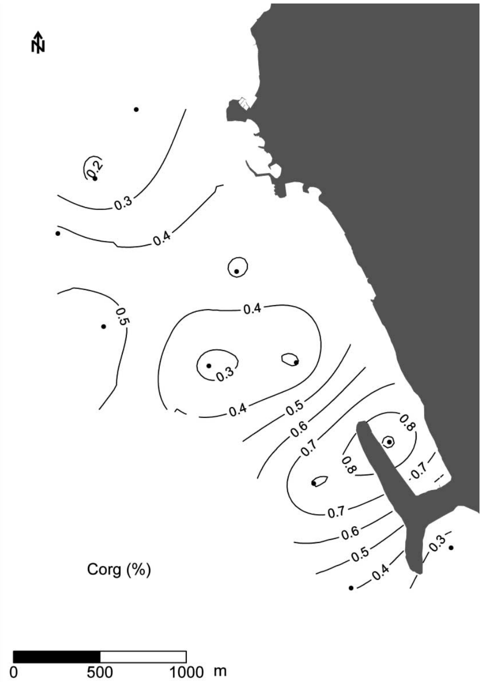

Fig. 4: Spatial distribution of organic carbon contents (%) in the surface sediments of the Agios Kosmas area.

maxima occur in the central and southern sectors (Fig. 3).

Organic carbon and total nitrogen

Organic carbon content was generally low (Table 1), between 0.18 % and 0.93 % (mean value 0.43 %). Its spatial distribution (Fig. 4) seems to follow the same pattern as the grain size distribution: i.e., the highest values were recorded in the muddy sediments in the southern sector of the study area, and close to/inside the existing marina. Lowest values were found in the area around the two reefs where the seabed is covered with coarse sand. The total nitrogen values were always below 0.09 % (mean value 0.04 %). The C_{org}/N ratios were slightly higher than expected for algal organic material, varying between 8.3 and 14.0 (mean value 10.9). These values could suggest influence from vascular land plants.

Trace elements

Geochemical analysis results of the bulk sediment are presented in Table 1. Spatial distributions were found to be similar to one another, except for Sr (Fig. 5). In general, higher trace element concentrations were observed in the southern part of the study area, in the immediate vicinity of the marina. All concentrations decrease in a northwestern direction and towards the open sea; high concentrations coincide with the presence of fine-grained sediments (muds, see Fig. 2a, b), which cover the seafloor inside and outside the marina, due to enhanced trace metal absorption to fine sediments as a function of the enhanced surface areas and/or mineralogical differences between fine and coarse sediment (e.g., HOROWITZ, 1991 and references therein). Organic carbon concentrations were also higher in this area, suggesting that part of the trace metals may be

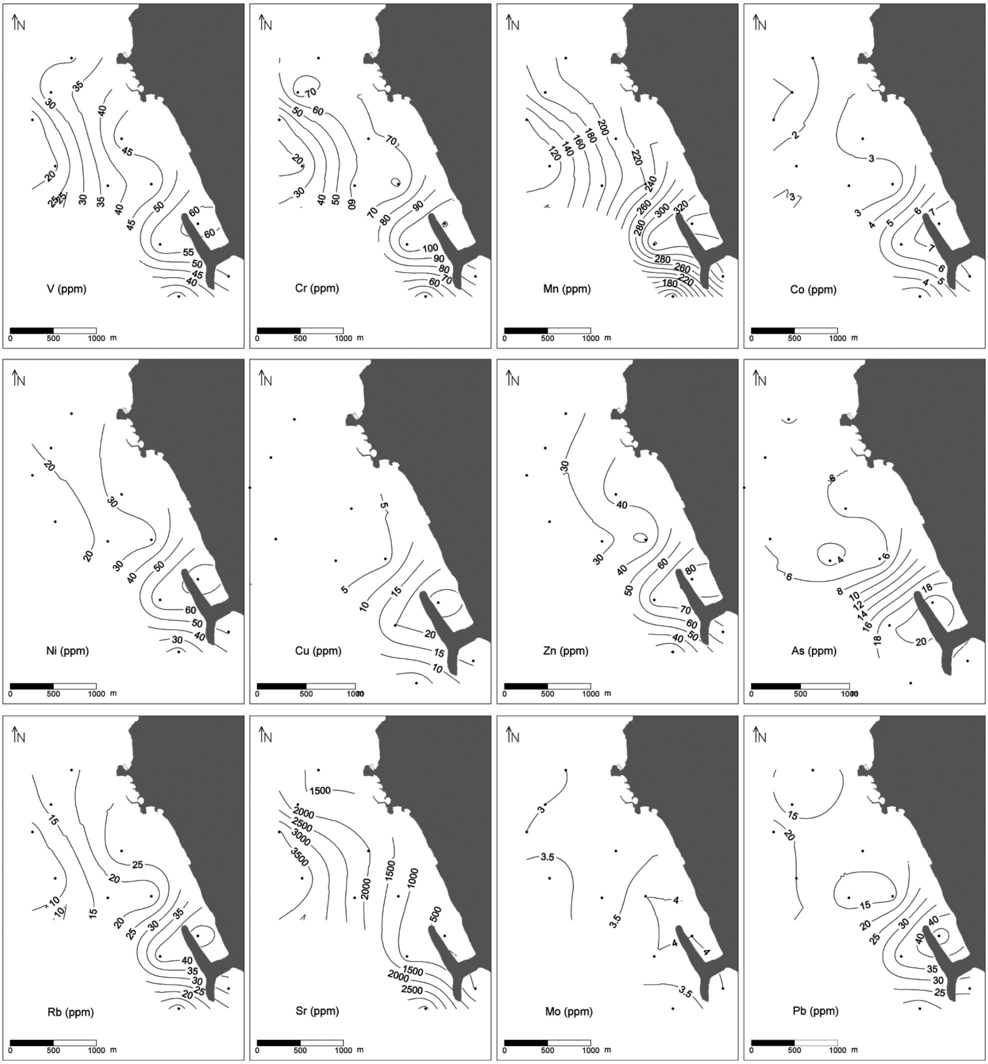

Fig. 5: Spatial distribution of trace metal contents in the surface sediments of the Agios Kosmas area. All contents are in ppm.

associated by adsorption to, or organometallic bonding with organic matter.

Elemental interrelations, as well as their affinity with mean grain-size and carbonate, organic carbon and total nitrogen concentrations, and aluminium, are discussed through the correlation coefficient matrix presented in Table 2. The statistical significance of the correlation coefficients was assessed by a *t*-test given by:

$$t = \frac{r\sqrt{n-2}}{\sqrt{2-r^2}}$$

where n is the number of observations and r the correlation coefficient (DAVIS, 1986); p values were determined at 1 and 0.1% significance levels.

Table 2
Correlation coefficient matrix for mean size, carbonate, organic carbon, total nitrogen and trace metals in the Agios Kosmas surface sediments (n = 11). Double underline: $p < 0.001$, single underline: $p < 0.01$.

	M_z	Carb.	C_{org}	N_{total}	Al	V	Cr	Mn	Co	Ni	Cu	Zn	As	Rb	Sr	Pb
M_z	1.000															
Carb.	-0.537	1.000														
C_{org}	0.664	-0.159	1.000													
N_{total}	0.479	0.102	0.946	1.000												
Al	0.723	-0.859	0.558	0.304	1.000											
V	0.639	-0.827	0.499	0.231	0.962	1.000										
Cr	0.734	-0.920	0.381	0.091	0.951	0.942	1.000									
Mn	0.749	-0.836	0.424	0.143	0.953	0.934	0.952	1.000								
Co	0.708	-0.592	0.656	0.478	0.877	0.840	0.754	0.858	1.000							
Ni	0.819	-0.751	0.652	0.410	0.971	0.931	0.914	0.953	0.923	1.000						
Cu	0.857	-0.558	0.710	0.524	0.861	0.802	0.777	0.869	0.936	0.953	1.000					
Zn	0.766	-0.693	0.645	0.434	0.949	0.892	0.856	0.927	0.957	0.982	0.964	1.000				
As	0.766	-0.667	0.744	0.673	0.943	0.917	0.964	0.981	0.959	0.976	0.971	0.981	1.000			
Rb	0.761	-0.837	0.613	0.370	0.996	0.949	0.937	0.946	0.894	0.981	0.889	0.959	0.939	1.000		
Sr	-0.626	0.891	-0.145	0.148	-0.840	-0.851	-0.925	-0.935	-0.654	-0.808	-0.680	-0.751	-0.846	-0.821	1.000	
Pb	0.824	-0.359	0.858	0.742	0.741	0.644	0.600	0.695	0.853	0.855	0.946	0.883	0.946	0.785	-0.440	1.000

Elements V, Cr, Mn, Co, Ni, Cu, Zn and As are significantly correlated to Al and Rb ($p < 0.001$), which are well-known proxies of the detrital fraction (e.g., CALVERT, 1976). Rubidium is principally associated with the aluminosilicates (Al: Rb $r = 0.996$, $p = 0.001$), is particularly immobile in the marine environment and exhibits uniform contents in the oceans (SMITH *et al.*, 1965). Moreover, the aforementioned elements are also positively correlated to the mean grain-size (in φ units), suggesting that they are preferably constituents of the fine alluminosilicates. We therefore assume that they mainly reflect a natural detrital origin and are not related to anthropogenic pollution. However, some elements, i.e. Pb, Cu, Co, Ni, Zn, and As, are positively (to a lesser extent) correlated to organic carbon, implying an association to the organic matter. Carbonates and strontium strong correlation ($r = 0.891$, $p < 0.001$) reflect their association to biogenic carbonates, which are abundant in the area; Sr can replace Ca due to similar ionic radii.

To better elucidate the factors governing the trace metal distribution in the area, we performed principal factor analysis on the data. The data set was log-transformed to ensure homogeneity of variance and overcome the consequence of different units (per-cent and ppm) (REIMANN *et al.*, 2002). The log-normalized variables were tested whether or not have a normal distribution (REIMANN

Table 3
Results of principal factor analysis with Varimax rotation.

Component	Factor 1	Factor 2
Corg	-.061	.917
V	.927	.190
Cr	.978	.005
Mn	.964	.223
Co	.590	.687
Ni	.911	.397
Cu	.621	.717
Rb	.932	.287
Sr	-.903	-.283
Pb	.296	.922
% of variance explained	74	18

& FILZMOSER, 2000) with a Kolmogorov-Smirnov test. A set of ten representative elements was selected to enter factor analysis with Varimax rotation, as the available number of measurements ($n = 11$) did not permit the use of all variables. Two factors were extracted, which explain 92 % of the total variance (Table 3). Factor 1 explains 74 % of the total variance. Geochemically Factor 1 is dominated by the alluminosilicate-related elements, expressed with high loadings for Rb (representative of detrital origin), Cr, Mn, V, and Ni. The other trace metals participate positively to this factor, but with relatively lower loadings. Organic carbon and Sr are negatively loaded in this factor, underscoring a negative relation to aluminosilicates. Strontium represents the authigenic biogenic carbonates abundance. Factor 2 accounts for 14 % of the total variance and is essentially an organic carbon factor. Lead, copper and cobalt are markedly loaded in this factor, underscoring their association to C_{org}. The organic matter plays an important role in the transport of metals, since it is able to bind trace metals and takes place in diagenetic processes after deposition (SALOMONS & FÖRSTNER, 1984; HOROWITZ, 1991). The aforementioned association suggests that, even though the organic carbon levels are relatively low in the study area (mean value 0.43 %), its potential to incorporate some trace metals is high.

Sedimentary heavy metal concentrations (e.g. Cr, Mn, Ni, Cu, Zn, Pb) were generally found to be low, around the levels normally expected in coarse sand-sized marine sediments (e.g., CALVERT, 1976; CHESTER, 1990). In fact, the heavy metal concentrations are lower than in other coastal areas of Greece marine sediment and the average shale (Table 4). In particular, the neighboring Elefsis Bay and port of Piraeus, exhibit several-fold higher mean heavy metal contents, due to anthropogenic pollution. The values reported here for Agios Kosmas resemble those found in south Evvoikos Gulf sediments, which are relatively unaffected by human activities (XRF analysis of bulk sediments characterized by increased sand content; KARAGEORGIS *et*

Table 4
Trace metal contents in sediments of various Hellenic sites and the average shale.

Element	Agios Kosmas[1]	Elefsis Bay and Piraeus Port[2]	Rhodes Harbour[3]	South Evvoikos Gulf[4]	North Evvoikos Gulf[5]	Hellenic Volcanic Arc[6]	Southern Aegean Sea[7]	Aegean Sea[8]	Average Shale[9]
Cr ppm	63	130	59	138	592	-	103	-	90
Mn ppm	213	360	175	510	3979	810	975	280	850
Ni ppm	34	90	-	110	1367	38	129	28	68
Cu ppm	8	100	65	12	34	18	32	13	45
Zn ppm	42	760	145	55	64	43	63	45	95
Pb ppm	22	210	135	22	-	20	11	38	20
Sr ppm	1636	-	-	1272	-	1144	577	-	140

[1]Present study; bulk; [2]VOUTSINOU-TALIADOURI *et al.* (1989); extraction with 2 N HCl; [3]ANGELIDIS & ALOUPI (1995); fraction <63 μm, extraction with 0.5 N HCl; [4]KARAGEORGIS *et al.* (1997); bulk; [5]VOUTSINOU-TALIADOURI & VARNAVAS (1993); bulk; [6]SIOULAS *et al.* (2000); bulk; [7]HODKINSON *et al.* (1994); bulk; [8]SMITH & CRONAN (1975); bulk; [9]TUREKIAN & WEDEPOHL (1961); bulk.

al., 1997). However, a direct comparison of heavy metal concentrations with reported values from other areas may be misleading, due to the different size fractions and digestion methods applied. In order to better evaluate possible element enrichment in the sediments, enrichment factors (EFS) versus average shale (TUREKIAN & WEDEPOHL, 1961) of V, Cr, Mn, Co, Ni, Cu, Zn, As, Rb, Sr, and Pb were calculated from:

$$EFS=(element/Al)_{sample}/(element/Al)_{average\ shale}$$

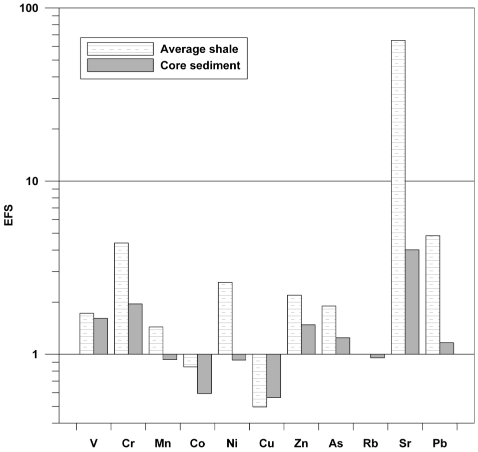

Fig. 6: Enrichment factors versus average shale (TUREKIAN & WEDEPOHL, 1961) and local core sediment for V, Cr, Mn, Co, Ni, Cu, Zn, As, Rb, Sr, and Pb analysed in the sediments of Agios Kosmas (median values from eleven samples).

According to this evaluation, the Agios Kosmas sediments were found to be enriched in all the elements, except for cobalt and copper (Fig. 6). This method, although very often used, generates uncertainties, mostly due to its inability to account for the local geochemical background. Therefore, it is more reliable to calculate EFS using element concentrations from local, non-contaminated sediment(s) (LORING & RANTALA, 1992; ANGELIDIS & ALOUPI, 1995). For this purpose, we used the deepest sample (40-43 cm) of a box-core recovered from the outer Saronikos Gulf at 228 m depth. Due to the low sedimentation rates observed in the area (max. 0.6 cm 100 y^{-1}; LYKOUSIS & ANAGNOSTOU, 1992), this sediment definitely represents pre-industrial period and can be considered as non-contaminated. The sample has been analyzed with exactly the same procedure as the Agios Kosmas sediments (Table 1). The recalculated EFS values are illustrated in Fig. 6. The EFS value for Sr was the highest observed ($EFS_{Sr} = 4.01$), indicating the abundance of biogenic carbonates. On average, the EFS values for vanadium, chromium, zinc, arsenic, and lead, suggest some enrichment ($2< EFS <1$). The highest EFS values appeared in the sandy sediments of the western part of the area (AK-4, AK-18, and AK-68, see Fig. 1 for location). Most likely, the additional source for these elements is heavy minerals, which are abundant in coarse-grained reworked sediments and are rich in metals (SALOMONS & FÖRSTNER, 1984). This is consistent with the results of the factor analysis, which groups these elements to the detrital factor. However, lead was grouped with organic carbon, therefore, its slight enrichment ($EFS_{Pb} = 1.17$) could be attributed to anthropogenic sources (e.g. industrial emissions, combustion of leaded fuel).

Summarizing the available evidence we may conclude that the Agios Kosmas sediments have not been considerably affected by anthropogenic activities. Apart from the absence of pollutant point sources along the Agios Kosmas coast, an important factor for the low heavy metal contents reported, is the relatively coarse grain-size, which results in a considerably lower tendency for heavy metal enrichment. In addition, the hydrological regime enables the dispersion of pollutants toward the open sea (NCMR, 2000).

Hydrocarbons

The analytical data of hydrocarbon analysis and some compositional parameters are given in Table 5. The concentrations of total aliphatic

Table 5
Hydrocarbon concentrations and some compositional parameters in the Agios Kosmas surface sediments. THC: total hydrocarbons, AHC: aliphatic hydrocarbons, CPI: carbon preference index, U/R: ratio of unresolved to resolved compounds, ΣPAH: total PAHs.

	AK1	AK2	AK4	AK1a	AK5a	AK5b1	AK5b2	AK5c
THC (μg/g)	65.7	114.3	111.1	135.5	94.5	84.8	113.4	67.9
AHC (μg/g)	65.2	112.9	110.1	133.9	92.6	82.5	111.9	66.4
n-alkanes (μg/g)	2.2	6.1	3.0	1.2	1.0	1.0	1.9	0.8
CPI	3.0	2.7	2.8	3.5	3.1	2.9	3.4	2.9
U/R	21.7	12.8	27.6	35.1	22.1	21.5	21.5	18.1
ΣPAH (ng/g)	497.7	1406.8	959.4	1553.5	1931.4	2270.7	1550.6	1538.7

hydrocarbons (AHC) found in the surface sediments of the Agios Kosmas area ranged between 65.2 and 133.9 μg/g dry weight (mean value 97.3 μg/g). These values are generally considered as elevated and hence indicate moderate petroleum pollution in the whole area. The highest values were recorded inside the marina in the southern sector of the study area, where fine-grained organic carbon-rich sediments prevail. The relatively low hydrocarbon concentration found at station AK1 does not seem to reflect lower pollution levels but it is possibly related to the presence of sandy sediments with very low organic carbon concentrations. As illustrated in Table 6, most Greek coastal and open sea studies observed lower hydrocarbon contents than those in Agios Kosmas sediments. Slightly higher values were recorded in Thessaloniki Bay (HATZIANESTIS *et al.*, 2001), whereas only Elefsis Bay, which is considered as a seriously polluted area, exhibits significantly higher mean hydrocarbon concentrations (SKLIVAGOU *et al.*, 2001). These increased hydrocarbon values were attributed to fossil fuel releases from both the intense ship traffic in the area and the various anthropogenic activities in the densely populated coastal zone.

The presence of an unresolved complex mixture (UCM) was evident in the chromatograms of the aliphatic fraction in all samples (Fig. 7). The UCM is considered as an elaborate mixture of branched and cyclic hydrocarbons and it is generally well correlated with degraded or weathered petroleum residues (BOULOUBASSI & SALIOT, 1993). The ratio of unresolved over resolved compounds (U/R) is widely used to identify the origin of the hydrocarbons in marine sediments. Values of U/R >4 are considered as clear evidence of petroleum residues (MAZUREK & SIMONEIT, 1984). In the

Table 6
Sedimentary aliphatic and polycyclic aromatic hydrocarbons in various Greek marine areas.

Area	Aliphatic (μg/g)	PAH (ng/g)	Reference
Agios Kosmas	97	1464	Present study
W. Saronikos Gulf	53	166	NCMR, 1997
Elefsis Bay	526	3037	SKLIVAGOU *et al,* 2001
Thessaloniki Bay	148	421	HATZIANESTIS *et al,* 2001, CATSIKI *et al,* 2001
S. Evoikos Gulf	31	208	NCMR, 2001
Nestos Estuary	37	174	HATZIANESTIS & SKLIVAGOU, 2000
Strymonikos Gulf	52	569	HATZIANESTIS & SKLIVAGOU, 2001
Evros Estuary	94	1560	KANELLOPOULOS *et al,* 2000
Igoumenitsa Gulf	64	620	LELEKIS *et al,* 2001
Open Aegean Sea	25	103	HATZIANESTIS *et al,* 1998

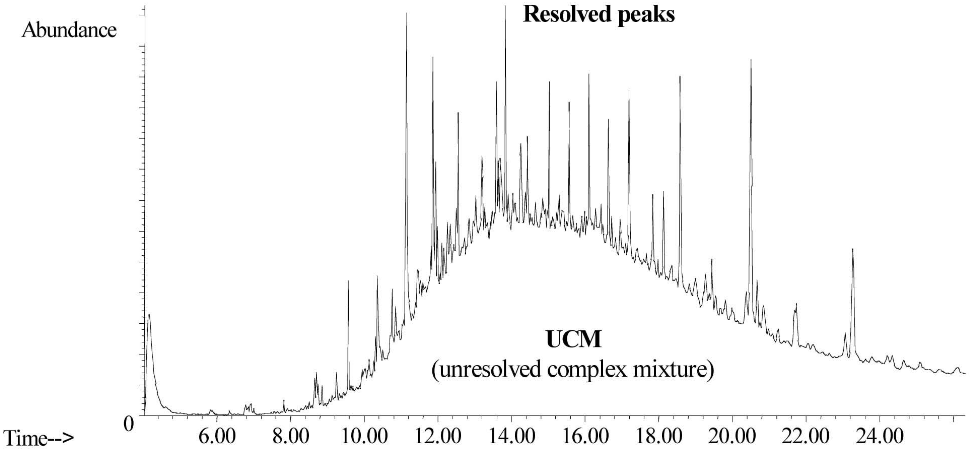

Fig. 7: Gas chromatogram of sedimentary aliphatic hydrocarbons from Agios Kosmas area.

sediments examined in this study, the U/R ratio ranged between 12.8 and 35.1, indicating a significant degraded petroleum component in all sediments of the study area. N-alkane concentrations were relatively low and varied between 0.8 and 6.1 μg/g accounting for the 0.9-5.4 % of the total aliphatics. N-C29 or n-C31 was always the dominant compound indicating terrestrial origin but a strong predominance of odd carbon numbered n-alkanes was not observed (CPI values ranged from 2.7 to 3.5), also confirming the fossil fuel influence.

Polycyclic aromatic hydrocarbons (PAH) also presented elevated values in comparison with other Greek marine areas (Table 6). Their total concentrations calculated as the sum of 25 individual compounds (parent PAHs with 2 to 6 aromatic rings, dibenzothiophene, and the alkylated derivatives of naphthalene, phenanthrene and dibenzothiophene) ranged from 497.7 to 2270.7 ng/g dry weight, and the

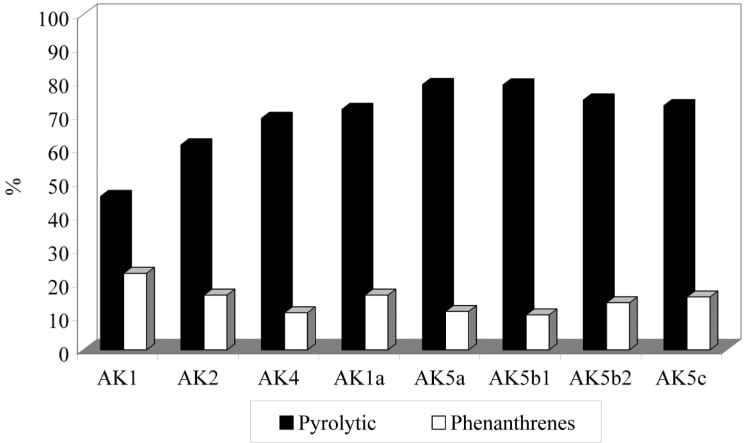

Fig. 8: Percent distributions of pyrolytic PAH and sum of phenanthrene compounds in surface sediments of Agios Kosmas area.

most abundant compound was always benzo(b)fluoranthene. The PAHs do not show any significant correlation with aliphatic hydrocarbons indicating different sources and/or particle associations. PAH composition profiles can be used in order to distinguish between different anthropogenic and natural inputs. Pyrolytic PAH, representing the compounds derived almost exclusively during the various combustion processes, are defined as the sum of parent compounds with MB 202, 228, 252, 276, 278 (BOULOUBASSI & SALIOT, 1993; PAGE *et al.*, 1999), except perylene which could also originate from biogenic sources (BUDZINSKI *et al.*, 1997). Petroleum originating PAHs are mostly represented by phenanthrene compounds. In Fig. 8, the percentages of pyrolytic PAH and sum of phenanthrene compounds are shown for the different stations. As it can be seen, pyrolytic PAHs were clearly predominant in all cases and accounted for 46-79 % of total PAHs. The lowest abundance of pyrolytic PAHs (< 50 %) was observed at the relatively remote station AK1, where the lowest total PAH values were also recorded, whereas the stations located very close to the coastline exhibited increased pyrolytic PAH values (above 75 % in all cases). All these observations clearly demonstrate that the main part of the PAH measured in this study was produced from various combustion processes on land and transferred into the sea through runoff.

Conclusions

The seabed of Agios Kosmas area is covered by sandy Holocene deposits. Their grain-size varies between -1 and 0 φ, and represent reworked sediments originating in the weathering of Plio-Pleistocene sedimentary sequences. In contrast, finer muddy sediments cover the seabed inside the sheltered marina. Carbonate content was high (mean 65.2 %), whereas organic carbon and total nitrogen contents were found to be low, as a result of the coarse sediment texture.

Spatial distributions of trace elements revealed that concentrations exhibited a generally common pattern: a decrease towards the open sea, and higher values inside the marina, where fine sediments prevailed. The detrital fraction was represented by V, Cr, Mn, Co, Ni, Cu, Zn, and As, which were significantly correlated to Al, Rb, and the mean grain-size, as well, suggesting element's relation with fine alluminosilicates. On the other hand, carbonates and Sr marked correlation was attributed to the abundance of biogenic carbonates. These findings were supported by the results of principal factor analysis. The latter analysis revealed the association of Pb, Cu, and Co with the organic carbon. The calculation of enrichment factors (EFS) have shown some enrichment for V, Cr, Zn, As, and Pb. Of all these elements, only Pb could be attributed to anthropogenic sources, whereas the rest were, most probably, related to heavy metal-rich heavy minerals found in the coarse-grained sediments. In general, sedimentary heavy metals exhibited relatively low concentrations, due to: (a) the absence of pollutant point sources; (b) the coarse texture of the sediments; and (c) the hydrological regime.

Both aliphatic and polycyclic aromatic hydrocarbon concentrations (AHC and PAH, respectively) were found to be relatively high in the sediments, indicating moderate petroleum pollution in the area. Higher concentrations were recorded within the fine sediments. This problem is expected, as the Saronikos Gulf is an area of high shipping, and fossil fuel releases are substantially elevated. In addition, high pyrolytic PAH values were attributed to combustion activities on the land. However, elevated contents of hydrocarbons do not seem to affect the quality of this coastal ecosystem, as COTOU *et al.* (2002) recently demonstrated, using simultaneously Scope for Growth and Microtox® methods; the authors suggest that the area of Agios Kosmas reflects minimal pressures, due to generally good regional hydrologic regime and absence of industrial inputs.

As the constructions for the 2004 Olympic Games are in progress, dredging material will have to be removed from the area. However, this material does not seem to pose any threats for the dumping sites, which are usually some deep sectors of the Saronikos Gulf. The design and construction of additional breakwaters and docks should take into account the maintenance of the local hydrological circulation, to prevent phenomena of anoxia inside the marina. Moreover, dumping of construction materials, chemicals, paints, oils, etc, should be strictly regulated during the period of works. In addition, we propose that continuous monitoring should be planned, in order to ensure that the Agios Kosmas marine area would remain in good environmental condition, although the Olympic Games facilities will inevitably add more pressure to the system.

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