

Distribution and sources of hydrocarbons in surface sediments of Gemlik Bay (Marmara Sea, Turkey)

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Abstract

Seabottom sediments from Gemlik Bay, one of the most polluted spots in SW Marmara Sea, were analyzed for parent polycyclic aromatic hydrocarbons (PAHs) using gas chromatography–mass spectrometry. The concentration of 14 PAH compounds in sediment samples collected from 61 locations are distributed in a broad spectrum from low to very high concentration levels (50.8–13482 ng g⁻¹). No significant correlation was found between \sum PAHs and organic carbon content while \sum PAHs increase slightly with silt/clay ratio. Therefore the distribution and concentrations of PAHs would be determined more by direct input, rather than by the type of sediment found locally. The most polluted areas are distributed nearshore eastern (Gemlik) and southern (Kursunlu, Mudanya and Trilye) coasts which are mainly influenced by rapid ecotourism development, direct discharges from rivers, surface run-off and drainage from port areas, domestic and industrial effluent discharges through outfalls and various contaminants from ships. Special PAH compound ratios, such as Phe/Anth, Flu/Py, B[a]A/Chry; LMW_{PAH}/HMW_{PAH}; Per/; Per/ \sum (PAH); Per/ \sum (penta-aromatics) and Flu/(Py + Flu), were calculated to evaluate different hydrocarbon origins and their relative importance. Pyrolytic activity is dominant along the highly-populated eastern and southern coasts. Meanwhile, petrogenic activity mixed with pyrolytic activity is a matter of fact in front of the main industrial–tourism ports and anchoring areas as well. Higher concentration of perylene are distributed along the mostly polluted eastern and southern coastal areas, however, the concentrations of perylene relative to the penta-aromatic isomers are dominant especially in the northern and deepest sectors of the bay, indicating diagenetic origin for the presence of perylene.

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1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are common organic contaminants and generally generated by natural and anthropogenic processes. They can be introduced into the marine environment by various ways; e.g. oil spill, urban runoff, domestic and industrial wastewater discharges and atmospheric deposition across the air–sea interface. The largest concentrations of PAHs are generally detected in urbanized and industrialized areas. It is believed that the environmental fate and behavior of hydrophobic

organic compounds is ultimately determined by the sediment retention capacity and physico-chemical properties such as particle grain size, organic matter and salinity (Baker et al., 1991).

According to the formation mechanism, PAHs can be classified as pyrolytic and petrogenic. Pyrolytic PAHs are formed as a consequence of incomplete combustion whereas petrogenic PAHs are mainly derived from crude oil and its refined products. PAH ratios have been used to determine PAH sources, classify samples by location and estimate the importance of petroleum-derived PAH and combustion wastes (Sicre et al., 1987; Lipiatou and Saliot, 1991; Yunker et al., 1996, 2002; Budzinski et al., 1997; Soclo et al., 2000).

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A similar work has shown that Izmit Bay (Fig. 1) is one of the most polluted inner waters in the Marmara Sea and heavily impacted by petrogenic PAHs (Ünlü and Alpar, 2004). The Gemlik Bay is the second most polluted hot spot in this semi-enclosed sea connecting the Black Sea to the Aegean Sea via the Turkish straits (Bosphorus and Dardanelles). It is surrounded by areas of high population growth and rapid economic developments in the Marmara Sea and receiving natural and anthropogenic discharges via rivers and atmosphere.

1.1. Geographical setting

Similar to Izmit Bay, the Gemlik Bay emerges as a 31-km-long tectonic trough between two topographic heights, with an increasing width westward (Fig. 1). It is 2–6 km wide in front of the Gemlik Town in the east of Tuzla Point and 12–24 km in the west between Trilye and Bozburun (Armutlu Town). The length of its coasts along the steep Samanlıdağ Mountains in the north, alluvial plains and deltas in the east and small hills along the southern coasts is about 76 km.

The regional winds, mainly controlled by the surrounding mountains, blow from northwest in winter and mainly northeast for the rest of the year. They play a dominant role in the dynamics of this semi-enclosed sea. Gemlik Bay is open to the waves coming from the band between northwest and southwest (Özhan and Abdalla, 1999). In winter, the dominant wave direction is from northwest with the significant wave heights less than 3 m. The dominant wave direction is from southwest in spring months with the significant wave height less than 2 m. The maximum hindcasted significant wave height for Gemlik wave is 3 m for the duration of wind data 1994–1998.

The maximum depth is 107 m in the middle of a small northwest-trending elliptical central trough which is a fault-controlled depositional area (Yaltırak and Alpar, 2002). The southern coasts of the Gemlik pull-apart basin are controlled by the central strand of the North Anatolian fault. Holocene alluvial fans in the east disturb the symmetry of this marine depression which is separated from the Marmara Sea by a sill with an average depth of 50 m in the west (Fig. 1). With its 27 600 km² drainage area and 158 m³/s average water flows, the Karasu River is the most important geographic element in the region. It carries 0.5–5.5 tons of suspended solids daily into the sea depending on the climatic conditions (Yıldız et al., 2003).

1.2. Oceanographic conditions

No long-term current data is available to represent the water circulation in the bay which controls sediment transportation and deposition. Some short-term historical measurements revealed two distinct water layers; the upper Black Sea water and the dense lower Mediterranean Sea water. In normal weather conditions, the surface flow is clockwise with an average current speed of about 13–17 cm/s at the entrance of Gemlik Bay and 2–6 cm/s in the central and inner parts (Fig. 1). These figures increase in spring. The interface layer takes place at 20–30 m water depth depending on the seasonal variations. In addition to the main Mediterranean water in deep Marmara Sea basins, a relatively thinner plume of dense lower layer flows through the southern Marmara shelf and reaching Gemlik Bay (Beşiktepe et al., 1994). The average speed of the lower layer is 9–10 cm/s at the entrance while they are 2.5–4.5 cm/s in the central and inner parts of the bay, but with varying directions.

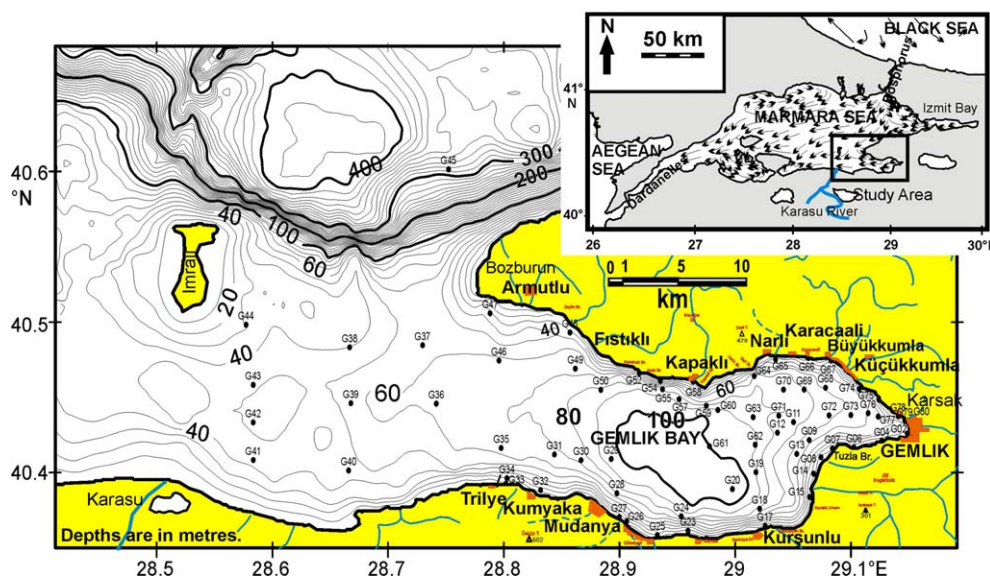


Fig. 1. Location of sampling stations in Gemlik Bay. Inset shows the study area and surficial flow of in the Marmara Sea (after Alpar et al., 1998). Bathymetry is reconstructed from Yaltırak and Alpar (2002) and using the data obtained during the recent multibeam bathymetric survey of the Ifremer RV Le Suroit vessel (Rangin et al., 2001).

1.3. Environmental conditions

The bay, with a total surface area of 349 km², is most particularly subject to high anthropogenic pressure due to inputs from rivers, atmosphere, coastal shipping and industrial activities. The most important industrial towns along the bay are the Gemlik Town, Mudanya and Trilye (Fig. 1). Mudanya port is the export gate of the second biggest industrial city of Turkey, Bursa. As opposed to the industrialization along the southern coasts, Armutlu, Fıstıklı, Kapaklı, Narlı, Karacaali, Büyükkumla and Küçükumla villages are tourism centers along the northern coasts. Total population exceeds 129 000 and doubles in summers. The most densely populated towns, however, are Gemlik (80 000) and Mudanya (24 000). The total of domestic wastewater discharge into the bay is as much as 7.5 million m³/y (Solmaz et al., 2000). Only Gemlik town and Küçükumla have their own deep sea outfall discharge system. Other coastal settlements use creeks or simple outfalls for their wastewater discharge. New systems are ready to operate for Mudanya and Armutlu.

The easternmost part of the bay is subject to chronic severe contaminations, among which hydrocarbons play a major role. The main sources are ship traffic, fishery activities, domestic and industrial sewage waters and riverine inputs. The Karsak creek which discharges into the Gemlik port is the most important pollution source. Not only the discharges of a wide range of industrial plants in Gemlik town, but this creek also carries the waters of Lake Izik, domestic and industrial wastewater discharges of Orhangazi town located 15 km in the west of the Gemlik Bay. The total load carried by Karsak River is therefore variable seasonally. The share of industrial waste water inputs is even higher, 13–20 million m³/y (Solmaz et al., 2000). The total discharge of textile and chemistry plants is seemingly lower, but they introduce an important industrial pollution into the bay since they do not use treatment systems. The impact of such an anthropogenic pressure can be observed often in summer with the phenomenon of red waters, resulting from eutrophication and disequilibrium processes for the exploitation of natural resources. No available measurement data, however, has been made for the content, composition and regarding the fate and potential sources of PAHs in the aquatic environment of Gemlik Bay.

The present study aims to determine the concentration and possible sources of PAHs in the sediments of Gemlik Bay. Diagnostic indices were utilized in identification of contamination sources.

2. Material and methods

2.1. Sampling

A total of 61 surface sediment samples were recovered throughout the bay using Orange Peel grab sampler (Table 1). Positioning errors of the research boat stayed within ± 10 m during cruise. The topmost 0–3 cm of the grab

sample was carefully removed using clean stainless steel spatula. Samples were placed either on ice or frozen immediately after sampling and remained chilled or frozen until analysis at the laboratory.

Approximately 30 g wet weight of sediments was placed in a labeled precombusted jar for chemical drying with anhydrous sodium sulfate until the sample was dry, free-flowing, and homogeneous, then Soxhlet-extracted with dichloromethane (150 ml) for 8 h with activated copper. Two grams of anhydrous sodium sulfate were added to remove water. The extracts were pooled and the volume reduced to approximately 1 ml by Rotary evaporation prior to column chromatography.

2.2. Sample extraction and cleanup

Sediment extracts were fractionated by adsorption chromatography, using a 1:2 alumina:silica column chromatography (6 g of 80–100 mesh fully activated silicagel, 3 g of 100–200 mesh fully activated alumina, topped with 0.5 g of sodium sulfate). The concentrated extract (1 ml) was carefully added to the top of the column and the following fractions were collected: (1) 25 ml of hexane (aliphatic hydrocarbons) and (2) 100 ml of 1:1 dichloromethane:hexane (aromatic compounds) (UNESCO, 1982). All the extracts were concentrated by gentle N₂ blow-down to approximately 100 μ l, and an aliquot (2 μ l). All solvents used for sample processing and analyses (dichloromethane and hexane) were of HPLC grade.

2.3. Analysis

Aromatic fraction was analysed by gas chromatography coupled to mass spectrometry (GC–MS). A HP6890 series gas chromatography (Hewlett–Packard, Palo Alto, CA, USA) with mass detector equipped with a split/splitless injector was used (splitless time: 1 min; flow: 0.8 ml/min). The injector and detector temperatures were maintained at 280 and 320 °C, respectively. The gas chromatography temperature program was maintained at 50 °C for 1 min, from 50 to 320 °C at 10 °C min⁻¹ and then held at this temperature for 5 min. The carrier gas was Helium at a constant flow rate of 0.8 ml/min. The capillary column used was a HP-5MS (Hewlett–Packard, Palo Alto, CA, USA): 30 m \times 0.25 mm ID \times 0.25 μ m film thickness. The gas chromatography was coupled to a HP 5972 mass selective detector (MSD). The mass spectrometer was operated under the selected ion monitoring mode (SIM) using molecular ions of the studied PAHs (electron impact at 70 eV, 2000 V, 1.4 scan/s; dwell time/ion 40 ms). The interface temperature was 290 °C. A computer system interfaced with the MS continuously acquired and stored all mass-spectral data during the analysis. This system also allowed display of a GC–MS data file for ions of specific mass and plotting ion abundances versus time or scan number. Response factors and retention times were determined in relation with deuterated internal standards

Table 1
Location, depth, textural features, total organic carbon (TOC) and ratios of different individual PAH compounds

Station	Latitude East (°)	Longitude North (°)	Depth (m)	Sand (%)	Silt (%)	Clay (%)	Silt/clay	Total PAHs (ng)	TOC (%)	Phe/Ant	Flu/Py	Flu/(Flu + Py)	B/C
G01	29.1511	40.4293	11	6.1	69.1	23.4	2.953	13481.0	2.2	3.44	0.90	0.47	0.61
G02	29.1486	40.4260	31	8.5	67.3	24.0	2.801	3119.0	3.0	NC	0.74	0.43	NC
G04	29.1267	40.4211	32	18.7	54.6	26.7	2.041	7222.0	0.6	7.75	1.27	0.56	0.72
G06	29.1027	40.4169	20	22.4	68.5	9.0	7.584	2039.0	2.2	2.98	1.13	0.53	0.67
G07	29.0840	40.4161	8	23.4	60.6	15.9	3.817	2082.2	1.0	5.92	1.65	0.62	NC
G08	29.0741	40.4103	6	80.8	6.7	4.4	1.529	3274.4	0.1	7.80	1.70	0.63	0.43
G09	29.0639	40.4217	53	41.2	33.4	24.3	1.374	1733.2	0.8	6.58	1.14	0.53	0.78
G11	29.0504	40.4336	74	1.0	50.3	48.7	1.035	1634.8	0.8	NC	1.08	0.52	NC
G12	29.0365	40.4266	80	0.7	43.9	55.4	0.793	2659.6	1.1	6.02	1.21	0.55	0.78
G13	29.0532	40.4125	55	13.1	53.2	33.7	1.580	1669.2	0.7	5.83	1.13	0.53	0.70
G14	29.0679	40.3992	15	4.9	66.4	28.5	2.332	1190.5	0.6	NC	1.62	0.62	0.82
G15	29.0667	40.3838	11	37.2	48.0	14.5	3.303	2200.7	1.4	NC	1.23	0.55	0.60
G16	29.0486	40.3732	54	1.8	56.9	41.2	1.382	3473.7	1.0	4.91	1.48	0.60	0.93
G17	29.0259	40.3644	32	39.8	50.1	10.1	4.971	8826.3	1.3	4.70	1.21	0.55	0.93
G18	29.0211	40.3760	82	1.1	47.7	51.1	0.933	806.9	2.3	2.62	1.20	0.54	1.03
G19	29.0179	40.4003	92	0.7	41.1	58.3	0.705	834.8	1.5	1.30	1.05	0.51	0.42
G20	28.9976	40.3891	105	0.8	38.8	60.4	0.643	1360.5	2.0	NC	1.26	0.56	0.70
G23	28.9592	40.3613	39	44.2	34.8	21.0	1.654	1149.3	1.0	4.69	1.40	0.58	0.77
G24	28.9533	40.3709	89	1.0	44.5	54.5	0.817	3392.3	3.0	4.37	1.13	0.53	0.89
G25	28.9327	40.3584	29	26.1	48.7	24.3	2.009	2269.6	1.5	4.86	1.24	0.55	0.97
G26	28.9063	40.3678	20	32.1	41.7	25.9	1.612	11032.3	1.3	3.87	1.18	0.54	0.88
G27	28.8998	40.3704	10	34.3	44.7	18.4	2.423	3008.8	1.9	3.78	1.10	0.52	0.90
G28	28.8977	40.3862	70	7.0	40.4	52.7	0.767	4273.3	1.6	8.20	1.07	0.52	0.62
G29	28.8928	40.4091	96	0.8	37.1	62.1	0.598	647.7	2.5	5.25	1.45	0.59	0.70
G30	28.8668	40.4082	76	1.5	42.0	56.6	0.742	602.2	2.1	5.25	1.30	0.57	0.64
G31	28.8438	40.4121	68	1.4	40.3	58.4	0.690	315.5	1.7	6.78	1.22	0.55	0.89
G32	28.8318	40.3884	24	9.6	53.8	36.4	1.481	2505.6	1.8	3.88	1.35	0.57	0.94
G33	28.8017	40.3926	8	20.7	52.6	25.7	2.046	2042.6	3.1	4.10	1.16	0.54	0.84
G34	28.8026	40.3963	25	9.1	53.1	37.1	1.430	862.4	1.5	3.60	1.33	0.57	1.01
G35	28.7977	40.4163	65	1.7	43.0	55.3	0.777	344.4	1.9	NC	1.37	0.58	0.72
G36	28.7417	40.4459	59	22.0	28.0	48.0	0.583	480.6	1.0	NC	2.40	0.71	NC
G37	28.7298	40.4847	54	59.5	17.5	11.5	1.522	528.8	0.3	NC	NC	NC	0.99
G38	28.6667	40.4834	40	11.8	63.3	22.6	2.801	695.3	1.2	NC	1.23	0.55	0.82
G39	28.6678	40.4461	58	1.5	48.3	50.2	0.962	514.1	1.5	NC	1.28	0.56	NC
G40	28.6658	40.4014	55	0.3	38.2	61.5	0.621	304.9	0.3	NC	1.25	0.56	1.01
G41	28.5834	40.4084	25	28.0	29.0	38.0	0.763	717.9	2.9	NC	1.30	0.56	0.94
G42	28.5834	40.4334	35	31.0	28.0	39.0	0.718	338.5	1.5	NC	1.11	0.53	NC
G43	28.5834	40.4583	50	34.0	25.0	38.0	0.658	604.8	1.1	4.71	1.36	0.58	NC
G44	28.5772	40.4984	38	52.5	13.4	15.1	0.887	687.6	1.6	NC	1.10	0.52	0.99
G45	28.7523	40.6014	320	24.0	60.0	12.0	5.000	486.1		NC	1.76	0.64	NC
G46	28.7958	40.4745	63	9.4	28.4	56.3	0.504	473.4	1.41	NC	1.12	0.53	0.66
G47	28.7881	40.5059	30	66.1	7.4	9.1	0.818	373.7	0.53	10.19	1.46	0.59	0.62
G48	28.8572	40.4932	41	67.9	22.3	9.2	2.412	223.3	0.38	4.35	1.25	0.56	0.85
G49	28.8618	40.4691	65	0.8	38.1	60.7	0.628	1.8	0.79	NC	1.18	0.54	NC
G50	28.8839	40.4551	81	1.5	37.2	61.1	0.608	307.0	1.34	5.42	1.19	0.54	0.72
G52	28.9171	40.4662	60	10.6	51.3	38.0	1.350	387.3	0.97	NC	1.24	0.55	NC
G54	28.9353	40.4609	63	3.6	47.8	48.5	0.986	923.8	1.29	2.78	1.37	0.58	0.74
G55	28.9372	40.4554	80	1.4	42.7	55.9	0.764	313.5	1.91	5.61	1.19	0.54	0.82
G57	28.9515	40.4488	84	0.6	36.0	63.5	0.567	345.4	2.37	NC	1.54	0.61	NC
G58	28.9636	40.4605	20	41.1	45.7	12.3	3.723	2258.9	1.09	4.89	1.27	0.56	0.98
G59	28.9750	40.4444	93	1.1	52.5	46.4	1.132	88.7	1.34	NC	1.52	0.60	NC
G60	28.9850	40.4416	91	1.0	35.0	64.0	0.547	164.1	0.78	6.42	1.23	0.55	0.85
G61	28.9777	40.4175	100	0.4	44.7	55.0	0.812	64.8	1.98	NC	1.28	0.56	NC
G62	29.0173	40.4186	94	1.5	42.8	55.6	0.770	50.0	1.52	NC	1.12	0.53	NC
G63	29.0155	40.4369	87	0.3	39.8	59.9	0.665	28.9	1.85	NC	1.89	0.65	NC
G64	29.0165	40.4643	71	1.1	43.9	55.0	0.798	180.3	1.52	NC	1.07	0.52	0.71
G65	29.0349	40.4776	40	26.5	61.9	11.5	5.366	468.8	1.01	4.50	1.33	0.57	0.84
G66	29.0633	40.4762	30	39.9	32.4	7.3	4.456	319.8	1.19	4.89	1.23	0.55	0.93
G67	29.0827	40.4745	32	16.8	62.6	20.3	3.086	78.1	1.55	NC	0.96	0.49	NC
G68	29.0781	40.4564	59	1.0	43.0	56.0	0.769	21.5	1.48	NC	1.72	0.63	NC
G69	29.0596	40.4553	70	0.6	39.1	60.3	0.648	8.7	0.97	NC	1.62	0.62	NC
G70	29.0418	40.4552	77	0.6	38.2	61.2	0.625	20.5	1.25	NC	1.27	0.56	NC

(Continued on next page)

Table 1 (continued)

Station	Latitude East (°)	Longitude North (°)	Depth (m)	Sand (%)	Silt (%)	Clay (%)	Silt/clay	Total PAHs (ng)	TOC (%)	Phe/Ant	Flu/Py	Flu/(Flu + Py)	B/C
G71	29.0377	40.4379	83	0.5	45.2	54.2	0.834	25.9	1.18	NC	0.87	0.46	NC
G72	29.0811	40.4381	63	1.0	49.5	49.4	1.002	301.8	1.89	NC	1.01	0.50	NC
G73	29.0999	40.4383	56	0.7	47.0	52.3	0.898	289.0	1.16	NC	0.95	0.49	NC
G74	29.1071	40.4555	50	1.2	47.2	51.6	0.916	517.1	1.39	NC	1.02	0.51	NC
G75	29.1241	40.4485	40	2.5	74.0	23.5	3.153	443.4	1.29	NC	1.30	0.56	0.66
G76	29.1149	40.4395	50	0.8	43.7	55.5	0.788	381.3	1.24	NC	1.19	0.54	NC
G77	29.1235	40.4373	48	1.1	45.7	52.9	0.863	1199.2	1.06	NC	1.20	0.55	NC
G78	29.1409	40.4374	35	1.1	56.2	42.7	1.315	2895.8	1.37	4.46	1.11	0.53	0.84
G79	29.1466	40.4342	28	3.8	61.4	34.6	1.774	5353.0	1.66	4.31	0.93	0.48	0.59
G80	29.1518	40.4312	11	18.2	66.3	15.4	4.311	6126.0	2.34	3.57	1.24	0.55	0.93

NC: not calculated due to concentrations below the detection limits.

(chrysene- d_{12} , perylene- d_{12}) and a standard PAH text mixture. Prior to sample analysis, the GC–MS was tuned with perfluorotributylamine (PFTBA) at the beginning of each analytical sequence.

The GC–MS was calibrated for the 14 priority pollutant PAHs using the internal standard calibration procedure described in US EPA method 8000 (PAH calibration mixture purchased from Supelco, a part of Sigma–Aldrich Corporation) and also using the major characteristic ion of each compound for quantitation. The studied parent PAHs ranged from the three-aromatics to hexa-aromatics. Method detection limit for Phe, Ant, Flu, Py, BaA, Chry + Triph, were of the order of 1 ng g⁻¹ dry sediment, while it was approximately 0.1 ng g⁻¹ for other PAH compounds. The abbreviations used for the PAHs are: Phe: phenanthrene, Ant: anthracene, Flu: fluoranthene, Py: pyrene, BaA: benzo[*a*]anthracene, Chry: chrysene, Triph: triphenylene, BbF: benzo[*b*]fluoranthene, BkF: benzo[*k*]fluoranthene, BeP: benzo[*e*]pyrene, BaP: benzo[*a*]pyrene, Per: perylene, BPer: benzo[*ghi*]perylene and IP: indeno[1,2,3-*cd*]pyrene.

2.4. Sediment texture and total organic carbon analysis

Sediment grain size analysis is broken down into several steps dealing first with the coarse fraction (sand and gravel) and then with the fine fraction (silt and clay). It was performed using a method adapted from Folk (1974) as described by GERG SOP-8908.

The total organic carbon (TOC) contents were measured by means of the Walkley–Black method, which involves the titration with ferrous ammonium sulfate of the dichromate left after a wet combustion of the sample with potassium dichromate (Gaudette et al., 1974; Loring and Rantala, 1992). The analytical precision of analysis was better than $\pm 4\%$ at 95% significance level from five replicates (Ünlü et al., 2005).

3. Results and discussion

3.1. PAH contamination of sediments

The PAH concentrations (expressed in ng g⁻¹ dry weight) were calculated for 61 sediment samples (Table 2).

The Σ PAH concentration varies from 50.8 to 13482 ng g⁻¹ (Fig. 2). The highest values are distributed as spot shape areas; sequentially they are in front of Gemlik harbour (stations G1, G2, G79 and G80) and ports (G4), nearshore the cable and petroleum plants at Güzelyali, 3 km east of Mudanya (stations G26 and G27), in front of a creek at Kurşunlu (station G17) and finally in Mudanya (G28) and Trilye (G33) villages (Fig. 2).

A quantitative comparison across reported PAH data is difficult because of variances in the number and type of individual species determined in each study, the sediment fraction analysed, and the analytical methods used. According to Baumard et al. (1998a), PAH levels can be characterized as low, moderate, high and very high when Σ PAH concentrations are 0–100, 100–1000, 1000–5000 and >5000 ng g⁻¹, respectively. PAHs < 100 ng g⁻¹ are indicative of low pollution, whereas values higher than 1000 ng g⁻¹ correspond to chronically polluted industrialized areas and harbours. However, this parameter is questionable in areas where significant inputs from petroleum occurred since it does not take account all alkylated homologue compounds derived from fossil sources. In this study the sum all PAH compounds is preferred due to the high proportion of fossil PAH. The comparison of the Σ PAH levels in the present study are similar to the international studies worldwide (Table 3). On the basis of classification adapted by Baumard et al. (1998a), the sediments from the Gemlik Bay can be considered low to very high polluted with PAHs. Due to their non-solubility, hydrophobic character ($\log K_{ow} = 3–8$) and long-lasting persistence, PAHs rapidly become associated with sediments and suspended particles (Law et al., 1997). The sum of two- and three-ring aromatic hydrocarbons varies from 1.0 to 10137 ng g⁻¹ with an average of 949 ng g⁻¹ while the sum of four to six ring hydrocarbons (perylene excluded) ranges from 1.7 to 5502 ng g⁻¹ with an average of 849 ng g⁻¹ dry weight.

Total PAH concentrations range in general from very low in offshore areas and unaffected coasts to very high in the vicinity of urban centers, industrial sources or river outflows. Highly polluted sediments coincide to the nearshore areas with high anthropogenic input coming from the marinas, ports, three local fuel storage terminals

Table 2
Petroleum hydrocarbons (Σ PAHs)

Station	2–3 Ring PAHs		4 Ring PAHs				5 Ring PAHs						6 Ring PAHs IP	Total PAH	LMW/HMW
	Phe	Ant	Flu	Py	BaA	Chry + Triph	BbF	BkF	BeP	BaP	Per	BPer			
G01	5995	1744	480	534	157	258	439	312	890	1718	240	143	571	13481.0	1.35
G02	178	NC	49	66	NC	14	1020	165	490	289	140	208	500	3119.0	0.06
G04	3076	397	660	520	210	291	195	69	270	135	275	470	654	7222.0	0.93
G06	384	129	288	255	98	146	204	73	98	141	49	78	96	2039.0	0.34
G07	361	610	495	300	NC	23	148	52	2	NC	16.9	29.3	45	2082.2	0.87
G08	1092	1400	115	68	108	251	42	22	17	54	25.6	23	56.8	3274.4	3.19
G09	565	86	385	338	110	141	33	14	5	NC	12	17.2	27	1733.2	0.60
G11	NC	45	766	710	NC	8.1	0.5	0.1	25	80	NC	NC	0.1	1634.8	0.03
G12	1780	295	139	115	121	156	0.4	0.2	13	40	NC	NC	NC	2659.6	3.55
G13	1016	174	156	138	56	80	0.1	0.1	12	37	NC	NC	NC	1669.2	2.48
G14	775	NC	144	89	30	36.5	14	6	22	74	NC	NC	NC	1190.5	1.87
G15	391	NC	885	720	33.6	56	0.5	0.4	28	46	8	13.2	19	2200.7	0.22
G16	738	150	892	603	34.4	32	6	0.3	19	62	209	345	383	3473.7	0.34
G17	6745	1435	51.6	42.7	39	42	64	18	7	45	90	102	145	8826.3	12.66
G18	399	152	54	45	28	27	7	5	0.1	NC	16	25.4	48.4	806.9	2.15
G19	218	167	168	161	7.5	18	6	4	NC	0.5	25	28.6	31.2	834.8	0.86
G20	NC	NC	702	557	32	46	0.1	0.1	0.2	NC	4	10.1	9	1360.5	NC
G23	765	163	52	37	9	11.6	24	9	9.9	32	7	12.3	17.5	1149.3	4.19
G24	2685	614	9	7.9	15	16.8	32	10	2.1	NC	0.2	NC	0.3	3392.3	35.36
G25	1493	307	21	17	65	67	79	26	0.1	NC	45	61.3	88.2	2269.6	3.83
G26	8056	2081	98	79	65	74	176	65	15.3	46	71	92	114	11032.3	11.32
G27	216	57	402	372	224	249	753	221	98	140.8	63	70	143	3008.8	0.10
G28	3417	416	130	121	14	23	18	7.8	27	45	12	15.8	26.7	4273.3	8.71
G29	467	89	37.7	26	4.3	6.1	12	5.2	0.3	NC	0.1	NC	NC	647.7	6.06
G30	357	68	14	10.7	58	91	2	1.4	0.1	NC	NC	NC	NC	602.2	2.40
G31	203	30	21	17.2	10.9	12.3	5	3.5	0.1	NC	4	NC	8.5	315.5	2.82
G32	469	121	620	470	12	13	304	89	3.4	11.2	97	106	190	2505.6	0.31
G33	307	75	540	465	129	153	119	40	14	42	34	58	66.6	2042.6	0.23
G34	186	52	210	157	8.41	8.33	92	68	NC	NC	18	22.7	40	862.4	0.38
G35	228	NC	6	4.3	12	16.6	45	32	NC	NC	0.5	NC	NC	344.4	1.96
G46	192	NC	84	75	5	7.5	6	4	0.1	NC	20	35.4	44.4	473.4	0.68
G47	103	10	28	19	1	1.6	0.1	NC	NC	0.1	52	57	101.9	373.7	0.43
G48	120	27	4.7	3.8	3.3	3.89	0.2	NC	0.1	0.2	12	20.1	28	223.3	1.93
G49	NC	NC	0.7	0.6	0.1	NC	0.1	NC	NC	NC	0.1	NC	0.2	1.8	NC
G50	116	21	0.8	1.5	2	3	1	0.5	NC	NC	35	59.2	67	307.0	0.81
G52	36	NC	34	25	0.3	NC	21	12	NC	4	59	78	118	387.3	0.10
G54	546	196	14	10.2	23.6	32	6	19	NC	4	14	26	33	923.8	4.08
G55	5.17	0.92	7	10.4	36	44	78	NC	NC	NC	27	45	60	313.5	0.02
G57	NC	NC	15	9.7	0.1	NC	68	29	5.2	16	45	67.4	90	345.4	NC
G58	176	36	220	173	671	685	NC	6	7.2	21.7	70	83	110	2258.9	0.10
G59	NC	NC	52	34.2	0.1	NC	0.5	0.4	NC	NC	0.9	0.2	0.4	88.7	NC
G60	77	12	27	21.9	12	14	NC	NC	NC	NC	0.2	NC	NC	164.1	1.19
G61	NC	NC	36	28.1	0.1	NC	NC	NC	NC	NC	0.5	0.1	NC	64.8	NC
G62	NC	NC	24	21.4	0.1	NC	NC	4.1	NC	0.1	0.1	NC	0.2	50.0	NC
G63	NC	NC	18	9.5	0.1	NC	NC	NC	0.2	0.4	0.2	NC	0.5	28.9	NC
G64	23	NC	9	8.4	9.9	14	31	17	0.1	0.3	18	7.6	42	180.3	0.15
G65	135	30	4.5	3.4	31.9	38	80	25	6	9	23	31	52	468.8	0.54
G66	52	11	2.1	1.7	42	45	17	9	0.3	1.5	32	44.2	62	319.8	0.25
G67	NC	NC	0.9	1	0.1	NC	4	3	NC	0.1	14	17	38	78.1	NC
G68	0.97	NC	10	5.8	0.1	NC	1.9	1.1	NC	0.1	0.8	0.4	0.3	21.5	0.05
G69	NC	NC	3.8	2.4	0.1	NC	0.99	0.97	NC	NC	0.3	NC	0.1	8.7	NC
G70	NC	NC	8.8	7	0.2	NC	2.5	1.4	0.1	0.2	0.1	NC	0.2	20.5	NC
G71	NC	NC	11.9	13.7	0.1	NC	NC	NC	NC	0.1	NC	NC	0.1	25.9	NC
G72	NC	NC	27.9	27.7	0.1	NC	NC	0.1	24	71	29	57	65	301.8	NC
G73	NC	NC	39.7	41.8	0.1	NC	0.5	NC	44.5	89	16	19.4	38	289.0	NC
G74	NC	NC	50	49.01	0.1	NC	NC	0.2	10.8	32	120	130	125	517.1	NC
G75	27	NC	52	40	37	25	NC	NC	26.4	79	18	59	80	443.4	0.06
G76	NC	NC	26	21.8	0.1	NC	18	10	33.6	56	72	45	98.8	381.3	NC
G77	NC	NC	35	29.1	0.1	NC	47	26	225	124	204	131	378	1199.2	NC
G78	312	70	82	73.8	97	82	845	302	88	160	146	117	521	2895.8	0.15
G79	1180	273	193	207	740	577	490	181	210	420	174	87	621	5353.0	0.37
G80	1300	364	126	101	108	120	1070	262	360	190	485	630	1010	6126.0	0.37

NC: not calculated due to concentrations below the detection limits.

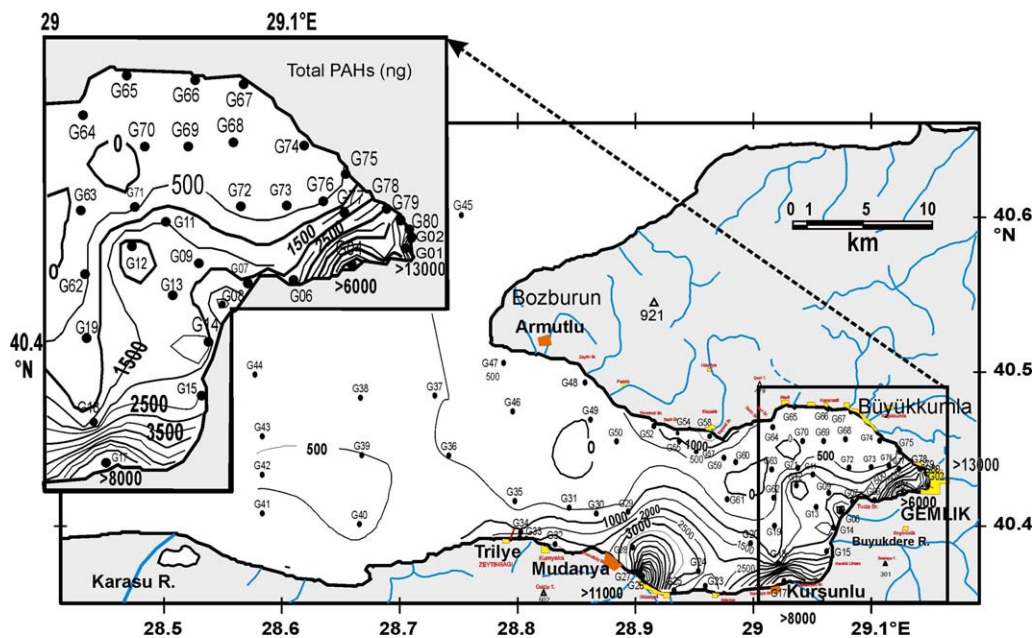


Fig. 2. Contour plots of the total petroleum hydrocarbon concentrations in sediment.

Table 3

Concentration ranges of polycyclic aromatic hydrocarbons (PAHs) in sediments collected from different locations

Location	<i>n</i>	\sum PAHs (ng g ⁻¹)	Pollution level	References
Kyeonggi Bay, Korea	23	10–1400	Low to moderate	Kim et al. (1999)
Baltimore Harbour, USA	21	2944–29 590	High to very high	Pereira et al. (1999)
San Diego Bay, USA	36	80–20 000	Low to very high	Anderson et al. (1996)
Santander Bay, Northern Spain	16	20–25 800	Low to very high	Viguri et al. (2002)
Taranto Gulf, Italy	8	335–5193	Moderate to high	Storelli and Marcotrigiano (2000)
West Mediterranean Sea	14	1.5–20 440	Low to very high	Baumard et al. (1998a,b)
Northwest Coast Mediterranean Sea	14	86.5–48 090	Low to very high	Benlahcen et al. (1997)
Western Harbour, Alexandria, Egypt	20	8–131 150	Low to very high	Mostafa et al. (2003)
Xiamen Harbour, China	9	70–33 000	Low to very high	Hong et al. (1995)
Izmit Bay, Turkey	17	2500–25 000	High to very high	Tolun et al. (2001)
Gemlik Bay, Turkey	14	50.8–13 482	Low to very high	This study

n: Number of PAH compounds analysed in each study. Pollution levels are assigned as low: 0–100, moderate: 100–1000, high: 1000–5000, very high: >5000 ng g⁻¹ (Baumard et al., 1998a).

(Gemlik town, Kurşunlu-Tuzla Point and Mudanya) and anchoring areas scattered in and around the Gemlik harbour. In sediments collected from the central, western exit and northern sectors of the bay, the PAH concentrations were generally much lower than those observed in the eastern and southern coasts. The contamination levels are lower for the sites far from the pollution source. On the other hand, the stations which are little influenced by human activities have shown the lowest concentrations of total petroleum hydrocarbon; e.g. northern coastal area extending from Büyükkumla to Bozburun, as well as central part and western exit of the bay (Fig. 2). Evidently the current speed of the dense lower layer flowing alongside the southern and eastern coasts seems not to be high enough to carry PAH/organic contaminants away and prevent their deposition. The concentrations of total petro-

leum hydrocarbon could also be related to different grain size distributions along the study area.

3.2. Relation between sediment PAHs concentration, organic carbon content and grain-size distribution

The surface sediments covering the study area are mostly composed of terrigenous material which consists of an admixture of sand, silt, clay and gravel (Fig. 3). Possibly due to its sheltered basin morphology and low-energy current conditions, Gemlik Bay is characterized by the overwhelming presence of silt and clay fractions (Table 1). Average percent silt–clay in sediments is rather high at the southern part of the study area (89.9% to the South 43.49°N latitude) and particularly in the bay itself (91.4% to the East of 28.8°E longitude). Two exceptions are small

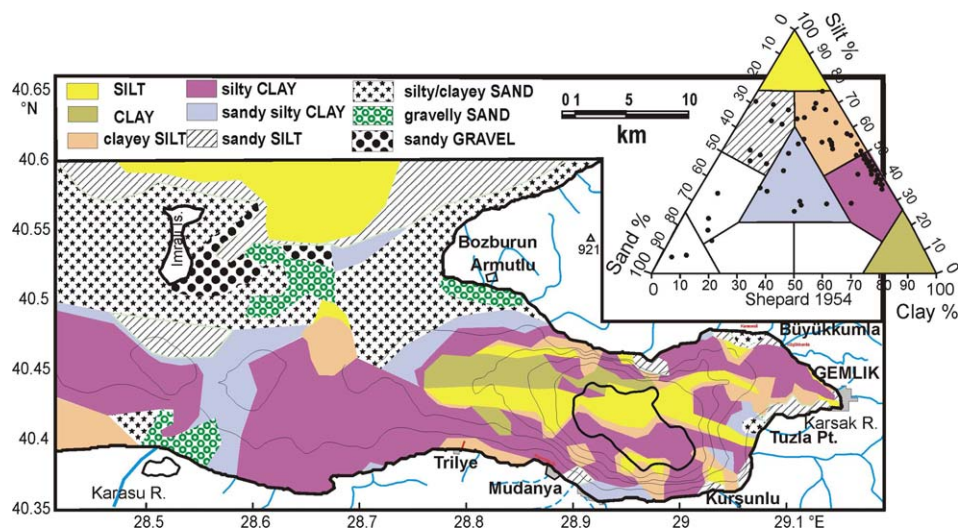


Fig. 3. Distribution of sediment grain size which were classified by designating a principal name describing the major textural component of the sediment with the addition of major and minor modifiers to either describe less abundant components (after Shepard, 1954 and Schlee, 1973).

and local distributions of muddy sand placed in front of the rivers discharging at the Tuzla Point and Büyükümle. The western part of the area is mainly subject to the strong riverine input of the Kocasu River. Mean percent silt–clay decreased northwest rapidly, as low as 30–40% offshore Armutlu Peninsula. The saddle-shaped seafloor between the Imrali Island in the west and the Bozburun village at the western tip of the Armutlu Peninsula forms the sandiest part of the study area with only 21.7% silt–clay. These coarser-grained sediments correspond to the relict deposits formed under shallower water–higher energy conditions. Gravel-sized material is locally present along the shores of the Armutlu Town, in the east of Imrali Island and off the mouth of the Kocasu River.

Sedimentary texture (e.g. mean grain size and silt/clay ratios) and organic carbon were analyzed in order to assess the role of geochemistry on PAH distribution. PAH concentrations may be influenced by physical sediment factors as well as proximity to sources. The organic carbon values of the sediments given in Table 1 range from 0.07% to 3.05% and are typical of marine environments. The organic carbon contents of sediments from both deep trough of the Gemlik Bay and near shore waters in front of Gemlik and Trilye harbours were in general higher than those from the shallow water area in the bay and southern shelf of the Marmara Sea. However, no significant correlation was found between \sum PAHs and organic carbon content beyond a slight positive linear relationship that confirms the presence of elevated total petroleum hydrocarbon concentrations in sediments with high levels of TOC (Witt, 1995; Evans et al., 1990). We suggest that the productive and varied benthic microfauna in Gemlik Bay contributed to the organic carbon level in the benthic sediment masking any relationship which may exist between \sum PAHs and organic carbon. Abnormal individuals of some species (*Spiroplectinella sagittula*, *Spiroloculina excavata*, *Bulimina elongata*, *Ammonia tepida*, *A. compacta*, *Elphidium com-*

planatum, *E. crispum* and *E. macellum*) were observed at eight stations (G6, G7, G17, G25, G26, G34, G36 and G47) (Meriç et al., 2005).

In general, sediments with more silt and clay (percent fines) and higher TOC have higher PAH concentrations than sandy sediments with low TOC (Luoma, 1990; Witt, 1995; SFEI, 2001). The silt/clay ratios range from 0.5 to 7.5, and are generally higher along the shores of the Gemlik Bay and at the NW exit of the bay (Fig. 4). It is lower in the centre of the Gemlik trough. The spatial distribution of the silt/clay ratio shows a distinct pattern in the bay similar to those bathymetric contours. The silt/clay ratio of 1.0 is slightly follows the 60 m isobath. In a general sense PAH concentrations increase with silt/clay ratio, but this relationship is not much stronger than 30% in our case.

3.3. Identifying the origin of PAHs

The study of the compositional patterns of PAH mixtures can provide useful information regarding their sources and transport pathways. Three types of PAHs are commonly found in marine sediments. Pyrolytic PAHs derived during the combustion of all the organic materials, petrogenic PAHs which are contained in petroleum and its products and biogenic PAHs coming from natural terrestrial or marine sources. Pyrolytic PAH mixtures are characterized by predominance of parent compounds with four or more aromatic rings, whereas in petrogenic PAHs the two to three aromatic ring compounds are most abundant components. The biogenic PAHs are retene originated from terrestrial conifer trees and perylene that is diagenetically formed from terrestrial precursors but it is also produced during pyrolytic processes (Baumard et al., 1998b; Guinan et al., 2001).

Several molecular ratios; such as naphthalene/fluoranthene (Nap/Flu); phenanthrene/anthracene (Phe/Ant); fluoranthene/pyrene (Flu/Py); benzo[*a*]anthracene/chrysene

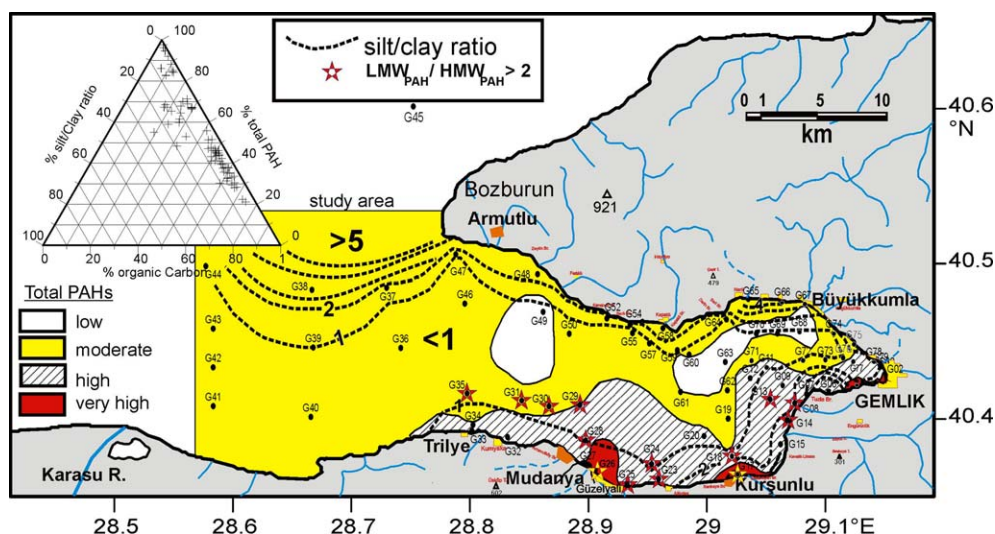


Fig. 4. The comparison of the distributions of silt/clay ratio with \sum PAH levels. Contrary to a symmetric spatial distribution of silt/clay ratios, the highest values of PAH are distributed in front of the Gemlik harbour and nearshore ports and creeks at Kurşunlu, Güzelyali (cable and petroleum plants), Mudanya and Trilye villages. Ternary diagram shows the relation between organic carbon, \sum PAH and silt/clay ratio.

(B(a)A/Chry) and pyrene/benzo[a]anthracene (Pyr/B(a)A) have been developed for interpreting PAH compositions and inferring the possible sources (Blumer and Youngblood, 1975; Sporstøl et al., 1983; Aceves and Grimalt, 1993; Simpson et al., 1995, 1998). Since no alkylated PAHs derived from oil were determined in this study; concentrations ratios of parent PAH including Phe/Ant; Flu/Py; (B(a)A/Chry); Flu/(Py + Flu), the low/high ratio (sum of the low molecular weight PAH (LMW_{PAH}) concentrations versus sum of higher molecular weight PAH (HMW_{PAH}) concentrations) LMW_{PAH}/HMW_{PAH} ; Perylene/sum of the PAH (Per/ \sum (PAH)); Perylene/sum of the penta-aromatics (Per/ \sum (penta-aromatics)) were used identified the possible PAH origins in sediments from Gemlik Bay (Table 1).

Petroleum often contains more thermodynamically stable compounds such as naphthalene; fluorine; phenanthrene and chrysene; while fluoranthene and pyrene are usually the most abundant compounds for pyrolytic PAHs. Therefore, the Flu/Py ratio is obviously related to pyrolytic origins as the values greater than 1; while values less than 1 are attributed to petrogenic sources (Sicre et al., 1987). The Phe/Ant ratio is observed to be very high in PAH petrogenic pollution, but low in pyrolytic contamination cases (Gschwend and Hites, 1981; Soclo et al., 2000). Budzinski et al. (1997) suggested that sediments with Phe/Ant > 10 were mainly contaminated by petrogenic inputs and Phe/Ant < 10 was typical of pyrolytic sources. The averages of the ratios of Phe/Ant and Flu/Py were calculated as 4.11 ± 0.47 ($n = 42$) and 1.09 ± 0.16 ($n = 71$), respectively, which indicate a strong pyrolytic input throughout the bay. Similar results were observed for the (B(a)A/Chry). Chrysene and benzo[a]anthracene are both derived from the combustion processes with (B(a)A/Chry) ratio lower than 1 (Gschwend and Hites, 1981).

The suggested ratio values for crude and fuel oil range from 0.24 to 0.40. The pyrolytic PAH inputs in Gemlik Bay are also confirmed by the B(a)A/Chry ratio, ranged between 0.42 and 1.03 with a mean value of 0.80 ± 0.15 ($n = 47$).

Chrysene, together with triphenylene, is another compound found in marine sediment and believed to be a natural origin aromatic compound and believed to be a natural origin aromatic compound formed mainly during combustion processes and only at low concentration during biosynthesis. In this study, chrysene (together with triphenylene) appeared mostly in near-shore sediments (e.g. stations G1, G2, G4, G6, G7, G8, G15, G27, G32, G33, G34, G47, G58, G79, G80) (Fig. 5), possibly due to the pyrolytic sources via direct input or after deposition in land.

While PAHs with LMW mainly came from petrogenic sources, those with higher molecular weight mostly come from pyrolytic sources when differentiating PAHs into lower (2–3 rings) and higher molecular weight (4–5 rings) fractions, significant differences could be observed in LMW_{PAH}/HMW_{PAH} values in coast and inner harbour samples (Table 2). The values of the ratio LMW_{PAH}/HMW_{PAH} is lower than 1 that indicates pyrolytic origin pollution in general. For example, it averaged 0.39 ± 0.33 for inner sector of Gemlik harbour, showing PAHs in that area to be more pyrolytic. This ratio is almost similar for the northern sector of the bay (0.30 ± 0.37), for Trilye harbour (0.31 ± 0.07), and for Mudanya harbour (about 0.10). On contrary, the LMW_{PAH}/HMW_{PAH} ratio for the stations (stations G35, G31, G30, G29, G28, G26, G25, G24, G23, G18, G17, G14, G13 and G8 from west to east) ranges from 1.9 to 35.3 with an average of 7.0 ± 8.5 , implying petrogenic activity along these stations (Fig. 4).

The compounds of PAHs with four or more aromatic rings (mainly fluoranthene, pyrene, benzo[a]anthracene,

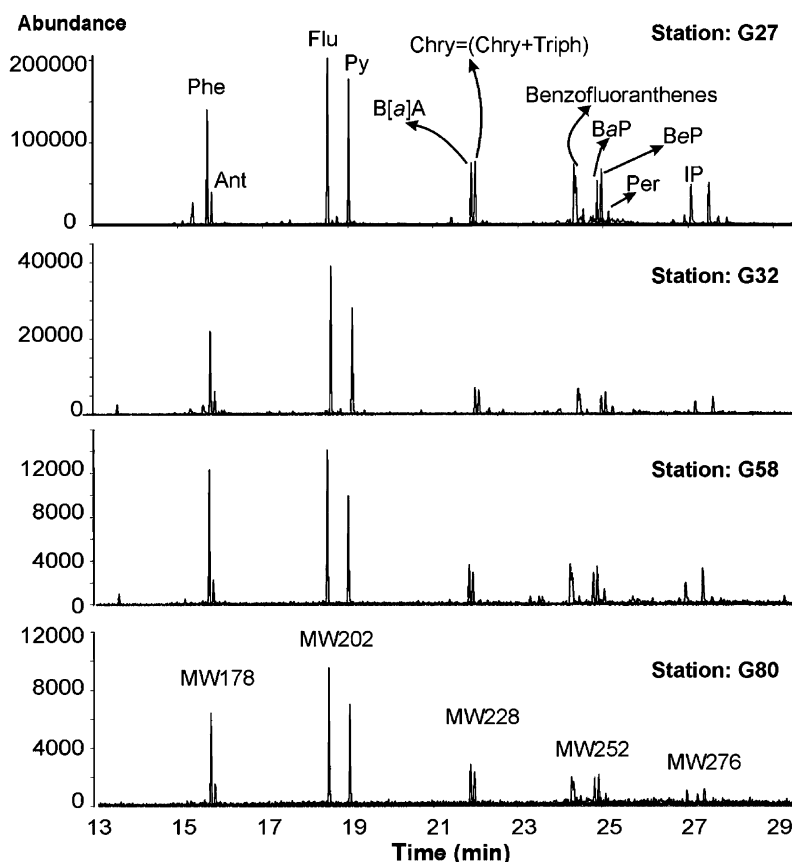


Fig. 5. Selected ion monitoring chromatograms of stations G27, G32, G58 and G80. The relative abundances of three- and more aromatic ring PAHs in the sediments are subgrouped according to their molecular weights: MW178 = (anthracene + phenanthrene), MW202 = (pyrene + fluoranthene), MW228 = (benzo[*a*]anthracene + chrysene), MW252 = (benzofluoranthenes + benzopyrenes) and MW276 = (indeno[1,2,3-*cd*]pyrene + benzoperylene). Abbreviations as stated in the text.

chrysene, benzofluoranthenes, benzo[*a*]pyrene, perylene, benzoperylene and indeno[1,2,3-*cd*]pyrene) were dominant through Gemlik Bay. Shown in Fig. 5 are the summed mass chromatograms of m/z (178 + 202 + 228 + 252 + 276) for selected sediment samples of this study. PAHs of molecular mass 178 and 202 are commonly used to distinguish between combustion and petroleum sources (Yunker et al., 2002). Most of the stations are characterized by almost similar relative abundance of the Phenanthrene series over four and more aromatic ring materials. This shows that there is a mixture of petrogenic (three-ring) and pyrolytic derivative (four- and more aromatic rings) PAHs. Pyrolysis/combustion of fossil materials yields such PAH assemblages, which are subsequently introduced into the marine environment by coastal and river runoff (Neff, 1979; Hoffman et al., 1984), direct dry or wet deposition from the atmosphere (Dichut and Gustafson, 1995). Industrial and/or domestic wastes are often other important sources. An abundance of high molecular weight PAHs was typically encountered in atmospheric particles and urban aerosols (Simoneit, 1985; Sicre et al., 1987) and is characteristic of pyrolytic origin. Anthropogenic combustion processes appeared to be delivered uniformly to sampling sites via atmospheric particulate transport, which may be transported long distances by wind and enriched

by river discharges (Youngblood and Blumer, 1975). This factor greatly contributes to the ubiquity of PAHs and as a result, PAHs have been found in locations remote from industrial/urban activities. If these particles settle on the surface of the sea, they can become incorporated into large fecal pellets or suspended matter, and this will result a rapid deposition in the marine sediment. The Flu/(Py + Flu) ratio (Tsapakis et al., 2003; Zhang et al., 2004) has no any systematic distribution in the Gemlik Bay sediment. However, for coastal sediments, this ratio range between 0.47 and 0.63, with a mean value of 0.56 ± 0.04 ($n = 22$), implying additional effect of atmospheric emission (e.g. combustion of fossil fuels) and deposition (Table 1). The currents and wind waves which are sensitive to the driving regional winds give rise to coastal transports of sediments and contaminants.

Benzo[*ghi*]perylene and indeno[1,2,3-*cd*]pyrene have been used by several researchers as a source identifier for aerosols from automobiles (Greenberg et al., 1981; Harkov et al., 1984). Four anthropogenic PAHs including benzo[*a*]pyrene, perylene, indeno[1,2,3-*cd*]pyrene and benzoperylene were most notable in the studied area.

In the present study, intercalated PAH origins, both pyrolytic and petrogenic, were demonstrated (Fig. 5). The relative amounts of the pyrolytic, fossil and diagenetic

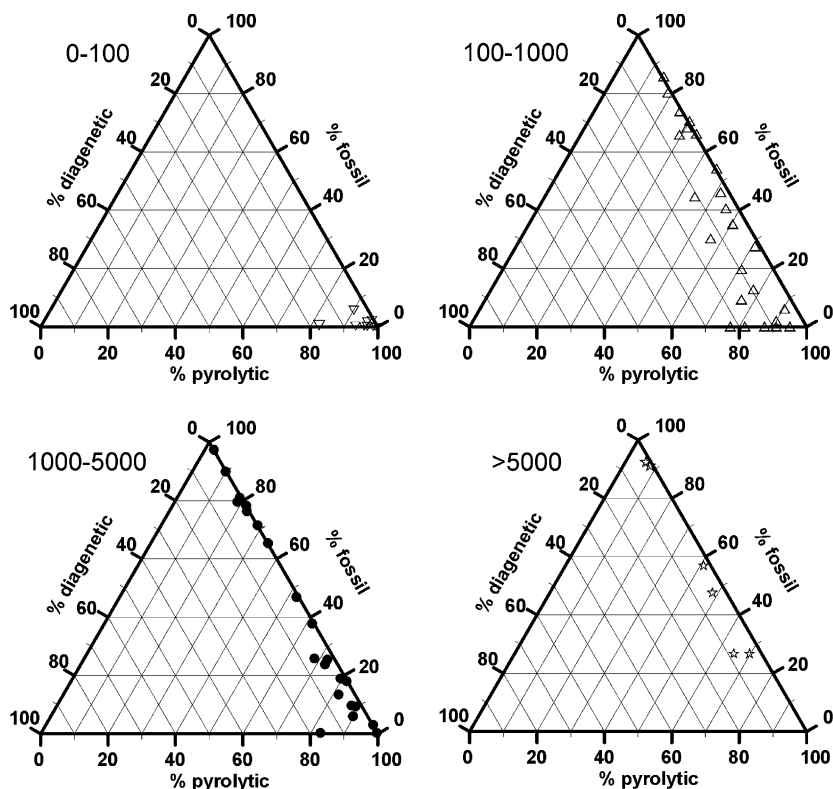


Fig. 6. Ternary diagrams showing the relative amounts of PAHs from different sources (fossil oil, combustion products and natural biological activity) for distinguished ratios of Σ PAH according to the classification adapted by Baumard et al. (1998a).

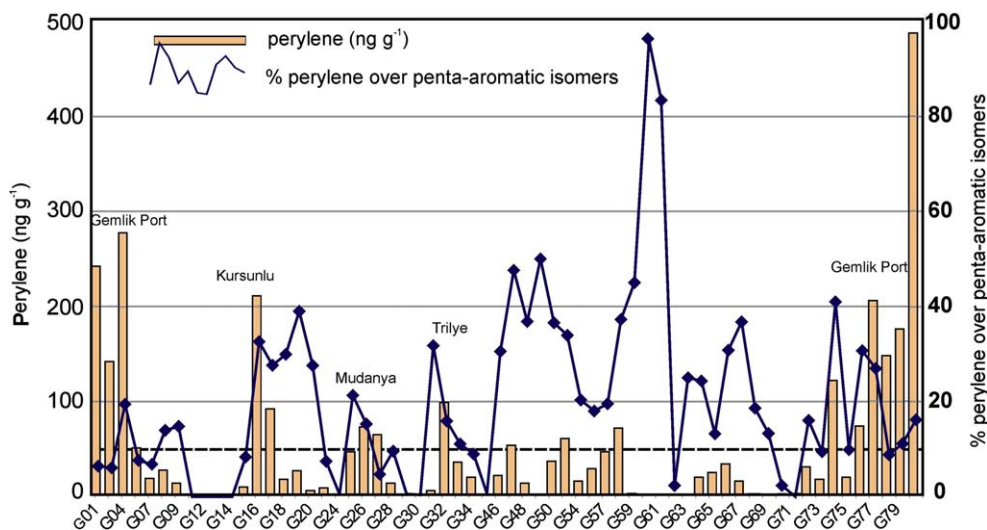


Fig. 7. Plot of the perylene concentration and percentage of perylene relative to the combined concentration of all penta-aromatic isomers for stations of Gemlik Bay.

PAHs are shown in four ternary plots representing each range of Σ PAH (Fig. 6). This diagram clearly shows the overwhelming importance of pyrolytic activity as a source of PAHs in the region. In addition, the sources of PAHs whether from pyrolytic or petrogenic contamination may be identified by ratios of individual PAH compounds based on peculiarities in PAH composition and distribution pattern as a function of the emission source.

In addition to pyrolytic and petrogenic sources, perylene is also produced by in situ degradation of biogenic precursors (Venkatesan, 1988; Baumard et al., 1998b). Indeed, perylene is probably the most important diagenetic PAH encountered in sedimentary environments and, thus a high abundance of perylene relative to the other PAHs can indicate an important natural origin of the compound. The highest concentrations of perylene were observed in front

of Gemlik harbour (stations G1, G2, G4, G77, G78, G79 and G80) and anchoring areas (G6, G76), Büyükkumla and Küçükkumla resort areas (G74 and G75), nearshore the cable and petroleum plants at Güzelyali, 3 km east of Mudanya (stations G25, G26 and G27), in front of a creek at Kurşunlu (stations G16 and G17) and finally in Trilye (G32) village. The large amount of perylene found in these near shore sediment was believed to originate mainly from terrestrial input. Perylene has been frequently associated with inputs from rivers and estuaries (LaFlamme and Hites, 1978; Baumard et al., 1998b). These authors have suggested that concentrations of perylene which are higher than 10% of the total penta-aromatic isomers indicate a probable diagenetic input whereas those in which perylene less than 10% indicate a probable pyrolytic origin of the compound. In the present study perylene was studied in all sediment samples and its concentrations ranged from 0.1 to 485 ng g⁻¹ dw (Fig. 7). Concentrations of perylene relative to the penta-aromatic isomers indicate only a few values are less than 10%, indicating a pyrolytic origin of the compound scattered along the southern sector of the bay. High values are, 10–75%, observed in the northern and deepest sectors of the bay, indicating diagenetic origin for the presence of perylene.

4. Conclusion

The present work represents the first detailed study on the distribution of PAHs in the Gemlik Bay sediment and their possible sources. Since the bay is an urbanized industrial area as well as ornamented by important tourism ports, the anthropogenic and environmental activities show some meaningful interactions. PAH concentrations encountered near the industrial areas were usually much higher than those normal values (>100 ng g⁻¹) observed in the bay. The dominant sources of PAH appear to be combustion processes through run-off, industrial and sewage discharges, and atmospheric input rather than the oil spills. The long-range atmospheric transport of PAHs is of particular importance, mainly due to the terrestrial ecosystems of this semi-enclosed bay.

Conclusions similar to those above could be made when the proportion of nine pyrolytic probable compounds (fluoranthene, pyrene, benzo[a]anthracene, chrysene + triphenylene, benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[e]pyrene, benzo[a]pyrene, benzo[ghi]perylene and indeno[1,2,3-cd]pyrene) to Σ PAH concentrations were used as indicators, percentage combustion determined (Prah and Carpenter, 1983). The present study indicated that the ratio of these pyrolytic compounds to the Σ PAHs is about 70.4% for the northern and central sectors of Gemlik Bay, while it is about 12.4% for the southern coastal area.

Two main sources of PAH in the study area are pyrolytic and petrogenic. The molecular indices of Phe/Ant, Flu/Py; B(a)A/Chry and LMW_{PAH}/HMW_{PAH} has shown, however, pyrolytic activity is dominant. The oil pollution

in sediment is serious at localities Gemlik, Mudanya and Trilye, which originates mainly from municipal effluents, local fuel storage terminals, spillage from vessels, urban vehicle traffic, other port operations and atmospheric deposition/transport. Flu/(Py + Flu) ratios suggest that PAHs contamination is mainly related to PAHs-rich atmospheric particulates produced by anthropogenic combustion processes. Local deposition or long-range transportation is also one of the important sources of pyrogenic PAHs in the bay. Perylene levels were high in many samples, and highest levels were found in areas of strong terrigenous influence. The present study and further researches will contribute to understand how PAHs behave in such kind of semi-enclosed basins; and enable assessment of the environmental stresses confronting the Gemlik Bay and its catchment.

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