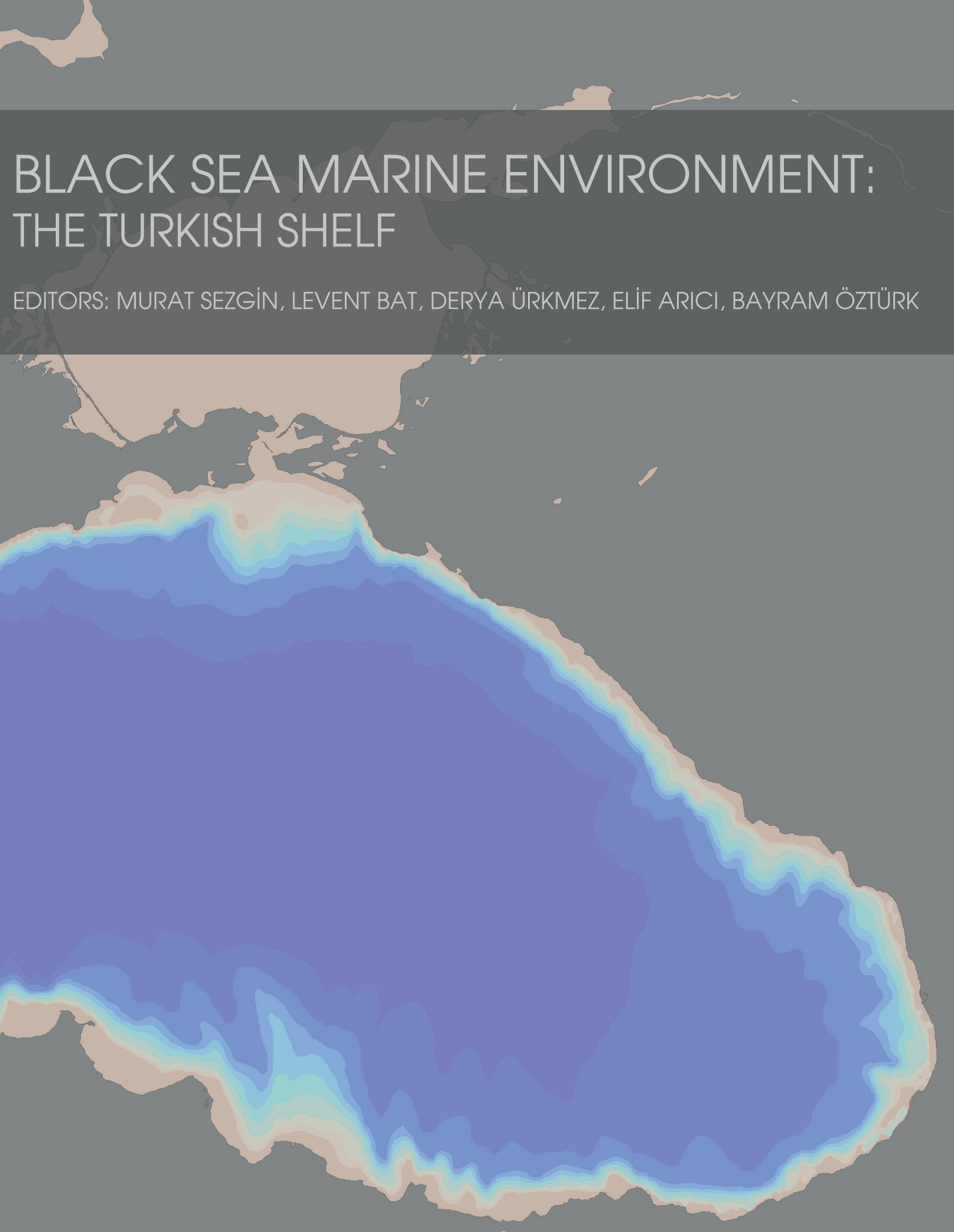
BLACK SEA MARINE ENVIRONMENT:
THE TURKISH SHELF

EDITORS: MURAT SEZGİN, LEVENT BAT, DERYA ÜRKMEZ, ELİF ARICI, BAYRAM ÖZTÜRK



TURKISH MARINE RESEARCH FOUNDATION
Publication No: 46

BLACK SEA MARINE ENVIRONMENT: THE TURKISH SHELF

Edited by

Murat SEZGİN – Sinop University

Levent BAT – Sinop University

Derya ÜRKMEZ – Sinop University

Elif ARICI – Sinop University

Bayram ÖZTÜRK – Istanbul University

Publication no: 46

Istanbul 2017

BLACK SEA MARINE ENVIRONMENT: THE TURKISH SHELF

ISBN- 978-975-8825-38-7

Citation: Sezgin, M., Bat, L., Ürkmez, D., Arıcı, E., Öztürk, B. (Eds) (2017). Black Sea Marine Environment: The Turkish Shelf. Turkish Marine Research Foundation (TUDAV), Publication No: 46 Istanbul, TURKEY.

Turkish Marine Research Foundation (TÜDAV)
P.O. Box: 10, Beykoz / Istanbul, TURKEY
Tel: +90 216 424 07 72
Fax: +90 216 424 07 71
E-mail: tudav@tudav.org
www.tudav.org

EVALUATION OF MONOAROMATIC HYDROCARBON POLLUTION IN SEDIMENTS OFFSHORE TURKISH BLACK SEA COAST

Selma ÜNLÜ and Bedri ALPAR

Istanbul University, Institute of Marine Sciences and Management, 34134 Vefa, Istanbul, Turkey
su@istanbul.edu.tr

1. Introduction

Monoaromatic hydrocarbons constitute an important fraction of volatile organic compounds in the aquatic environment. The volatile mono aromatic hydrocarbons, a collective name for benzene, toluene, ethylbenzene, and *o*-xylene, *(m+p)*-xylenes (light aromatic BTEX compounds) are also major constituents of re-refined petroleum products and other common environmental contaminants. They are highly volatile and are quickly lost through evaporative processes. The BTEX compounds are among the most abundantly produced chemicals, and majority of them released into the environment enter the atmosphere directly (Buczynska *et al.* 2009). In addition to some natural sources (*e.g.* superior plant wax, algae and plankton), they are generated by incomplete combustion of organic matter from mobile (vehicle exhaust) and stationary (wood, coal and waste burning, heating, oil refining) sources (Hinwood *et al.* 2006). They are included in the US Environmental Protection Agency (EPA) purgeable priority pollutants list (USEPA 1989, 1993).

2. Study Area

The major environmental problems of the Black Sea, a marine basin virtually dead below a depth of about 100-150 m where high concentrations of hydrogen sulphide and sulphate-reducing bacteria are present (Murray *et al.* 1991), are markedly differrent from those in other seas. Having excess nutrient loads via the rivers (320-350 km^3 per year) and directly from land-based sources of domestic, industrial and agricultural sources and having anoxic conditions accounting for 87% of it, the Black Sea is now the largest natural anoxic water basin in the world and ranked among the most threatened inland seas of the world.

Oil pollution is another problem of the Black Sea especially at places close to well-known sources. The highest levels of petroleum hydrocarbons (>0.18 mg l^{-1}) detected in the surface waters of the Black Sea are located in three distinct areas. They are offshere the Georgian oil terminals, Danube River, and Turkish coast from Bulgarian border to the Zonguldak industrial area (BSERP 2007). Even the region along the northern exit of the Strait of Istanbul (Bosphorus) is not an industrial region but it is placed on the main shipping routes. Oil contamination in sediments, however, is

considerably less (5.5 – 60 μg g^{-1}) than those found in surface waters. High-speed Black Sea currents and clean Mediterranean water within the two-layer water exchange should be preventing most of the deposition in sediment. To the east, petroleum hydrocarbon contamination in sediments becomes more crucial mainly due to major land-based sources and maritime transport of petroleum carrying tankers (Ünlü *et al.* 2009).

Land-based pollution sources (mainly rivers, domestic and industrial discharges and dumping) account for more than 70% of the sediment pollution in the Black Sea. The large river systems drain 87% of its catchments and provide the 60% of the freshwater input. The water input and sediment load of the Turkish rivers are estimated annually at 41 km^3 and 28 million tons, respectively (Hay 1994). Oil waste discharged annually into the Black Sea is estimated >110,000 tons; half-transported by the Danube River (>53,900 tons) and the rest from land-based sources of its coastal states. Moreover, all maritime activities, including petroleum transport and operational discharges of vessels, contribute to the environmental pollution (Palshin 1998).

The sedimentogenesis situation in the basin is greatly influenced by the runoff fluctuations of Black Sea Rivers, which display a wide range of seasonal variations with a maximum in spring, and by the characteristic features of the watershed. Most of the sediment is carried by the rivers around the periphery and the total annual sediment load into the basin is at least 145 million ton, 20% of which enters into the Anatolian shelf region (Hay 1994). These coasts are mostly polluted with oil particularly close to seaports and river mouths (*e.g.,* Sakarya, Filyos, Kızılırmak Yeşilırmak, Filyos and Bartın).

If compared to the others, Turkey's Black Sea region is not heavily industrialized. Various types of small-scale industries, *e.g.* textile, food, forest products, metal, etc., are scattered in and around the settlement areas usually occupying nearly the whole of the space between the sea and the backside mountains. Some of the larger industrial establishments are located between Ereğli and Zonguldak, the coastal cities of affected from interdependent processes of modern economic development, i.e. industrialization, urbanization and immigration (Ünlü and Alpar 2010).

Iron and steel complexes composed from many separate plants, hard-core production, coke plant, ore processing, mine quarries, mining machine industries and thermal power plants are responsible for the major coastal "hot spots". These areas still suffer from the impacts of air and water pollution from industries mostly due to the difficulties involved in enforcing environmental laws on the existing facilities (Özhan 1996).

Oil waste discharged into the Black Sea because of unlawful disposal of ships' wastes and accidents, as well as through land-based sources is estimated to be 110,840 tons annually; nearly half of it is transported by the Danube River (53,300 tons) and the rest from land-based sources of the Black Sea coastal states (BSERP 2007). Even

though oil levels are not very high in the open Black Sea, unacceptable levels can be detected near polluted harbours and some river mouths. However, there is no sufficient measurement data including the content and potential sources of the aromatic fuel oil components in the aquatic environment of the Turkish Black Sea coast of Turkey.

The Turkish coast of the Black Sea is not a heavily industrialized region excluding some well-known hot spot areas. During the last decades, however, the Black Sea has been subjected to strong environmental impacts that may lead to serious changes in the ecology. The main scopes of the present study are to define the archieval database of monoaromatic hydrocarbon (BTEX) compounds in sediments offshore the Turkish coast of this inland sea, to understand their distribution characteristics according to other parameters such as depth and texture, and to identifiy their possible major sources.

3. Materials and Methods

3.1. Sampling procedure

The surface samples were collected in September 2005 from 48 stations along the Turkish Black Sea shelf areas. The sampling depths were between 9 and 113 m (Figure 1). The topmost 3 cm parts of the grab samples were removed carefully using clean stainless steel spatula. The samples were boxed on a dry ice bed immediately after sampling and transported to the laboratory as soon as possible for analyses.

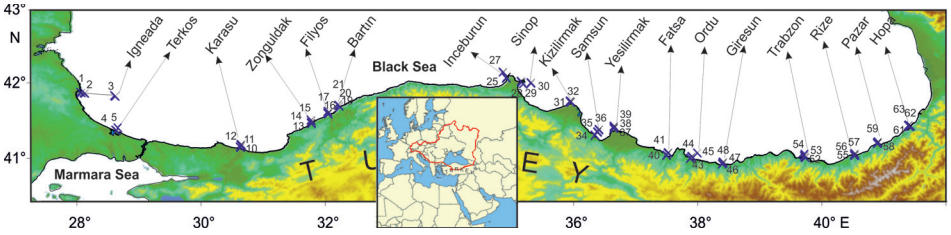


Figure 1. Map showing the sampling stations along the Black Sea shelf of Turkey. Inset shows drainage area of the Black Sea basin

3.2. Sample prepration for chemical analysis

Approximately 10 g of wet sediment was placed in precombusted jar for chemical drying with anhydrous sodium sulfate until it is dry, free-flowing, and homogeneous, then automatic Soxhlet-extracted with dichloromethane (100 ml) for 8h with activated copper. Two grams of anhydrous sodium sulfate were added to remove water. The combined extracts were dried with anhydrous sodium sulphate, and the volume was reduced to 2 ml by rotary evaporation. Aromatic fraction is obtained by adsorption chromatography, using alumina: silica (1:2 volume) column chromatography

(UNESCO 1982). Standard response curves of fluorescence intensity versus concentration are generated for 1) seven different crude oils (from Libya, Saudi Arabia, Egypt, Syria, Cas-pian basin, Iran and Iraq) representing their usage and transportation in the Black Sea region (Ünlü and Güven 2001), and 2) chrysene (Merck), the standard aromatic hydrocarbon. As the geological source of the seven different crude oils used and transported in the Black Sea region is the Thetis Ocean, a huge paleogeographical sea dominant in the periods of Jurassic and Cretaceous, in this study, a com-bined name of Thetis-Oil is given for the seven crude oils (Ünlü *et al.* 2009, Alpar and Ünlü 2010).

3.3. Chemicals and reagents

Standard solutions containing benzene (99.99%), toluene (99.5%), ethyl benzene (99.97%), *m*-xylene (99.8%), *p*-xylene (99.9%) and *o*-xylene (99.3%) were purchased from Merck (Darmstadt, Germany). For qualitative and quantitative recognition of the BTEX compounds in samples, standard curves have been generated for different concentration ranges using benzene, toluene, ethyl benzene, *m-, p-* and *o*-xylene standards in hexane. Detection limits and recoveries were obtained from analysis of three replicates standard solutions at concentrations of 1.5, 3.12, 6.25, 12.5, 25, 50 µg L^{-1}, respectively.

3.4. Analyses

3.4.1. Volatil aromatic hydrocarbons (BTEX compounds)

The qualitative and quantitative identification of BTEX compounds were conducted by Finnigan Thermo trace DSQ gas chromatography/mass spectrometry (GC/MS) using a modified EPA Method 5021 for the detailed molecular characterization of gasoline-derived contamination. This method describes an automated headspace analysis for soils and other solid matrices.

The concentrations in the sediment samples were determined at MERLAB Central Research Laboratory of Istanbul University using a static headspace autosampler (Thermo Finnigan model HS 2000) equipped with 10 ml glass vials. HS-GC–MS reference procedure set was in accordance with the description of Esteve-Turrillas *et al.* (2007). For qualitative and quantitative identification of the BTEX compounds in the sediment samples, standard curves have been generated for different concentration ranges using benzene, toluene, ethyl benzene, *m-, p-* and *o*-xylene standards in hexane. One gram of sediment sample was weighted in glass vial. The sample heated in headspace autosampler at 90°C for 10 min with shaking (headspace syringe temperature: 100°C). The initial oven temperature was 40°C (held for 10 min), then increased up to 200°C (rate 20°C min^{-1}) and held at this temperature for two minutes. Electron impact ionization was used at 70eV and helium flow is 1 ml min^{-1}. Transfer line temperature was held at 250°C. The detector temperature was set to

230°C. In order to obtain the reference data by chromatography a Hewlett Packard HP 5MS (Palo Alto, CA, USA) column was used (30m x 0.32mm i.d., film thickness: 0.25µm).

3.4.2. Analytical Quality Assurance

The vendor software Xcalibur from Thermo (Waltham, MA, USA) and TurboQuant Analyst 6.0 software (Thermo Nicolet Corp. Madison, USA) was employed for measurements and calibration. The mass spectra were obtained at a mass-to charge ratio (*m/z*) scan range from 75 to 200. The specific ions generated at *m/z* 77 and 78 for benzene, *m/z* 91 and 92 for toluene and *m/z* 91 and 106 for ethylbenzene and xylenes. The recoveries of compounds were found to be between 70 and 130%. The repeatability (n=3) varied between 14.9 % (benzene), 7.0 % (toluene), 3.1 % (ethylbenzene) and 13.7 % (xylene). %. The limit of detection (LOD) was between 0.25-0.5 µg kg^{-1} dw for each component.

3.4.3. Other analyses in the sediment samples

Particle grain size (PGS) analysis was applied to samples using the method described in standard operating procedures SOP-8908 at GERG. Granulometric fractions influence the chemical composition in sediment significantly and considered as a normalization parameter. Organic carbon content of samples were measured by Thermo Finnigan FLASH EA 1112 model CHN analyzer at the MERLAB Central Research Laboratory of Istanbul University, after removing the inorganic carbonate fractions, and were replicated within runs and over time with a confidence interval of 0.1%. TOC data was also measured by means of the Walkley-Black method (Loring and Rantala 1992). The analytical precision of analysis was better than ±4% at 95% significance level from five replicates.

3.4.4. Statistical Analyses

Pearson's correlation coefficients calculated the strength of relationships between the monoaromatic hydrocarbon concentrations, and principal component analysis (PCA) quantified spatial/temporal variability of BTEX sources for Turkish Black Sea coast sediment samples (n=48). The first few components explain the inherent variances to largest possible extent (Varmuza and Filzmoser 2008). In the present study, PCA was conducted with varimax rotation. The first three eigenvalues retained were greater than one; as 3.86, 1.95 and 1.49 (n=48).

4. Results and Discussion

4.1. Textural characteristics of sediment

The southern shelves of the Black Sea extend northwards until a shelf break at about 100-130 m water depth. The sediment samples collected above 100 m stay within the oxygenated surface layer of the Black Sea, which is only 50-100 m thick (Table 1). The samples are mainly composed of various size-grained sediments, mainly mud (Figure 2). The depth seems not to be the sole restraint parameter on the grain size distribution, possibly due to rapidly changing morphology incised by canyons and the chaotic physical processes in the water column especially above the sea surface.

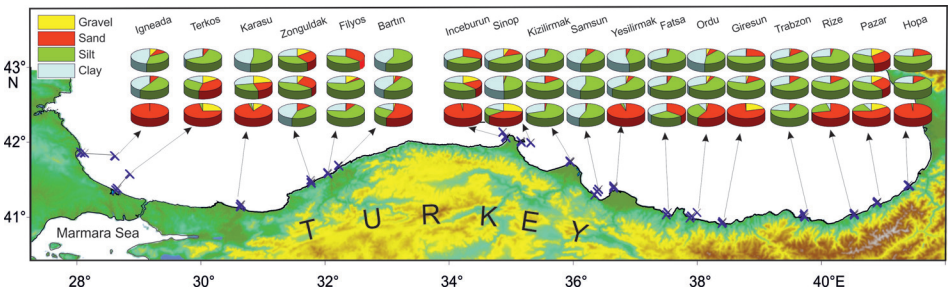


Figure 2. Distribution of textural characteristics of sediments offshore Turkish Black Sea coast

4.2. TOC and TPH Distributions

The TOC content in sediments ranges from 0.5 to 3.2% with an average of 1.54±0.67% (n=48) (Table 1). The highest values of TOC content were recorded offshore the harbours of Zonguldak and Ordu (3.2%), due to coal production and port activities.

The levels of total hydrocarbon, which are calculated using the equation given by Ünlü *et al.* (2009), are scattered in a wide range from 6 to 1546 µg g^{-1} (dry weight) (Table 1). The high values (>100 µg g^{-1} dw) confirm chronic oil pollution, especially those measured near the Zonguldak port (1546 µg g^{-1} dw), Inceburun peninsula (1292 µg g^{-1} dw), Sinop port (915 µg g^{-1} dw) and Trabzon port (330 µg g^{-1} dw). According to Readman *et al.* (2002) the concentrations higher than 100 µg g^{-1} dw are mainly related with port activities or riverine (terrestrial) inputs.

Table 1. The depth (Dep in m), mud (%), sediment water content (Swc in %), total organic carbon (TOC in %), total petroleum hydrocarbon (TPH in μg g^{-1} dw) and concentrations of light aromatic BTEX fractions and total BTEX (μg kg^{-1} dw) in the sediment samples given in Figure 1.

Region	St.	Dep	Mud	Swc	TOC	TPH	B	T	EB	*(m+p)*-X	*o*-X	Total
	1	23	0.1	14.4	0.5	10	BC	BC	BC	BC	BC	BC
	2	50	92.5	57.8	1.5	80	0.3±0,1	0.7±0,1	BC	BC	BC	1.0
Igneada	3	100	84.3	47.4	2.4	102	BC	BC	BC	BC	BC	BC
	4	21	3.1	16.5	1.2	143	BC	BC	BC	BC	BC	BC
Terkos	5	53	46.7	37.4	2.4	43	BC	BC	BC	BC	BC	BC
	10	21	4.1	27.7	1.1	8.2	0.7±0,1	16.4±1,9	3.3±0,5	43.8±3,9	13.2±1,2	77.4
	11	50	54.2	38.0	1.5	29	BC	BC	BC	BC	BC	BC
Karasu	12	98	100	59.3	2.7	46	0.4±0,1	1.5±0,6	BC	0.6	BC	2.5
	13	23	87.3	25.7	3.2	1546	6.2±0,1	9.3±3,1	5.1±2,8	21.7±7,3	2.3±3,2	44.5
	14	51	64.0	38.2	2.1	390	4.2±0,7	9.0±1,4	0.8±0,1	16.6±3,1	1.4±0,0	32.0
Zonguldak	15	103	59.3	43.5	1.4	25	BC	BC	BC	BC	BC	BC
	16	21	91.3	21.3	1.0	513	BC	BC	BC	BC	BC	BC
Filyos R.	17	50	85.5	36.0	2.1	207	0.2±0,1	0.5±0,1	BC	BC	BC	0.7
	19	21	44.0	29.5	0.7	9	2.6±1,8	3.3±2,5	BC	BC	BC	5.9
	20	54	92.5	40.5	1.2	294	0.5±0,1	0.7±0,2	BC	1.3±0,2	BC	2.6
Bartın	21	103	100	45.1	1.3	286	0.3±0,0	1.9±0,5	BC	BC	BC	2.2
	25	21	1.9	20.1	0.8	1292	BC	0.3±0,0	BC	BC	BC	0.3
Inceburun	27	101	69.6	46.9	1.5	164	2.0±0,3	6.1±1,0	0.7±0,1	3.9±0,6	0.9±0,0	13.6
	28	21	36.2	32.7	1.0	915	BC	0.3±0,1	BC	BC	BC	0.3
	29	49	97.6	53.8	1.6	59	1.3±0,2	2.5±0,6	BC	BC	BC	3.8
Sinop	30	97	81.0	43.9	1.6	100	0.3±0,0	0.9±0,1	BC	BC	BC	1.2
	31	25	98.4	32.1	0.7	28	0.3±0,0	0.9±0,2	BC	BC	BC	1.1
Kızılırmak	32	38	85.9	37.1	0.8	62	0.2±0,0	0.7±0,2	BC	BC	BC	0.9
	34	13	98.6	8.9	2.0	119	4.4±0,3	147±16,8	22±4,0	148.2±23,9	18.5±1,6	340
	35	51	100	46.1	0.9	34	0.1±0,0	0.3±0,0	BC	BC	BC	0.4
Samsun	36	103	91.4	50.4	1.7	77	0.2±0,0	1.4±0,4	BC	1.0±0,1	BC	2.6
	37	12	4.8	17.9	0.8	32	BC	BC	BC	BC	BC	BC
	38	51	92.7	34.7	1.3	43	BC	0.4±0,2	BC	BC	BC	0.4
Yesilırmak	39	103	96.5	47.9	1.3	122	BC	14.3±2,7	2.9±0,3	36.5±10,5	13.0±2,5	67
	40	21	63.7	43.1	0.7	100	BC	BC	BC	BC	BC	BC
Fatsa	41	51	95.5	44.3	1.6	63	0.2±0,0	0.7±0,1	BC	BC	BC	0.8
	43	9	42.6	23.7	0.7	96	BC	14.5±1,2	2.4±0,6	19.5±8,4	10.0±1,9	46.4
	44	53	92.9	45.2	3.2	64	0.3±0,1	0.2±0,0	BC	BC	BC	0.6
Ordu	45	100	90.1	55.5	1.9	123	0.7±0,0	16.3±1,3	3.5±0,7	32.3±3,9	15.8±1,1	69
	46	21	0.7	20.8	0.7	94	BC	12.6±0,4	2.5±0,6	23.2±1,8	10.7±2,4	49.0
	47	53	84.9	48.1	1.7	64	BC	13.1±1,2	1.9±0,8	17.7±4,4	8.3±1,0	41.0
Giresun	48	98	75.1	44.8	2.1	88	BC	BC	BC	BC	BC	BC
	52	10	93.6	38.4	0.9	330	2.2±0,2	8.2±2,1	0.7±0,1	4.5±1,2	0.8±0,1	16.4
	53	52	90.0	50.6	1.7	40	BC	BC	BC	BC	BC	BC
Trabzon	54	93	87.1	40.8	1.4	57	BC	13.4±3,5	3.3±0,9	34.7±12,6	13.8±3,8	65.1
	55	21	28.9	28.8	1.1	269	BC	15.4±2,1	2.4±0,8	19.2±11,9	9.2±5,1	46.2
	56	53	87.6	53.2	2.1	201	BC	0.5±0,1	BC	BC	BC	0.5
Rize	57	113	97.4	48.6	1.9	12	BC	BC	BC	BC	BC	BC
	58	21	25.3	11.5	1.4	12	BC	14.7±1,9	1.8±1,0	11.5±1,2	6.0±1,6	34.0
Pazar	59	52	59.6	45.8	2.4	88	BC	BC	BC	BC	BC	BC
	61	22	1.5	17.5	1.3	7	BC	BC	BC	BC	BC	BC
	62	52	88.1	47.4	2.6	132	BC	15.4±1,1	BC	7.8±0,6	6.1±0,8	29.3
Hopa	63	101	79.4	47.4	2.3	86	0.7±0,1	0.6±0,1	BC	BC	BC	1.3
Min		9.0	0.1	9.0	0.5	7.0	0.1	0.2	0.7	0.6	0.8	BC
Max		113	100	59	3.2	1546	6.0	147	22	148	18	340
Mean		53	67.6	38	1.5	185	1.3	10.1	3.8	24.7	8.7	20.8

BC: not calculated due to concentrations below the detection limits. B: Benzene, T: Toluene, E: Etylbenzene, (*m+p)*-X: (*meta+para)*-Xylene, *o*-X: *ortho*-Xylene.

4.3. BTEX compounds in sediment samples

Distributions of concentrations of volatile gasoline-related compounds were different in the sites sampled and they varied between concentrations below the detection limits and 340 μg kg^{-1} dw along the southern Black Sea shelf (Figure 3). The distribution of BTEX concentrations may depend on various factors such as petroleum hydrocarbon distribution, distance to the hot points, water depth, sediment texture, land-based pollutant sources and the variability of biodegradation processes. The total BTEX concentrations, in general, were much higher in the Eastern Black Sea (EBS) region than the western Black Sea (WBS) region and the maximum value was (340 μg kg^{-1}) at station 34 near-shore sediments in Samsun. Median concentrations of BTEX compounds in the EBS region and the WBS region were 32.4 and 8.3 μg kg^{-1}, respectively (Table 1).

4.4. Statistical relationships between parameters

The regression analysis revealed the relationships between the concentration of individual BTEX compounds, percentage of grain size, sediment water content, TOC and total petroleum hydrocarbon levels (Table 2). The TOC concentrations increase slightly with the increasing depth and finer grain size. The finer grained sediments (i.e. silt and clay) have much ability to carry and store pollutants than coarse-grained sandy sediments. Therefore, the samples with low TOC values are mostly made up of coarse-grained sediments (r^2=0.48, $p<0.01$). The samples taken from higher depths (93-113 m) contain higher TOC contents (1.8-2.7%), with a correlation of r^2=0.43 ($p<0.01$). Clay is better correlated with TOC for shallow depths than 25 m ($r^{2=}$0.55, $p<0.05$). The organic matter sedimentation rates are highest in anoxic systems. Therefore, in addition to seaport areas, most of carbon preservation in sediment occurs in anoxic systems.

The correlation matrix exhibits moderate to high similarities between the BTEX compounds ($0.47>r^2>0.99$; $p<0.01$), except weak correlation between benzene and *o*-Xylene. There is a moderate correlation between the levels of TPH and benzene (0.45, $p<0.01$), while no meaningful correlations have been detected with other light aromatic hydrocarbon compounds.

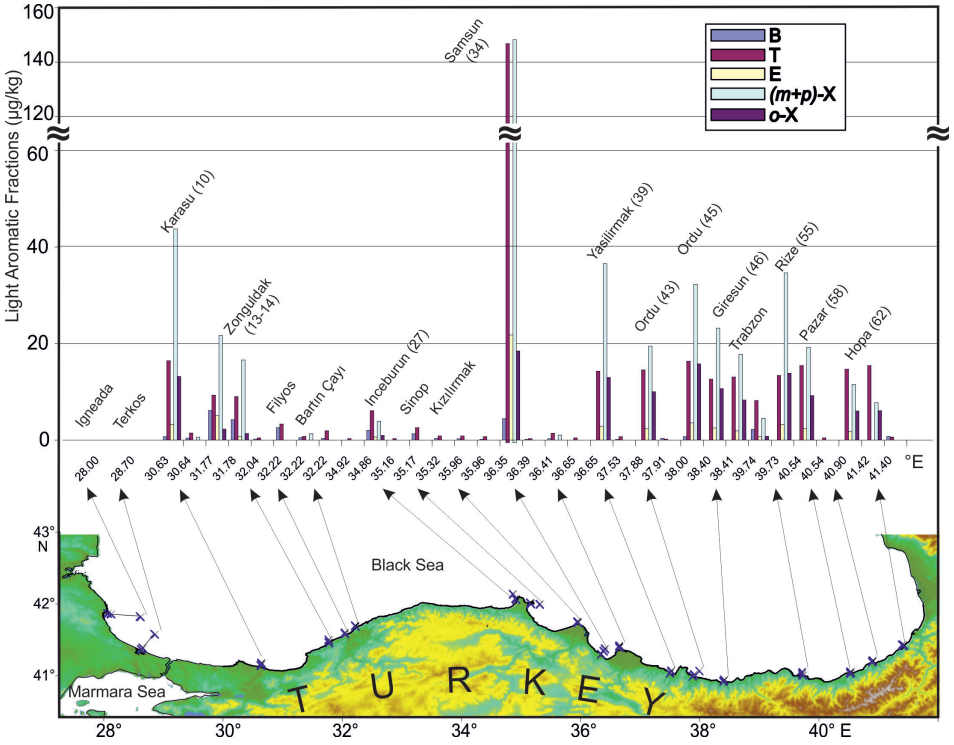


Figure 3. Contributions of BTEX levels of sediments offshore Turkish Black Sea coast.

4.5. Source identification of the BTEX compounds in sediment samples

PCA technique reveals if relevant relationships exist between the cases. Three principal components were retrieved for the Black Sea shelf sediments. Including the loadings of different BTEX congeners, TPH, and some physicochemical parameters in sediment samples and considering all of the stations from Western and Eastern Black Sea, the variance loading of the first three factors is 42.9, 21.7 and 16.6% of the total variability respectively (accumulative variance 81.2%, n=48). If we separate the stations into two clusters, as the western (n=23, stations 1-32) and the eastern Black Sea (n=25, stations 34-63), the main two factors used to identify the source categories and the loadings are shown in Figures 4a and b.

Factor 1. Accounting for 46.4 and 48.4% of total variance in the western and eastern Black Sea region, respectively, this factor exhibits higher loadings for light aromatic fractions and TPH, influenced from anthropogenic inputs either from point or non-point sources.

Table 2. Pearson-coefficient correlation matrix (r) between concentrations of BTEX compounds, TPH, and some physicochemical parameters in sediment samples (n = 48).

	Depth	Gravel	Sand	Silt	Clay	swc	TOC	TPH	B	T	E	*(m+p)*-X	*o*-X
Gravel	-.158												
Sand	-.516**	.260											
Silt	.376**	-.452**	-.899**										
Clay	.570**	-.342*	-.852**	.603**									
swc	.719**	-.252	-.683**	.590**	.646**								
TOC	.426**	-.029	-.457**	.381**	.389**	.426**							
TPH	-.247	.026	.082	-.115	-.017	-.231	.108						
B	-.173	-.176	-.144	.083	.247	-.174	.295*	.447**					
T	-.195	-.090	-.085	.053	.134	-.342*	.089	-.022	.468**				
E	-.192	-.085	-.073	.015	.161	-.362*	.115	.079	.536**	.975**			
(m+p)-X	-.154	-.071	-.043	-.013	.132	-.325*	.073	.006	.468**	.957**	.976**		
o-X	-.062	-.010	.072	-.103	.003	-.202	-.046	-.091	.156	.660**	.701**	.806**	
∑BTEX	-.172	-.079	-.055	.009	.131	-.334*	.079	.001	.476**	.979**	.985**	.995**	.780**

*Correlation is significant at the 0.05 level (2-tailed). **Correlation is significant at the 0.01 level (2-tailed).

Factor 2. This factor showed the similar distribution pattern in both regions (with 22.6 and 22.1% of total variance). It controls different weathering degrees of light aromatic fractions and TPH. This includes rapid aerobic/anaerobic biochemical degradation under the control of nitrate or sulfate as the terminal electron acceptor, or desorption in the water column during the mixing, transportation and deposition of organic matter from point and non-point sources. The depth of the station, sediment texture and TOC control this factor. Mud and TOC, however, is only correlated for shallow depths (<25 m).

Factor 3. The third factor is responsible for 15.6% of the total variance in the western Black Sea, slightly higher than the eastern coasts (12.0%). This factor predominantly composed by TPH pollution solely, coming from point sources. They were observed at the western (4, 16, 17, 20, 21, 25, 28 and 30) and eastern (40 and 56) stations. These stations are close to the coast, except the station 30. Their TPH levels were greater than 100 μg g^{-1}, implying occurrence of oil spill or leakage pollution caused by vessels, possible discharges from municipal and industrial wastewater or occasional surficial runoff.

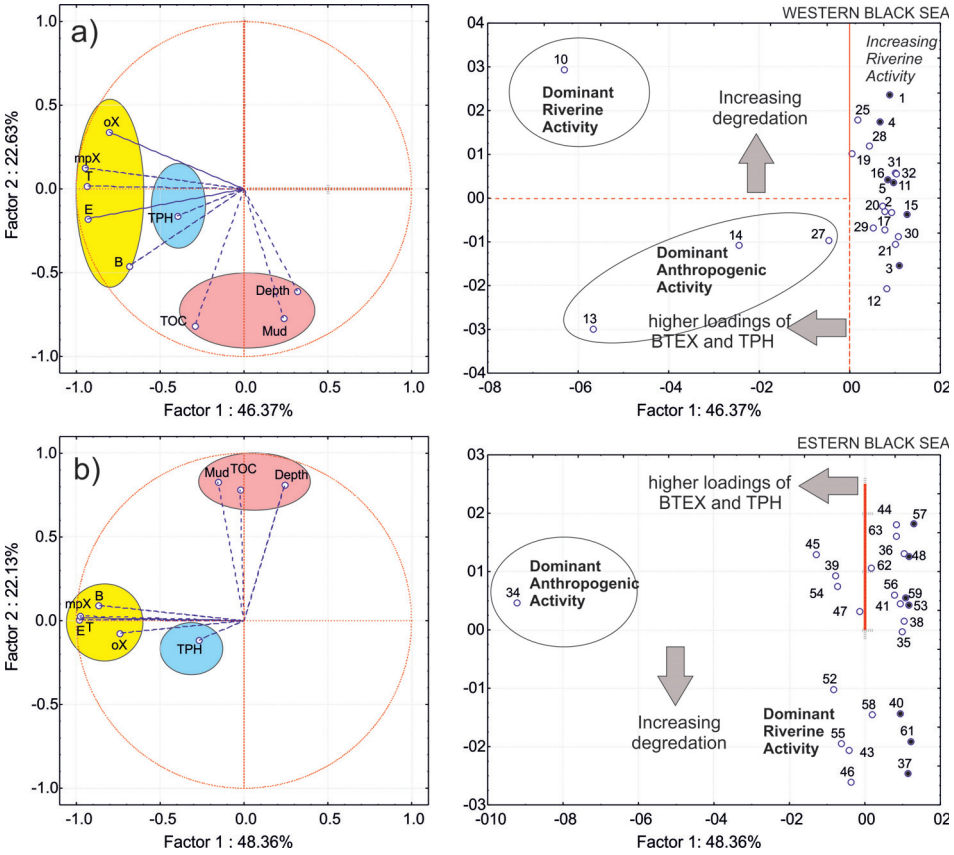


Figure 4. The projection of the variables and cases on the factor plain 1x2 for a) western and b) eastern basins of the Black Sea.

5. Conclusion

The exceptional geography, characteristic hydrographic features and intricate oceanographic conditions make the Black Sea region a unique but sensitive ecosystem. It is more vulnerable to various environmental problems facing humankind. Hydrocarbon (crude oil, diesel and gasoline oil etc) pollution in sediment is not a common phenomenon along the Turkish coast, but usually determined by various reasons. In addition to increasing ship transportation, for example, various land-based sources, such as commercial ports, fuel storage terminals, and anthropogenic inputs from industrial point sources or diffuse emissions are the most serious impacts of pollution on the Black Sea environment.

The highest concentrations of total BTEX were observed at the stations offshore the Zonguldak Industrial Zone, the Samsun Port and the river mouths, especially the Karasu River. If compared to the non-polluted stations, the concentrations close to such point sources were higher up to 4-8 times in the Eastern Black Sea, and 11-65 times in the Western Black Sea. There was not meaningful correlations between the levels of TPH and light aromatic hydrocarbon compounds, except a moderate one with benzene. In terms of the component scores and loadings, the main factors responsible for the incorporation, distribution and fate of the hydrocarbon pollution in the Turkish Black Sea coastal sediments are the high loading of anthropogenic / riverine inputs, the differences in the rate of weathering of light aromatic fractions and TPH and finally individual TPH pollution usually coming from point sources.

It is imperative that planned and continuous monitoring of pollutants be carried out at the polluted areas specified in this study and other vulnerable regions. Such kind of systematic programs will provide a basis for environmental impact assessment and control.

Acknowledgements

The sediment samples were collected within the framework of Water and Sediment Quality Monitoring Project supported by the General Directorate of Istanbul Water and Sewerage Administration. Authors are indebted to the staff of R/V Arar-1 for their efforts in sediment recovery. A financial support was also provided by the Research Fund of Istanbul University (Project BEK-21558) for scientific analyses.

References

Alpar, B. and S. Ünlü. 2010. Volatile aromatic compounds (BTEX) in sediments offshore Zonguldak Industrial Region, Black Sea, Turkey. Asian J. Chem., 22: 3531-3540.

BSERP. 2007. Black Sea Transboundary Diagnostic Analysis, Black Sea Ecosystem Recovery Project, Blck Sea Commision, GEF, UNDP, UNOPS. RER/01/G33/A/1G/31, Programme Coordinating Unit, Istanbul, Turkey.

Buczynska, A.J, A. Krata, M. Stranger, A.F.L. Godoi, V. Kontozova-Deutsch, L. Bencs, *et al.* 2009. Atmospheric BTEX-concentrations in an area with intensive street traffic. Atmos. Environ., 43: 311-318.

Esteve-Turrillas, F.A., S. Armenta, S. Garrigues, A. Pastor, and M. de la Guardia. 2007. Headspace-mass spectrometry determination of benzene, toluene and the mixture of ethylbenzene and xylene isomers in soil samples using chemometrics. Anal. Chim. Act., 587: 89-96.

Hay, B.J. 1994. Sediment and water discharge rates of Turkish Black Sea rivers before and after hydropower dam construction. Environ. Geol., 23: 276-283.

Hinwood, A.L., H.N. Berko, D. Farrar, I.E. Galbally, and I.A. Weeks. 2006. Volatile organic compounds in selected micro-environments. Chemosphere, 63: 421-429.

Loring, D.H. and R.T.T. Rantala. 1992. Manual for the geo-chemical analyses of marine sediments and suspended particulate matter. Earth-Sci. Rev., 32: 235-283.

Murray, J.W., Z. Top,. E. Özsoy. 1991. Hydrographic properties and ventilation of the Black Sea. Deep-Sea Res., 38 (2A): 663-690.

Özhan, E. 1996. Coastal Zone Management in Turkey. Ocean Coast. Manage., 30: 153-176.

Palshin, G. 1998. Black Sea in Crisis. In Proceedings from the 23rd Session of the International Seminars on Planetary Emergencies, ICSC-World Laboratory Rep. No. 23, Erice, Sicily, August 19-24.

Readman, J.W., G. Fillmann, I. Tolosa, J., Bartocci, J.-P. Villeneuve, C. Catinni, and L.D. Mee. 2002. Petroleum and PAH contamination of the Black Sea. Mar. Pollut. Bull., 44: 48-62.

UNESCO. 1982. The determination of petroleum hydrocarbons in sediments. Manuals and Guides, Intergovernmental Oceanographic Commission. 11: 1-35.

Ünlü, S. and K.C. Güven. 2001. Role of reference materials used in measurement of oil pollution and a correlation equation to determine oil in seawater. Bull. Environ. Contam. Toxicol., 67: 1-5.

Ünlü, S., B. Alpar, and Ş. Aydın. 2009. Spectrofluorometric characterization of aromatic hydrocarbon contamination in the sediment from the Zonguldak Industrial Region, Black Sea, Turkey. Fresenius Environ. Bull., 18: 474-480.

USEPA. 1989. Method 503.1 Volatile Aromatics. Environmental Monitoring and Support Laboratory, Cincinnati, USA.

USEPA. 1993. Provisional Guidance for Quantitative Risk Assessment of Polycyclic Aromatic Hydrocarbons. EPA/600/R-93/089, Washington, DC.

Varmuza, K. and P. Filzmoser. 2008. Introduction to Multivariate Statistical Analysis in Chemometrics. CRC Press, Taylor and Francis Group, Boca Raton, FL.