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Volatile Aromatic Compounds (BTEX) in Sediments Offshore Zonguldak Industrial Region, Black Sea, Turkey

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The coastal area off the Zonguldak Industry Region is one of the most-polluted "hot spots" in the anoxic water basin of Black Sea, which is ranked under great anthropogenic pressure among the most ecologically threatened water bodies of the world. Quantitative analyses of volatile aromatic compounds using Finnigan Thermo trace DSQ gas chromatography/mass spectrometry (GC/MS) indicated considerable levels of BTEX (benzene, toluene, ethylbenzene and the mixture of *o*-, *m*- and *p*-xylenes) contamination in the sediment close to many well-identified pollution sources on land. BTEX contamination of seabed sediment was due mostly to benzene except a station off the Zonguldak sea port where xylene was dominant with toluene. The varying concentrations of the contamination throughout the region indicate sea port activities, industrial inputs and partly maritime petroleum transport as the main sources of pollutants.

Key Words: Volatile aromatic compounds, Pollution, BTEX, Sediment, Contamination, Black Sea, Zonguldak.

INTRODUCTION

The first step needs to be taken to deal with the continuing environmental deterioration of the Black Sea is environmental monitoring of pollutants which can be toxic to organisms. Pollutants, however, never occur as single pollutants, but nearly always as pollutant mixtures. One of the most prominent environmental groups of pollutants is BTEX (benzene, toluene, ethyl benzene and mixture of *o*-, *m*- and *p*-xylenes) compounds often found in discharges and petroleum products. These volatile aromatic compounds are severely toxic to aquatic organisms if contact is maintained[1]. They are generated by incomplete combustion of organic matter and their major sources to the urban environment include vehicle exhaust (mobile source), coal burning and residential heating, waste incineration, petroleum refining processes, coke and aluminum production (stationary sources). Most light crude oils contain BTEX usually from about 0.5 up to 5 % or more. Gasoline can contain large amounts of BTEX (up to 40 %). BTEX compounds are therefore indicators of gasoline contamination and consequently are the chemicals for which sediment samples are analyzed when gasoline contamination is suspected.

BTEX compounds, however, are volatile and, if discharged into the sea, are quickly lost through evaporative processes. Because of their volatility, the time exposure to aquatic organisms may be short enough to avoid toxic effects. Even though volatile organic compounds in marine sediment should, in general, not be regarded as a major problem, elevated local concentrations may be a cause of concern. BTEX compounds are generally neurotoxic to target organisms. Benzene, in particular, has also been found to be carcinogenic to mammals and humans. BTEX compounds are therefore important in monitoring programs and contamination studies.

In Black sea, there is neither a regular monitoring programme that fully conforms to the international standards nor any specific previous research is known on the impact of BTEX pollution in the region even though this knowledge is critical in understanding BTEX emission sources. After a brief review of the Black sea's current environmental conditions, this paper try to assess the extent of BTEX compounds in sediment from the shelf area off the Zonguldak Industry Region (ZIR), one of the most polluted hotspots along the Black Sea (Fig. 1). The results are also correlated with some other parameters such as sediment texture, total organic carbon (TOC) and total petroleum hydrocarbon concentration levels.

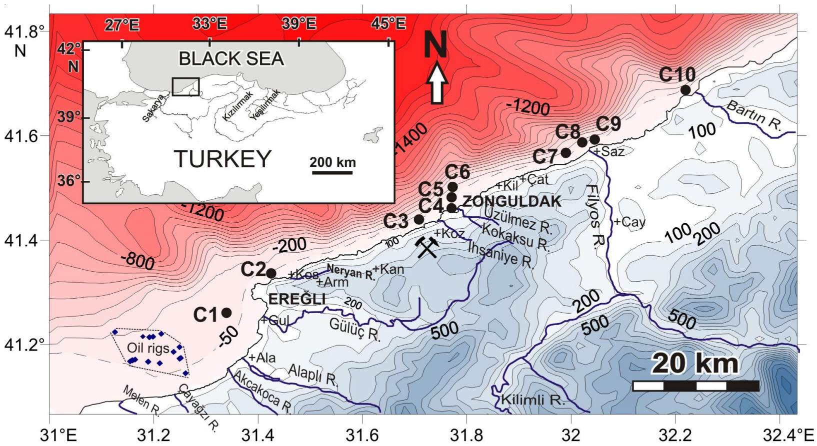

Fig. 1. Sampling stations (C1-10), bathymetry and main rivers. Inset shows the study area. Elevations are in meters. Ala: Alapli, Arm: Armutcuk, Cat: Catalagzi, Cay: Caycuma, Gul: Guluc, Kan: Kandilli, Kil: Kilimli, Kos: Koseagzi, Koz: Kozlu, Saz: Sazkoy

EXPERIMENTAL

In order to investigate past and existing industrial conditions of the ZIR, an environmental site assessment work was performed along the entire coastal area from Eregli in the west and Bartin river in the East. The surface sediment samples were then recovered in September 2005 from the shelf areas mostly off the hot spots defined in land (Fig. 1). The sampling stations were chosen close to river mouths which are the main sources both of sediments and pollutants as they are used as natural discharge elements. The topmost 0-3 cm of the grab sample was used for analyses. Because of the nature of the contaminants, special attention was paid to analyte losses and contamination of the samples during storage aboard the research vessel. Samples were frozen immediately after sampling and analyzed within 48 h of collection.

The particle grain size analysis was performed using petrographic procedures adapted from Folk[2], as described by GERG SOP-8908. Total organic carbon contents (TOC) were measured by means of the Walkley-Black method[3]. The analytical precision of analysis was better than ± 4 % at 95 % significance level from five replicates.

The qualitative and quantitative identification of BTEX compounds were conducted by Finnigan Thermo trace DSQ gas chromatography/mass spectrometry (GC/MS) using EPA Method 8260 modified for Selective Ion Mode (SIM) for the detailed molecular characterization of gasoline-derived contamination. The need to compare values with low benchmark concentrations, detection limits should be as low as possible and in all cases no higher than 0.025 ppm in sediment[4]. BTEX compounds are readily adaptable to gas chromatographic detection which provides low detection limits, but sediment samples are difficult to analyze. Volatilization during sample handling and homogenization can result in losses. BTEX concentrations in marine sediments are usually low and there is a lack of information on standardized methods for their determination in hazard assessment works[4]. Therefore volatile compound laboratory methods with low detection limits were used. Detection limit of the BTEX compounds in SIM mode was as low as 0.01 ppm. The repeatability (n = 3) varied between 14.9 % (benzene), 7.0 % (toluene), 3.1 % (ethyl benzene) and 13.7 % (xylene).

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 (Fig. 2).

RESULTS AND DISCUSSION

During the last 30 years, the coastal areas of the Black Sea, which form a complex system at the land-sea-atmosphere interface, have undergone a continuous process of landscape degradation and loss of resources. Depending on the estimations by the World Bank, economic losses from pollution exceed 500 million US dollars/ year, not including the value of lost species and the cost of rehabilitation and cleanup of coastal areas.

Most pollutants enter from rivers, which bring down nutrients, oil, heavy metals, pesticides, surfactants and phenols and threaten coastal ecosystems. The best estimate of annual unrecoverable oil discharged into the Black Sea is more than 110,000 tonnes, which is nearly one twelfths of the worldwide estimation[5,6]. Most of the oil enters the environment as a result of domestic (> 30,000) and industrial sources (> 15,500), land-based runoff and washed down rivers (> 65,000). Other significant sources are bilge water oil and sludge from vessels, drilling operations and oil spills, at least 150 tonnes[6].

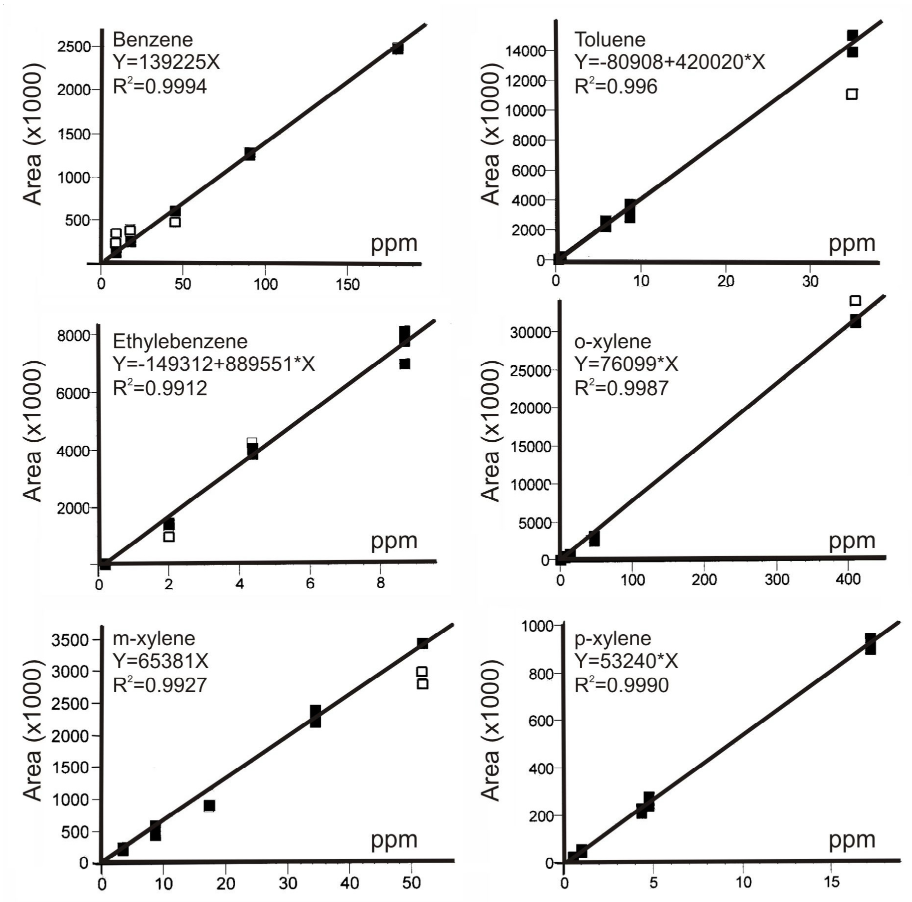

Fig. 2. Standard curves generated for different concentration ranges using benzene, toluene, ethylbenzene, *m*-xylene, *p*-xylene and *o*-xylene standards in hexane

Oil levels are not very high in the open Black Sea but unacceptable in many coastal areas perilously close to polluted harbors and many river mouths[5]. These areas, however, present the highest levels of bio-diversity and have a high socio-economic importance due to human use of coastal resources. There are about sixty sources of pollution which resulted in "hot spots" having disastrous impacts on sensitive marine and coastal areas and needed immediate priorities for action such as heavy investments in building wastewater treatment plants. The term of "hot spot" is employed to indicate a place with exceptionally high levels of pollution. Such a large number of small sources of pollution have been caused from a wide range of small industries, including such things as chemical plants, clothes and textile manufacturing units, metallurgical works and food processing. Many of the discharges from these plants are currently poorly regulated.

Pressures on coastal areas are growing both in terms of land use and population density and will grow more in the near future, increasingly leading to conflicts between coastal users of countries, cities and even towns. Fortunately, the Turkish coasts of the Black Sea are not much heavily industrialized, except a number of hot spots. Only small-scale textile, food, forest products and metal industries are scattered in and around the settlement areas. The average oil contamination in the sediments at the northern approaches of the Istanbul Strait (Bosphorus)[7] varies from 5.5-60 µg/g. It becomes > 190 µg/g towards the cities of Eregli and Zonguldak in the east, which are leading provinces of Turkey in terms of industrial production and known as Zonguldak Industrial Region. It is one of the important hot spots where some large scale plants were placed. The most important ones are an iron and steel complex located in Eregli and a 600 MW thermal power plant located at Catalagzi, 20 km east of Zonguldak. The sediment samples collected for this study represents this specific area having the highest industrialization and urbanization rates.

Textural and total organic carbon characteristics of sediment: The sea bottom in study area is under the control of the longshore currents supplied with river alluvium and coastal abrasion material and composed of mainly sand and silt mixtures with small amount of clay. The TOC content is variable and ranges from 0.9-3.1 % with an average of 1.89 ± 0.66 % (n = 10) (Table-1). The samples with lower TOC values are mostly coarse grained. The highest content of TOC was recorded offshore Zonguldak sea port (stations C3 and C4).

BTEX compounds in sediment samples: The highest total BTEX concentration (3.25 ppm) was observed at C4 off the Zonguldak port, followed by the stations of C3, C7, C8, C5 and C10 (Table-1). Other stations contain very low level of total BTEX (0.07-0.21 ppm).

Benzene is the most dominant gasoline compound with a median (range) concentration of 0.75 ppm (0.04-2.56 ppm). Excluding C4, benzene is directly related with the total BTEX ($r^2 = 0.997$). Toluene concentrations were low and only at C4 it was high (0.27 ppm). Even the metabolism of simple compound mixtures of BTEX under environmental conditions is by far not understood yet. Toluene often degrades under all redox conditions. Even ethylbenzene is often found together with benzene, no ethylbenzene was detected in present samples at a detection limit of 0.025 ppm. Finally mixed xylene was detected only in the station C4, offshore the Zonguldak sea port.

The overall appearance shows some gasoline contaminations in 4 stations; C3, C4, C7 and C8. Extracted ion chromatograms of BTEX compounds at m/z 78, 91, 106 for surface samples show that low-molecular mass hydrocarbons attributed to a light petroleum product eluting before 6 min (Fig. 3).

TABLE-1
DEPTH, TEXTURAL FEATURES, WATER HOLDING CAPACITY, ORGANIC CARBON, TOTAL PAH AND BTEX COMPOUNDS (µg/g, DRY WEIGHT) IN THE SEDIMENT SAMPLES

Station	Depth (m)	Texture	Moisture (%)	TOC (%)	TPH	B	T	E	*m*-	*p*-	*o*-	Total
C1	57	Sand	40.5	1.5	98	0.04	0.02	ND	0.00	0.01	ND	0.07
C2	35	Silty Sand	28.9	2.6	1589	0.19	ND	ND	0.01	0.01	ND	0.21
C3	67	Sandy Mud	36.2	1.7	468	2.33	0.03	0.02	0.08	ND	0.01	2.47
C4	23	Sandy Mud	25.7	3.1	1546	0.20	0.27	0.03	ND	2.35	0.40	3.25
C5	51	Sandy Silt	38.2	2.3	390	0.73	0.02	0.02	0.01	0.01	ND	0.78
C6	103	Muddy Sand	43.5	1.4	25	0.13	0.02	0.02	ND	0.01	ND	0.17
C7	96	Silt	29.8	1.8	459	2.56	0.03	0.02	0.07	ND	0.01	2.69
C8	37	Sand	31.7	1.4	158	0.77	0.03	0.02	ND	0.14	0.02	0.98
C9	50	Sandy Silt	36.0	2.2	208	0.05	0.02	0.02	ND	0.01	ND	0.09
C10	21	Muddy Sand	29.5	0.9	9	0.45	0.02	0.02	ND	0.02	0.00	0.51

B: benzene, T: toluene, E: ethylbenzene, *m*: *m*-xylene, *p*: *p*-xylene, *o*: *o*-xylene, ND: not detected.

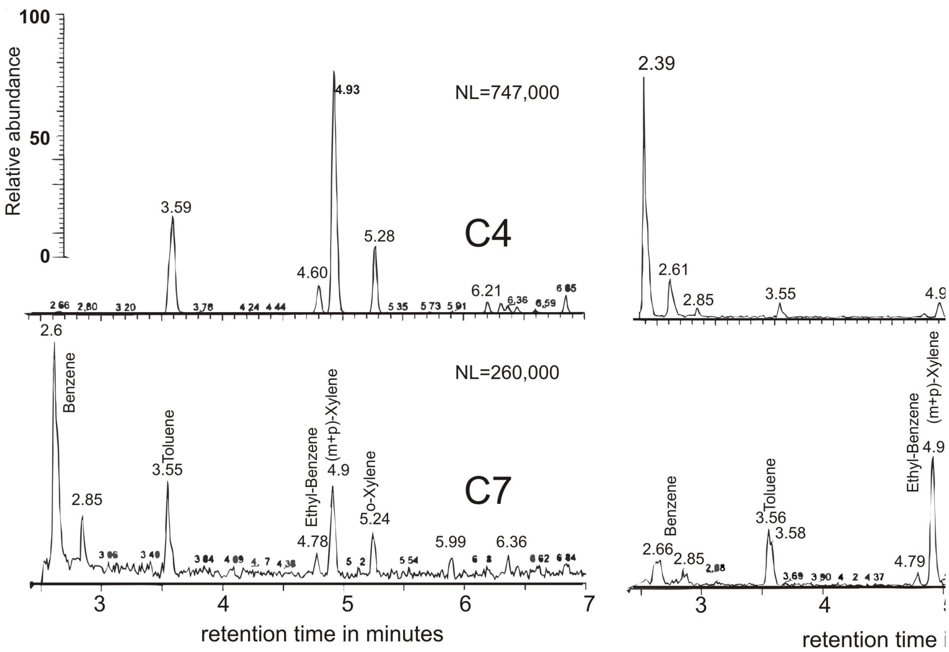

Fig. 3. Extracted ion chromatograms of BTEX compounds at m/z 78, 91 and 106 for some surface samples contaminated with gasoline NL: normalization level

The variability of BTEX levels ranging from 0.07-3.25 μg/g dw may depend on various causes such as total petroleum hydrocarbon (TPH) distribution, distance to the hot points, water depth, sediment texture, variability of biodegradation processes, *etc*. The levels of total petroleum hydrocarbon, given by Unlu *et al*.[8] on the basis of different crude oils used and transported in the region, show wide-range of distributions ranged from 10-1590 μg/g dw (Table-1). The highest levels (1550-1600 μg/g dw) were observed at two distinct spots; offshore the Zonguldak sea port (C4) and a cement factory in Eregli (C2). Excluding these two extreme stations, there is a moderate correlation between the concentrations of BTEX and TPH (r^2 = 0.663).

The changes in grain size fractions influence the chemical compositions of the sediments. Fine-grained sediment samples carry higher levels of BTEX compounds (Table-1), because sandy sediment will not adsorb the volatile organic compounds (VOCs) as strongly as sediment samples with a large clay or organic fraction. Meanwhile the level of BTEX concentrations usually decreases with increasing depth (r^2 = 0.285), especially for less polluted (0.07-0.51 μg/g) areas far from hot points such as ports and river mouths.

Identification of pollution sources: The most important pollution sources in the region are the rivers which are used as natural discharge elements without any treatment. Their contributions are obviously small if we consider that the catchment area of the Black sea discharging main rivers is five times greater than the Black sea surface area and they drain industrial and agricultural wastes of 22 countries[7,9-11]. The total annual sediment load of the Anatolian rivers into the Black sea basin, however, is as high as the 20 % of the total load (Table-2). The total annual waste load entering from the ZIR, for example, is very high (126,292 tonnes) compared to the other industrialized coastal cities[12].

TABLE-2
ESTIMATED CAPACITY AND PRODUCTIVITY OF THE RIVER RUNOFFS[7,9-11]

Rivers	Drainage area (10^3 km^2)	Annual water load (km^3)	Annual sed. load (10^6 m^3)
Western rivers [1]	3.6	1.2	0.3
Filyos port	13.3	2.9-3.3	2.5-5.1
Bartin river	2.1	1.3	0.1
Anatolian	250	40	10
Black sea	1.850-2.350[2]	350-420[2]	50-55

([1]) Includes Melen, Akcakoca, Kozlu, Alapli, Guluc, Neryan and Ihsaniye (see Fig. 1).
([2]) Includes Azov Sea.

Depending on the main hot-spots, the region can be classified into four major industrial zones from west to east.

Industrial zone of Eregli: This area is the center of big iron and steel complexes with a big port close to C1. The complex annually discharges waste waters of 220,000 tonnes. Other industrial facilities were developed in early 1940 s as separate plants. These zones 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[13]. While domestic waste waters of the towns of Guluc and Eregli are discharged into the deep water separately, untreated waste waters of the town of Alapli and the treated industrial waste of textile factories discharged into the sea *via* Alapli river (> 10,000 m^3/day).

A cement grinding and packaging factory operates in Eregli (close to C2) with waste about 50 m^3/day (annually 2 tonnes of waste oil). The Neryan river is used as a natural discharge element for the domestic waste waters of Armutcuk and Kandilli villages and also industrial waste waters of the Armutcuk establishment of the Turkish Coal Corporation. Its pollution can be seen visually along the beaches at Koseagzi.

In this region no BTEX compounds were detected in the sample C1 possibly due to its coarse grained texture (sand) and its distance to the shore. There were no effects of the oil rigs operated to the west of this site (Fig. 1). Similarly the station C2, offshore the Neryan River, has no BTEX compounds even its TPH is elevated.

Industrial zone of Kozlu and Central Zonguldak: This zone bears old industrial complexes for hard coal production since 1848. Due to poor dispersion of air masses especially during stagnant conditions, air pollution cause serious effects in the region. Coal combustion is the major pollutant source with contributions of 80.8 % of the total variance for fine and 53.8 % for coarse airborne particulate matter collected in this zone[14]. Vehicular emissions (21.4 %) and stationary combustion (21.4 %) constitute secondary sources. Domestic and industrial waste waters of Kozlu town reach the sea directly or *via* Kozlu river (49,200 m^3/day) and other small creeks[10].

Discharges of both treated and untreated industrial waste water and possibly leachate from the landfill at Kozlu coast may be the reason of higher level of benzene concentration in C3. Beyond coal dusts and debris extracted from coal galleries dumped to the rivers and to the sea (close to C3). All kinds of municipal solid wastes, mostly organic, paper, plastic and ash are dumped into this wild waste deposition area (2.5 ha and 750,000 m^3) which is also washed out by the sea waves. The station C4 is very close to the Zonguldak port (1.2 km), an important and busy terminal for domestic and international transportation. Unfortunately, domestic and industrial wastes of this big city are also discharged into this port through Uzulmez and Kokaksu rivers. Meanwhile, the sediments from the stations C5 and C6, which are 1.1 and 4.4 km far to the Zonguldak port have no BTEX compounds. To the east, the waste water (240,000 m^3) of the Catalagzi thermal power plant is dumped to the sea at Kilimli. Its boiler slag and fly ash (2500 tonnes/day) was stated to be deposited on land[10].

Industrial zone of Filyos: The station sample from C7 is close to the Filyos port and to its terminal. The sources of benzene found in this station (C7) may be gasoline leaks from the storage tanks of the terminal or due to untreated industrial wastewaters.

The stations C8 and C9 are located close to the Filyos river. Domestic waste waters carried by Filyos river and industrial waste waters such as a paper mill in

Caycuma (21,400 m^3/day) and an oil station (< 50 m^3/day) are discharged into the sea close to C8 at Sazkoy[10]. The source of benzene observed in C8 may be these discharges of untreated industrial waste waters.

Industrial zone of Bartin: At C10 offshore the Bartin river benzene was the only BTEX compound that could be detected. The Bartin river is usually clean with very small amount of sediment load, but the morphological features of its basin have very adequate conditions for floods and flash floods. By means of some engineering mistakes experienced during the construction of its port, these floods show an increment year by year especially in bad weathers.

Conclusion

Due to its special geographical, hydrographic and oceanographic peculiarities, which make the Black Sea a unique ecosystem, the environmental problems of the Black Sea are exacerbated every day. There are some local "hot spots" along the coastal areas of the Black Sea which are indicative of anthropogenic inputs from industrial point sources or diffuse emissions, over a long period of time. Zonguldak Industry Region is one of them between the cities of Eregli and Zonguldak where some large scale plants were placed.

Although there is a lack of information on methods for determining BTEX concentrations in seabed sediment, the current method was successful in their determination in the study area with an acceptable error. The BTEX concentrations vary from 0.074-3.252 µg/g dw, with an average of 1.123 µg/g dw and reflect industrial and urbanized history of the area. The maximum concentration of BTEX compounds in some samples, *i.e.* the ones close to the Zonguldak sea port and a port of cement plant in Eregli, increases up to 4-5 times the average concentrations. Higher concentrations may cause toxicity, especially with regard to benthic organisms. BTEX assemblages were mainly comprised of the benzene, except for the case of C4, where *p*-xylene was dominant. This may indicate local effects (unburned fuel and paint) due to busy seaport activities.

On the basis of the geographic distribution of BTEX compounds along the study area, which is not systematic or system-wide, it can be considered that the main pollution of sediment by BTEX compounds is mainly induced by the industrial discharges from the coastal zone. Meanwhile, port facilities seem to be posing a serious threat with increasing transportation of crude oil to international markets *via* Black Sea. It is especially troublesome because contaminants tend to settle rapidly, accumulating in sediments close to these places. The study area and other similar hot spots along the Black Sea coasts need urgent and particular actions.

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