J. Black Sea/Mediterranean Environment
Vol. 31, No. 3: 236-259 (2025)

RESEARCH ARTICLE

Spatial distribution of biogenic and lithogenic sediment components in İzmit Bay: Assessing eutrophication dynamics and anthropogenic pollution sources in a stratified coastal ecosystem

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Abstract

In the present study, the spatial distribution and interrelationships of major biogenic and lithogenic components—biogenic silica (BSi), calcium carbonate ($CaCO_3$), total organic matter (TOM), total organic carbon (TOC), lithogenic matter (LM), calcium (Ca), and phosphorus (P)—were examined in İzmit Bay surface sediments (0–4 cm). The research assessed their utility as proxies for tracing eutrophication and contamination in the heavily industrialized part of the Marmara Sea. Sediments from 56 stations were analysed using classical wet-chemistry and combustion methods, and Ca and P concentrations were determined by ICP-MS. Distributions were mapped using Kriging interpolation. Results indicate that complex hydrodynamics and intense anthropogenic pressures drive spatial partitioning. BSi, a proxy for diatom activity, reached its highest average concentration (12.5%) in the shallow Eastern Basin. Elevated BSi and TOC/TOM near wastewater discharge points signal nutrient (specifically TN and TP) enrichment, excessive primary production, and severe eutrophication. $CaCO_3$ peaked (16.0%) along the northern coast, linked to cement industry inputs and dolomite deposits. High TOC and TOM in deep, hypoxic/anoxic zones reflect mixed autochthonous (phytoplankton-derived) and allochthonous (land-based/industrial) organic-matter inputs. The negative correlation between LM and biogenic components confirms the dilution effect of fluvial mud. Notably, the 61% increase in TOC levels in the surface sediments since 1987 indicates ongoing environmental deterioration in İzmit Bay. In conclusion, elevated BSi, TOM, TOC, and P values collectively signal nutrient-driven eutrophication, while high $CaCO_3$ reflects industrial discharge. An immediate reduction of nutrient inputs is essential to mitigate eutrophication, chronic algal blooms, mucilage occurrence and prevent widespread hypoxia/anoxia in İzmit Bay.

Keywords: İzmit Bay, the Sea of Marmara, biogenic silica, total organic carbon, sediment biogeochemistry, eutrophication, pollution

Received: 02.11.2025, **Accepted:** 04.12.2025

Introduction

Biogenic components, such as biogenic silica (BSi), calcium carbonate ($CaCO_3$), total organic carbon (TOC), and total organic matter (TOM), are essential parts of marine ecosystems and are closely linked to biotic and abiotic processes. These particles are important vehicles for nutrient transport and may control the distribution of particle-bound contaminants; hence, determining biogenic component fluxes helps to understand the distribution and fate of contaminants and nutrients, and accordingly pollution and eutrophication processes (Mayer 1994; Officer and Ryther 1980). Pollutants from wastewaters adsorb onto settling particles, including biogenic particles like diatom frustules, detritus material, $CaCO_3$, and lithogenic matter, and consequently sink into the surface sediment. These compounds can be transported laterally after resuspension, metabolized at the sediment-water interface, or harm benthic habitats due to oxygen consumption during the decomposition of organic matter, leading to hypoxia or anoxia throughout the water column (Aktan *et al.* 2005; Hargrave *et al.* 2007; Mayer *et al.* 2007). Recent studies (Amann *et al.* 2014; Raimonet *et al.* 2013; Struyf and Conley 2013) indicate that organic matter deposition occurs mostly in the continental shelves, and estuaries.

Siliceous organisms, primarily diatoms, dominate the marine silica cycle, and influence the global carbon cycle by sequestering CO_2 via photosynthesis. Therefore, BSi is extensively used as an indicator of diatom biomass and primary production (Tréguer *et al.* 1995; Conley 1997; DeMaster 2002). The determination of TOC, TOM and $CaCO_3$ in marine sediments is crucial for evaluating anthropogenic impacts and enhancing the comprehension of natural matter cycling which is essential for mitigating environmental issues such as the accumulation of toxic substances, harmful algal blooms, and oxygen depletion events. Consequently, understanding the spatial distribution of these pollutants and their effects is critical for developing and implementing effective nutrient reduction strategies (like advanced wastewater treatment and controlling agricultural runoff) necessary to mitigate the risks of algal blooms and subsequent oxygen depletion. Along with lithogenic matter (LM), biogenic particles provide valuable data regarding sediment characteristics and the dynamics of particulate cycling in a coastal marine ecosystem (Benner 2004; Hargrave *et al.* 2007).

Kocaeli Province, which currently houses a population exceeding two million and encircles İzmit Bay, has undergone rapid industrial expansion since the 1960s. This growth has resulted in the establishment of over 400 large-scale industrial facilities, including Türkiye's largest plants for metallurgy, paper production, fertilizer manufacturing, cement, and petrochemicals. Furthermore, the bay area is home to approximately 60 shipyards and 40 ports. Since the 1980s, this substantial industrial and demographic growth has unfortunately led to significant domestic and industrial discharges into the İzmit Bay drainage basin. Riverine inputs, particularly from Dil Creek, are among the elements that contribute to pollution and nutrient load as well. Consequently, intensified anthropogenic activity has exerted considerable environmental pressure on the bay's ecosystem. Current data indicate that eight operational Wastewater Treatment Plants (WWTPs) discharge an annual average of 165 million cubic meters of treated wastewater, contributing an estimated 2010 tons of total nitrogen (TN) and 227 tons of total phosphorus (TP) to the bay yearly (İÇDR 2024). However, quantification of untreated nutrient inflows from non-point sources, such as agricultural runoff and atmospheric deposition, remains unavailable.

Previous studies confirm that the presence of excessive nutrients (e.g. silicon, phosphorus and nitrogen), as well as organic and inorganic compounds, has caused eutrophic and anoxic conditions to occur in İzmit Bay (Ediger *et al.* 2009; Ergul *et al.* 2018; Morkoç *et al.* 2001). Furthermore, phytoplankton blooms, causing the water surface to turn red, and mucilage occurrence have been reported in the bay (Ergül *et al.* 2010, 2014, 2021; Taş *et al.* 2016). However, although studies have been undertaken on pollutants in the sediments of İzmit Bay (Balkis *et al.* 2007; Ergül and Karademir 2020; Ergül *et al.* 2013-a; Karademir *et al.* 2013; Tolun *et al.* 2006), few studies have examined biogenic components (Morkoç *et al.* 2008; Tolun *et al.* 2001).

Therefore, the present study aims to (1) determine the concentrations and spatial distribution of lithogenic and biogenic components in surface sediments collected from İzmit Bay and (2) examine the relationships between those parameters and pollution and eutrophication.

Materials and Methods

Study Area

İzmit Bay is a 49 km long bay that covers an area of approximately 300 km² and is divided into three basins by shallow narrow passages (Figure 1). The Eastern Basin is the smallest part of the entire system. It is approximately 5 km wide, 13.4 km long, and has a surface area of 47 km². It is relatively shallow, with a maximum depth of around 40 meters. The Central Basin is the largest part of the system. It is around 9.5 km wide and 22 km long, with a surface area of 165 km². The bottom topography of this basin varies considerably from north to south, with depths of up to 208 m in the southern section. A narrow, shallow area (55 m deep) off the coast of Dil Creek separates the Central and Western Basins. This area is approximately 8.5 km wide, 14 km long, and has a surface area of 87 km². The bottom topography of the Western Basin slopes downwards towards the Marmara Sea, reaching a depth of around 100 meters at the edge of the bay (Figure 1) (Morkoç *et al.* 2001).

Due to limited water exchange, the residence time of water in İzmit Bay is longer than in the rest of the Marmara Sea. The residence time of the upper layer waters (i.e. 0-40 m) is estimated to be 10 to 15 days in İzmit Bay and is relatively long compared to other areas in the Marmara Sea (Ediger *et al.* 2009). Consequently, domestic and industrial discharge tends to accumulate because of the low current velocity within the bay. Stratification of the water column occurs throughout the year owing to differences in salinity. Saltier water from the Mediterranean Sea (about 38 ppt) is found in the lower layer, while less saline water from the Black Sea (about 18 ppt) is found in the upper layer (Ergül 2016; Morkoç *et al.* 2001). Vertical mixing between these two layers is restricted over the Marmara basin, playing a key role in determining the bay's physicochemical characteristics, and anoxic conditions may occur in the lower layer (Algan *et al.* 1999; Balkıs 2003).

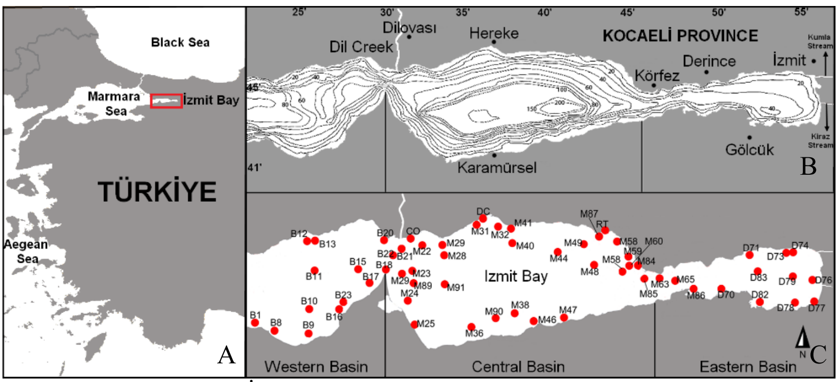


Figure 1. The location of İzmit Bay (A), districts and main streams of Kocaeli Province (B), and a bathymetrical map with the locations of 56 surface sediment sampling points in the Western, Central and Eastern Basins of İzmit Bay (C)

Surface Sediment Collection

Surface sediment samples were collected from 56 locations in the Western, Central, and Eastern Basins of İzmit Bay (Figure 1) using Ekman-type grab samplers. Sediments were collected over years, since 2010 and the most recent sample obtained in 2020. The uppermost 0-4 cm of surface sediment was sliced and placed into polyethylene cups. All sediment samples were stored in a cooler and were immediately transported to the laboratory for subsequent analysis.

Analytical procedures

Particles larger than 1500 µm were removed using a stainless-steel sieve. Wet sieving was performed to obtain total clay and silt (<63 µm), very fine (>63 µm), fine (>125 µm), medium (>250 µm), and coarse sand (>500 µm) particles using a Fritsch Analysette 3 Spartan model sieving equipment. The samples were washed with distilled water at least three times, dried at room temperature to a constant weight, gently homogenized, and kept in a deep freezer at −25 °C until analysis. Since organic and inorganic substances adsorb more readily on fine-grained particles (Horowitz 1991), fractions measuring 63 µm or less (i.e. clay and silt particles) were used in the analysis due to their higher adsorption capacity. This also enabled a better comparison to be made between different samples.

BSi analysis was performed by digesting 0.05 g of dry sediment sample with 1% Na_2CO_3 and analysed spectrophotometrically using the heteropoly blue method (DeMaster 1981). For TOC analysis, 0.5 g of homogenized, dry sediment was treated with 2 M HCl to remove inorganic carbon, and the remaining was oxidized to CO_2 and measured using a non-dispersive infrared analyser (Shimadzu TOC-V equipped with a Shimadzu SSM 5000A solid matter module). Classical combustion method (i.e. at 550 °C, 6 hours) was used for TOM analysis. The $CaCO_3$ content was determined gravimetrically after digestion 1 g of dry sediment with 0.5 N HCl (Strickland and Parsons 1972) The results were calculated as BSi%, $CaCO_3$%, TOC%, and TOM%. Standard deviations were calculated for at least three measurements. The formula below was used to estimate the LM concentration as total dry weight (TDW) in the sediment samples:

$$TDW_{LM}\% = 100 - (TDW_{TOM}\% + TDW_{CaCO3}\% + TDW_{BSi}\%) \quad (1)$$

The calcium (Ca) and phosphorus (P) concentrations were determined using a PerkinElmer Elan DRC-e ICP-MS equipped with a CETAC ADX-500 autosampler and diluter. The microwave digestion method was employed for liquid-phase extraction. To validate the accuracy and precision of the method, standard reference material (SRM DS8) was analysed for the corresponding elements and recovery values of 93% and 98% were determined for Ca and P, respectively.

The Map Viewer software was utilized to plot interpolated maps. The parameters associated with the locations of the sampling stations were interpolated to create a spaced grid using the Kriging method. The raw graphs were combined with the base map of Izmit Bay using a photo-editing software.

Statistical analysis was performed using the SPSS software package. The data collected were assessed for distribution normality. Non-parametric correlation analysis, specifically Spearman's rank correlation (ρ), was employed to determine the spatial correlation coefficients between variables.

Results

Spatial Distribution of Components in Surface Sediment

The surface sediment in İzmit Bay was predominantly composed of mud, including clay and silt particles, with an average composition of 69.2%, ranging from 7.39% to 99.1% (n=56). The presence of smaller sand particles was also observed, with varying degrees of contribution (Figure 2).

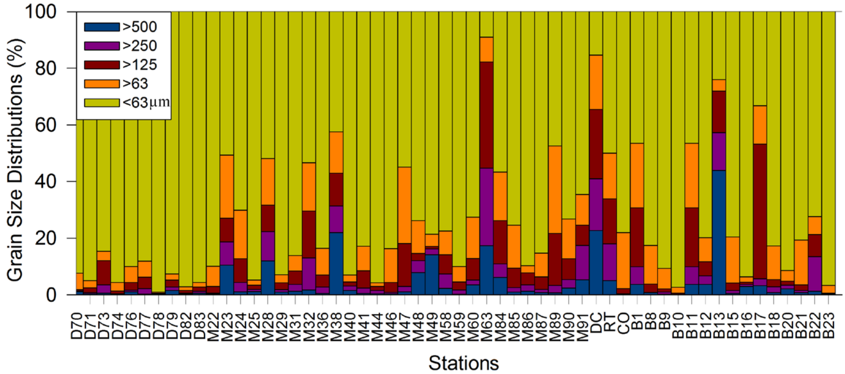


Figure 2. Sediment grain size distribution in the surface sediments of İzmit Bay

The Eastern Basin demonstrated the highest mean clay and silt particles content (93.1%, *n*=10), followed by the Central (75.1%, *n*=31) and Western Basins (69.8%, *n*=15). Sediment was typically grey to black in appearance, except for stations situated in close proximity to loading-discharging ports (i.e. DC, RT, and CO sites, Figure 1). At these stations, the sediment exhibited distinct colour variations, including brownish-red, greenish-grey, and light-grey hues, respectively. These colour variations suggest localized contamination or physical disturbance. Specifically, the presence of brownish-red hues indicates the accumulation of metal oxides, most notably iron oxides, which likely originate from metal processing or port-related activities (Schwertmann 2000). Conversely, the typical black, dark, or greenish-grey coloration signifies the abundance of sulfide compounds. This coloration is indicative of severe anaerobic conditions driven by high organic matter decomposition and the subsequent formation of iron sulfides within the sediment matrix (Ye *et al.* 2025).

With certain exceptions (e.g. M63, DC, B10, B23, Figure 1), the sediment grain sizes exhibited a tendency to increase from east to west and from south to north (Figure 3a).

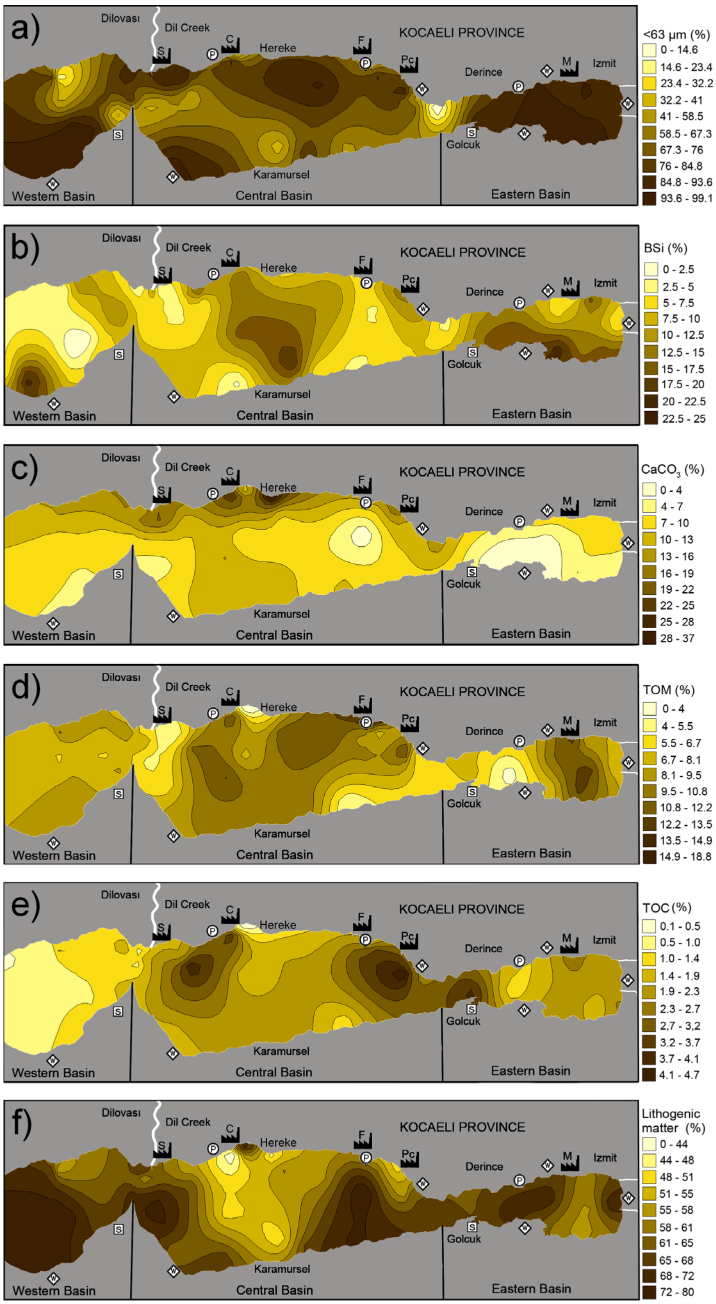
In the surface sediment, BSi concentrations ranged between 0.99% and 24.8% with an average of 9.26% throughout İzmit Bay. Relatively higher BSi concentrations were observed in the Eastern Basin particularly along the bay's southern coastline (Figure 3b). Average BSi concentrations (and ranges) were calculated as 12.5% (5.36-20.93), 9.12% (0.99-22.3) and 7.38% (1.48-25.8) in the Eastern, Central, and Western Basin, respectively (Table 1). Average TOM and TOC concentrations (and ranges) were 9.66% (3.55-18.84) and 1.96% (0.25–4.65) respectively, across İzmit Bay. Among the basins, the highest average TOM concentration was in the Eastern Basin (10.3%), followed by the Central (9.74%) and the Western Basins (9.02%). However, the highest average TOC concentrations were in the Central Basin (2.32%) followed by the Eastern (1.94%) and Western (1.22%) Basins. Relatively higher TOM and TOC levels were found on the northern coastline of the bay and their concentrations tended to decrease from the inner (i.e., eastern and central) to the outer (i.e., western) basin (Figures 3d, 3e). The $CaCO_3$ concentrations ranged between 4.69% and 37.7% with average 14.4% throughout İzmit Bay. Unlike BSi, $CaCO_3$ was found predominantly on the northern coastline. Average $CaCO_3$ concentrations were higher in the Central (16%) and lower in the Eastern Basin (9.21%), while it was an average of 14.4% in the Western Basin (Figure 3c). Average Ca and P concentrations (and ranges) were calculated as 5.30% (1.07-17.6) and 0.06% (0.04-0.15), respectively, in the surface sediment of Izmit Bay. LM was a dominant component in the surface sediment of Izmit Bay. Minimum and maximum LM concentrations were 42.0% and 79.8% (both in the Central Basin), respectively, with an overall average of 66.7% across all basins. Among the basins, the minimum average LM concentration was in the Central Basin (65.1%), while the averages were 69.1% and 68.0% in the Western and Eastern Basin, respectively. The LM concentrations showed significant negative correlations with the other components and tended to increase from east to west and north to south directions of İzmit Bay (Figure 3e).

Table 1. The sediment component concentrations in the Eastern (D), Central (M) and Western (B) Basin of İzmit Bay (% dry weight)

St	BSi	$CaCO_3$	TOM	TOC	LM	Ca	P
D70	16.9±4.3	4.69±0.5	4.54±0.1	1.16±0.1	73.9	1.07±0.1	0.06±0.003
D71	8.54±3.9	12.2±3.1	9.53±0.4	1.42±0.1	69.7	3.31±0.3	0.06±0.003
D73	5.36±0.9	12.8±0.4	14.4±0.2	2.79±0.2	67.5	4.31±0.4	0.08±0.004
D74	17.7±0.1	11.3±0.4	9.98±0.9	2.33±0.0	61.1	3.43±0.3	0.07±0.003
D76	3.99±5.4	11.7±0.4	8.49±0.3	1.85±0.2	75.9	3.66±0.3	0.06±0.003
D77	15.2±1.0	8.17±0.5	9.53±0.4	2.41±0.1	67.1	2.16±0.2	0.07±0.003
D78	16.2±2.5	9.28±0.6	12.2±0.7	1.44±0.1	62.3	2.17±0.2	0.05±0.003
D79	13.8±4.1	11.0±0.7	14.1±0.1	2.10±0.1	61.1	3.26±0.3	0.06±0.003
D82	20.9±7.7	5.21±0.4	8.81±0.2	2.14±0.1	65.1	1.81±0.2	0.06±0.003
D83	6.43±3.5	5.83±0.6	11.8±0.1	1.72±0.1	75.9	1.66±0.1	0.06±0.003
Mean Eastern	**12.5±3.4**	**9.21±0.8**	**10.3±0.3**	**1.94±0.1**	**68.0**	**2.68±0.2**	**0.06±0.003**
M22	3.80±1.9	24.3±1.8	5.60±0.5	2.21±0.1	66.3	8.33±0.7	0.06±0.003
M23	3.61±1.1	14.0±1.7	6.90±1.7	2.24±0.4	75.5	5.12±0.0	0.05±0.002
M24	7.16±0.5	9.77±0.1	7.32±0.1	2.37±0.0	75.8	3.38±0.0	0.05±0.001
M25	9.89±2.4	12.9±0.1	10.3±0.5	1.69±0.0	66.9	3.85±0.3	0.05±0.002
M28	4.76±0.1	13.8±0.4	12.5±0.2	4.09±0.0	68.9	4.96±0.0	0.05±0.002
M29	15.4±0.0	16.3±0.6	6.96±0.6	1.90±0.2	61.5	5.12±0.5	0.06±0.003
M31	12.9±1.7	31.4±1.5	13.8±1.5	3.61±0.1	42.0	10.6±0.9	0.08±0.004
M32	6.87±0.4	13.5±1.9	3.55±0.2	0.25±0.1	76.1	14.9±1.3	0.06±0.003
M36	1.77±0.0	16.0±0.3	11.4±0.9	2.08±0.1	70.8	5.63±0.5	0.06±0.003
M38	20.3±8.7	16.1±2.6	11.4±1.7	2.07±0.4	52.2	6.93±0.1	0.06±0.002

Table 1. Continued

St	BSi	$CaCO_3$	TOM	TOC	LM	Ca	P
M40	9.88±0.2	13.9±1.0	13.4±0.6	1.82±0.2	62.9	4.62±0.1	0.07±0.003
M41	5.54±1.3	37.7±1.7	7.87±1.1	1.17±0.1	48.9	13.0±0.2	0.05±0.003
M44	12.7±0.6	13.4±1.7	13.5±0.2	2.03±0.3	60.4	6.11±0.1	0.06±0.002
M46	5.81±2.5	12.8±2.9	12.1±0.2	2.06±0.3	69.3	6.03±0.5	0.07±0.003
M47	4.57±0.5	14.4±18	5.13±0.2	1.11±0.1	75.9	5.59±0.5	0.06±0.003
M48	3.92±0.1	4.81±1.5	11.5±1.7	3.30±0.0	79.9	4.31±0.0	0.06±0.002
M49	6.44±1.6	10.7±0.7	10.5±0.6	3.10±0.1	72.4	2.91±0.0	0.05±0.001
M58	15.2±1.9	21.9±0.3	9.53±0.3	3.03±0.0	53.4	4.64±0.4	0.11±0.005
M59	12.1±2.1	15.1±0.0	13.2±1.3	3.37±0.0	59.7	4.52±0.4	0.09±0.004
M60	11.6±0.8	16.5±0.3	13.3±0.4	4.64±0.2	58.7	4.45±0.4	0.09±0.004
M63	2.94±0.9	18.9±12	7.96±0.5	2.78±0.3	70.2	2.28±0.2	0.05±0.003
M84	11.7±1.3	13.1±0.2	7.48±0.5	2.94±0.1	67.7	3.24±0.3	0.06±0.003
M85	9.3±3.9	14.5±0.3	7.53±0.7	2.78±0.1	68.7	3.61±0.3	0.08±0.004
M86	14.7±0.6	8.33±0.2	8.60±0.2	3.85±0.1	68.4	1.94±0.2	0.06±0.003
M87	11.9±0.2	15.1±0.3	8.74±1.9	3.01±0.2	64.2	3.92±0.5	0.09±0.004
M89	6.05±2.5	12.7±1.8	6.20±0.4	1.70±0.1	75.0	4.53±0.1	0.06±0.003
M90	24.8±11	10.3±0.3	8.74±0.8	1.54±0.0	56.1	3.74±0.1	0.05±0.003
M91	15.8±0.2	17.2±3,0	13.8±1.0	2.38±0.2	53.3	6.82±0.1	0.06±0.002
DC	6.25±2.2	20.7±3.2	7.28±0.8	0.75±0.1	65.8	14.2±0.1	0.10±0.003
CO	1.48±2.0	16.4±2.8	7.11±0.3	0.65±0.0	75.1	17.6±0.3	0.07±0.004
RT	3.76±1.3	19.5±0.8	18.8±0.2	1.38±0.1	57.9	9.52±0.2	0.15±0.008
Mean Central	**9.12±1.8**	**16.0±2.1**	**9.74±0.7**	**2.32±0.1**	**65.1**	**6.34±0.3**	**0.07±0.003**
B01	3.70±2.7	10.6±0.1	8.05±0.5	1.65±0.1	77.6	3.77±0.3	0.05±0.003
B08	22.3±11	13.7±0.9	7.65±0.1	1.64±0.1	56.4	4.14±0.4	0.05±0.003
B09	7.69±0.5	12.5±3.6	8.34±0.6	1.22±0.0	71.5	3.99±0.0	0.05±0.000
B10	0.99±0.2	11.9±0.1	9.79±0.4	0.92±0.0	77.4	3.40±0.0	0.04±0.001
B11	4.67±0.1	12.7±0.4	7.81±0.7	0.73±0.0	74.9	3.98±0.0	0.05±0.001
B12	3.83±1.1	16.2±0.4	8.89±0.4	0.65±0.2	71.1	4.73±0.0	0.05±0.001
B13	11.9±4.1	17.4±0.2	11.2±0.3	1.50±0.1	59.5	5.68±0.5	0.06±0.003
B15	13.5±8.4	12.1±0.2	7.72±0.2	1.04±0.3	66.8	3.43±0.0	0.05±0.001
B16	7.79±3.2	9.27±0.9	9.98±0.4	1.09±0.1	73.0	3.07±0.3	0.05±0.003
B17	8.42±1.7	11.3±0.2	9.90±0.1	1.49±0.0	70.4	3.65±0.3	0.05±0.003
B18	5.42±0.5	13.0±4.2	8.10±0.6	1.32±0.1	73.5	4.01±0.4	0.05±0.002
B20	1.22±1.1	20.4±0.7	10.1±0.5	1.63±0.0	68.2	6.83±0.6	0.05±0.003
B21	6.34±1.8	23.5±3.2	9.73±0.2	1.84±0.1	60.4	13.0±0.1	0.08±0.001
B22	6.38±0.4	18.7±1.0	9.03±0.2	0.65±0.0	65.9	6.29±0.1	0.06±0.002
B23	6.65±3.5	13.4±4.1	9.08±0.7	0.94±0.1	71.0	3.32±0.1	0.05±0.003
Mean Western	**7.38±2.7**	**14.4±1.3**	**9.02±0.4**	**1.22±0.1**	**69.2**	**4.89±0.2**	**0.05±0.002**
Mean Total	**9.26±2.3**	**14.4±1.6**	**9.66±0.5**	**1.96±0.1**	**66.7**	**5.30±0.3**	**0.06±0.003**



C:Cement, F:Fertilizer, M:Paper mill, Pc:Petrochemical, S in square: Shipyards, S:Smelting processing facilities, W:Wastewater Treatment Plant, P:Port

Figure 3. Interpolated maps of a) <63-µm particles b) BSi, c) $CaCO_3$, d) TOM, e) TOC, and f) LM distributions in surface sediment within İzmit Bay

Table 2. Spearman's rho correlation coefficients among the component concentrations throughout in the surface sediment of İzmit Bay (a) and its subbasins (Eastern (b), Central (c) and Western (d))

All Basins n=56	BSi	$CaCO_3$	TOM	TOC	LM	Ca	P
BSi	1.00	-.24	.13	.24	**-.60****	**-.31***	.16
$CaCO_3$		1.00	.01	-.00	**-.48****	**.79****	**.37****
TOM			1.00	**.36****	**-.41****	.03	.21
TOC				1.00	**-.28***	-.16	**.37****
LM					1.00	**-.29***	**-.41****
Ca						1.00	**.34***
P							1.00

a)

Eastern n=10	BSi	$CaCO_3$	TOM	TOC	LM	Ca	P
BSi	1.00	-.60	-.26	-.03	-.60	-.49	-11
$CaCO_3$		1.00	.44	.31	-.09	**.95****	.26
TOM			1.00	.40	-.40	.38	-.14
TOC				1.00	-.41	.46	**.70***
LM					1.00	-.21	.07
Ca						1.00	.38
P							1.00

b)

Central n=31	BSi	$CaCO_3$	TOM	TOC	LM	Ca	P
BSi	1.00	-.09	.27	.24	**-.62****	-.21	.07
$CaCO_3$		1.00	.07	-.09	**-.56****	**.57****	**.49****
TOM			1.00	**.42***	**-.53****	-.01	.26
TOC				1.00	-.11	**-.54****	.09
LM					1.00	-.22	-.35
Ca						1.00	.33
P							1.00

c)

Western n=15	BSi	$CaCO_3$	TOM	TOC	LM	Ca	P
BSi	1.00	-.08	-.13	.16	**-.63***	-.14	.28
$CaCO_3$		1.00	.16	.10	**-.66****	**.86****	**.56***
TOM			1.00	.10	-.14	.096	.34
TOC				1.00	-.28	.30	**.52***
LM					1.00	**-.55***	**-.65****
Ca						1.00	**.66****
P							1.00

d)

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

Discussion

The particulate dimensions of the surface sediment, which are predominantly characterized by mud content, suggest that the sedimentation regime within İzmit Bay is largely low-energy and fine-grained. The spatial distribution of this muddy matrix, which reaches its maximum concentrations in the Eastern Basin (Figure 3a), strongly reflects the bay's function as a sediment sink. This role is likely attributed to the relatively restricted water circulation, a condition supported by the long residence time of the upper water column of İzmit Bay, which has a stratified structure (Ediger *et al.* 2009). The observed trend of increasing sediment grain size from the inner (east) to the outer (west) bay and from south to north. This suggests a gradual transition from the sheltered, river-influenced eastern zone to the more energetic, open western zone. While coarser sediments dominate the steep northern coastline of the Western Basin, particle size tends to decrease at depths greater than 50 m in the Central and Western Basins. The accumulation of fine-grained sediments in the inner bay (Eastern Basin) is likely a direct result of the low hydrodynamic regime, proximity to fluvial inputs, and wastewater discharges (Figure 3a). This basin, characterized by the finest sediment particles, is surrounded by dense human settlements. It receives a considerable load of domestic and industrial wastewater, estimated at approximately 86 million m^3 per year (İÇDR 2024). This volume is significant, accounting for more than half (50.3%) of the total wastewater released across the Kocaeli Province, with major inputs made from the Kumla Stream via the Doğu Channel (Figure 1). These fine particles likely settle in the Eastern Basin rather than moving to the outer basins due to decreasing current velocities from west to east (Algan *et al.* 1999; Balkis 2003) and flat bottom topography of the Eastern Basin.

Particulate Characterization in Surface Sediment of İzmit Bay

<u>Biogenic Silica (BSi)</u>

Biogenic silica concentrations exhibited a clear spatial gradient, peaking in the Eastern Basin and gradually decreasing westward (Table 1, Figure 3b). Furthermore, while BSi showed an insignificant correlation with other biogenic components (p>0.05), it was significantly and negatively correlated with LM throughout the bay (Table 2a).

These data indicate that BSi-forming materials (such as diatom frustules and siliceous fragments) follow distinct sedimentation dynamics compared to other components in İzmit Bay, except LM. Consistently, stations distant from river influence and/or proximal to WWTPs (e.g. D74, D82, M29, M38, M90, M91, B08, Figure 1) registered higher BSi and lower LM concentrations. Surrounded by the heavily populated and industrialized Kocaeli Province, İzmit Bay receives substantial nutrient loads from treated and untreated domestic and industrial wastewater discharges, approximately 2,010 tons of TN and 227 tons of TP annually (İÇDR 2024). These loads stimulate the growth of phytoplankton, such as diatoms and silicoflagellates, which are well-established components of the bay's ecosystem, particularly in the Eastern Basin (Aktan and Aykulu 2005; Aktan *et al.* 2005; Ergul *et al.* 2018; Kucuk and Ergul 2011). The observed correlation between BSi occurrence along the coastline and the proximity of wastewater discharge points confirm that nutrient availability is a key factor driving biogenic silica production. Hence, the second and third highest BSi concentrations (at stations D82 and B08) were recorded near the discharge points of wastewater treatment plants at the corresponding sites (Figure 3b). High BSi concentrations in the Eastern Basin's surface sediment are likely linked to intense biological activity in the water column, particularly the proliferation of siliceous organisms (e.g., phytoplankton and silicoflagellates), supported by the nutrient-rich condition of the basin (Aktan *et al.* 2005).

In the Central Basin, a BSi-rich zone, located between the offshore area of the Hereke District and the southern coastline, supports the production of amorphous silica stimulated by marine organisms, such as diatoms and/or silicoflagellates (Figure 3b). This finding is corroborated by prior studies reporting relatively higher silica concentrations (Morkoç *et al.* 2007) and frequent phytoplankton blooms (Ergul *et al.* 2018) specifically in this region. Moreover, the consistently low current velocities (Algan *et al.* 1999) of the Eastern Basin enhance the accumulation of BSi in its surface sediments compared to the other basins of İzmit Bay. However, the maximum BSi concentration was recorded at station M90 located in the Central Basin at a depth of 80 m. In addition, sediments collected from depths greater than 40 m (including stations M31, M29, B15, B13, M40, M38, M90, M44, and M91) had an average BSi concentration of 15.2%, remarkably higher than the basin average. These depths (>40 m) are characterized by hypoxic conditions (Algan *et al.* 1999; Balkis 2003; Ergül 2016). On the other hand, notable exceptions were observed at stations B10, M36, B12, and M41. Although these stations are in deep waters, they are situated on steep slopes and yield a low mean (3.08%) BSi concentration lower than the overall bay average (Table 1). While deeper, hypoxic (low-oxygen) environments are known to favour BSi preservation (Dale *et al.* 2021), the resulting BSi concentration in the present study is also clearly influenced by physical parameters like bottom topography, slope and current velocity.

Consequently, the present study indicates that BSi accumulation in surface sediments is primarily driven by the proliferation of siliceous organisms, such as diatoms and silicoflagellates, which are stimulated by the nutrient load originating from wastewater discharges. The Eastern Basin, which receives more than half of the total wastewater discharged into İzmit Bay, has the highest BSi concentrations in its surface sediments, suggesting excessive phytoplankton proliferation in this area. This finding, combined with previous studies that reported occasional significant decreases in regional oxygen concentrations (Ergül 2016), collectively points to a possible severe eutrophication problem within the bay.

TOM and TOC

Total organic carbon and TOM concentrations were significantly and positively correlated throughout the İzmit Bay surface sediment. This relationship extended to Phosphorus (P), which also showed a significant positive correlation with TOC. Although the correlation coefficient is not very high, the distribution of TOM and TOC is highly diagnostic of both depositional processes and anthropogenic influence. In contrast, (LM) was significantly and negatively correlated with both TOM and TOC (Table 2a).

Based on basin averages, the highest mean TOM concentration was recorded in the Eastern Basin. Conversely, the Central Basin exhibited the highest mean TOC concentration (Table 1). The mean TOM and TOC concentrations in the Western Basin surface sediments were relatively lower than those in other basins. These concentration differences suggest that the organic matter present in the Central Basin possesses a higher relative carbon content. This higher TOC concentration is likely attributable to a substantial presence of organic carbon derived from autochthonous biological production (e.g. phytoplankton blooms). This material is subsequently deposited and better preserved in the Central Basin's relatively deeper, low-oxygen environments, where it is less susceptible to aerobic decomposition (Mayer 1994). In contrast, the elevated mean TOM concentration in the Eastern Basin may be associated with a greater abundance of allochthonous (land-based) organic matter (Yu *et al.* 2015), such as that originating from factories, and wastewater discharges, which is often complexed with mineral matter. As a matter of fact, the highest TOM concentration in the Eastern Basin was recorded near a decommissioned paper mill (D73). This location is significant as it is an example of allochthonous TOM input as the paper mill has been previously documented to generate elevated TOM levels and radionuclide contamination in the surface sediment (Ergül *et al.* 2013a). Furthermore, the Eastern Basin is characterized by sediment containing a high proportion of fine-grained particles (93.1% are <63µm, Figures 2, 3a). This high percentage of fine material provides an ample surface area that facilitates the effective adsorption and accumulation of TOM.

The highest TOM concentration among all surface sediment samples in the Central Basin was recorded near the RT station, which is situated close to both a fertilizer factory and its port. Elevated TOM levels were also detected at a cluster of stations: M58, M59, and M60, located approximately 1 km offshore from the Türkiye's largest oil refinery. High concentrations persisted further offshore at stations M48, M49, and M40, which are located 3, 5, and 10 km from the refinery, respectively (Table 1, Figure 3d). The highest TOC concentration also recorded in the Central Basin was found at station M60, located offshore from the aforementioned oil refinery (with a crude oil processing capacity of 11 million tons/year). This refinery is a known source of contamination, having suffered a major fire and a catastrophic oil spill following the 7.4 magnitude earthquake in 1999 (centered in the Gölcük district, Kocaeli Province) (Güven and Ünlü 2000;

Okay *et al.* 2001). Additionally, elevated TOC levels were determined at other stations (M58, M85, M63, M48, and M49) situated relatively close to the refinery, ranging from 0.5 to 5 km (Table 1, Figure 3e). In a previous study, Tolun *et al.* (2001) reported approximately 5% TOC concentrations from the offshore of the refinery and indicated that TOC levels were constant in the region. Relatively high TOC levels were also recorded at the naval port entrance (M86) and a site (M28) that is suspected to discharge bilge water and other substances (Table 1, Figure 3e).

Elevated Total Organic Matter (TOM) concentrations were also observed at several other sampling points, indicating dispersed anthropogenic impact across the area. These specific high-concentration locations are situated in close proximity to various sources: a wastewater treatment plant (M25, 1.8 km distant), a solid load handling port (M31, 0.3 km distant), organized shipyard sites (B10, B16, and B23, ranging from 0.2 to 2 km distant), and an active ferry/shipping lane (B13). Additionally, high TOM was found at M28, which lies approximately 2 km from both untreated wastewater discharge points and an asphalt transfer port. The consistently high TOM values at these sites are likely attributable to the combined effects of domestic and industrial discharge and the accumulation of organic residue from marine organisms whose production is enhanced by the nutrient loading from these nearby discharge points (Table 1, Figure 3d).

In addition, some TOC is received from the Black Sea, with an estimated TOC input of 0.57×10^6 tons annually (Tugrul and Polat 1995). These data indicate that the activity of marine organisms alone is not responsible for TOC; rather, external sources that alter TOM and TOC levels, including anthropogenic discharge, petroleum, and petroleum-derived products, are also significant.

In the present study, the average TOC concentration in İzmit Bay was 1.96%, which was 1.6 and 1.2-fold higher than that reported by Ergin and Yoruk (1990) in 1987 and Yaşar *et al.* (2001) in 1997. In a study performed in Chesapeake Bay (USA), 3-m sediment core sampling revealed that TOC levels rapidly increased 2-fold (3.65% of the surface sediment) over a 60-year period following industrialization and urbanization (Zimmerman and Canuel 2000). In addition, current average TOC settling particle levels, i.e. 2.37%, obtained from offshore of Dil Creek (Ergul *et al.* 2013-b) are 2.04 and 1.49-fold higher, respectively, than those reported in the aforementioned studies. These results indicate that TOC levels in Izmit Bay have noticeably increased (i.e. by 61% on average) since 1987. Since organic matter (OM) exhibits a strong tendency to bind to various pollutants, including heavy metals, radionuclides and persistent organic compounds (Ergül and Topcuoglu 2009; Ergül *et al.* 2006, 2008; Mayer 1994; Tolun *et al.* 2006, 2001), surface sediments with high OM content can effectively serve as a trap for these contaminants. Consequently, these results collectively indicate that İzmit Bay ecosystem has been under significant and continuously escalating anthropogenic pressure in recent decades.

CaCO$_3$, Ca, and P

Significant positive correlations were observed between CaCO$_3$ and Ca throughout İzmit Bay (Table 2a). This strong relationship confirm that the vast majority of the Ca budget in the sediment is bound in the form of CaCO$_3$, and this finding suggests that the CaCO$_3$ content in Izmit Bay is primarily controlled by biogenic deposition, originating from coccolithophores and skeletal fragments of marine organisms. However, CaCO$_3$ were found at relatively higher levels along the northern coastline of İzmit Bay, reaching their highest average in the Central Basin, remarkably higher than its average in the Eastern Basin (Table 1). In fact, elevated CaCO$_3$/Ca ratios particularly along the north coast of İzmit Bay suggest substantial inputs originating from both natural biogenic and industrial sources. This local enrichment is directly linked to the presence of dolomite ($CaMg(CO_3)_2$) ore in the area, with the mineral's affinity to hydrolytic ionization and its industrial utilization primarily due to its porous molecular structure (Dalgic 2006). In addition, one of Türkiye's largest cement factories located in the region (near M41, Figures 1, 3) exploits voluminous mine beds to produce construction materials. Since the most common hydraulic cements are based on easily hydrated calcium compounds produced from rock-based CaCO$_3$ mixed with clay (Gartner and Macphee 2011), the combination of the region's geological richness and probable industrial discharge from both dolomite processing and cement production is the most likely driver of the elevated CaCO$_3$ flux in İzmit Bay. Also, industrial activities, such as those involving steelmaking treatment, are a probable source of significant Ca release into the sediment (Presern *et al.* 1991). In this respect, it is particularly noteworthy that, one of Türkiye's largest rolling-mill facilities also on the northern coasts of the Central Basin is very close to the stations CO and M22 (Figures 1 and 3). Consequently, the region's dominant geological structure and probable industrial inputs are likely contributors to the elevated CaCO$_3$ levels observed in Izmit Bay. However, these high concentrations suggest that this anthropogenic calcium loading potentially influences the bay's pH and overall buffering capacity. Furthermore, excessive CaCO$_3$ input may indirectly impact the mobility of contaminants by altering the precipitation and binding behaviour of various metal ions.

Another significant correlation was found between CaCO$_3$ and Phosphorus in the surface sediments of İzmit Bay (Table 2a). This statistical relationship was strongly supported by the localized data, specifically demonstrating elevated Ca and P concentrations near a fertilizer factory (M58). This localized anomaly suggests that the overall CaCO$_3$ - P association is likely to be driven by an external, anthropogenic input, where the deposition of commercial phosphate-containing fertilizers acts as a primary source, binding or co-precipitating with Ca in the local sediment matrix. High Ca and P levels in sediment may also be explained by contamination from calcium phosphate ($Ca_3(PO_4)_2$), which is employed as an additive in the fertilizer industry (Guelfi *et al.* 2022). The analysis of surface sediment revealed that the highest Ca concentration was recorded at the CO site, which is located adjacent to one of Türkiye's largest rolling-mills and associated port. Similarly, elevated Ca levels were observed at the DC station, which lies in close proximity to a separate iron-steel facility port and cement factory (Figure 1, Table 1). For P, the maximum concentration in the bay's surface sediment was measured at the RT station. This site's location near the largest fertilizer facility in Türkiye and its handling port suggests an industrial source (Figure 1). Furthermore, stations M58 and M87 also displayed elevated P concentrations, as both are situated near the fertilizer factory. Collectively, besides natural cycles, these spatial associations indicate contamination originating from industrial facilities, associated ports, and mine beds as the principal cause of the observed high $CaCO_3$, Ca, and P levels throughout the region.

On the other hand, the negative correlation observed between $CaCO_3$ and BSi in the Central Basin's surface sediments (Table 2b) suggests that biogeochemical processes vary regionally. This is likely driven by ecological competition between calcareous and siliceous organisms, and the influence of external discharges. The high $CaCO_3$ concentrations along the northern coasts are attributable to the area's geology and nearby industrial inputs; in contrast, the high BSi concentrations on the southern coasts of the Central Basin indicate that local conditions favour siliceous organisms, such as diatoms, allowing them to outcompete other primary producers in this region. The relatively high LM content in this same southern region (Figure 3e) further suggests that this BSi is subject to rapid burial, which enhances its preservation by protecting it from dissolution.

The positive significant correlation between P and TOC in the Eastern Basin surface sediments highlights a crucial mechanism driving eutrophication in İzmit Bay (Table 2b). This relationship confirms that the sediments act as a vast nutrient reservoir, with P primarily bound to organic matter (and thus TOC), and potentially to $CaCO_3$. The decomposition of TOC at these high levels is a significant problem, particularly in the anoxic lower layer of the layered structure of the bay or under seasonally occurring anoxic conditions. This degradation causes the reductive dissolution of iron and manganese oxides, which subsequently leads to the large-scale release of bound P (Yli-Hemminki *et al.* 2016). This nutrient mobilization results in the free P returning to the water column, accelerating the eutrophication process and potentially triggering harmful algal blooms. This cycle represents a significant, long-term ecological risk, capable of creating a continuous pollution problem in the bay for decades even if external pollution sources are eliminated. Therefore, the ongoing massive sediment cleanup project in the Eastern Basin, which involves removing approximately 8.5 million cubic meters of contaminated bottom sludge (KBB 2022), aims to eliminate the historical P and TOC as well as other organic and inorganic contaminants from the reservoir directly, thereby breaking the detrimental internal nutrient cycling mechanism and fostering the long-term ecological recovery of İzmit Bay. However, it should be noted that this cleanup has been carried out in a limited area of the Eastern Basin, so the persistent presence of contaminated surface sediments ensures that the risk of eutrophication remains a critical threat throughout the entire bay area. Therefore, operative measures to substantially reduce all discharges, particularly anthropogenic inputs including nitrogen and phosphorus compounds flowing into the bay, are essential.

<u>Lithogenic matter (LM)</u>

Across the basins, the average Lithogenic Material (LM) concentration exhibited distinct variations. The Central Basin recorded the minimum average LM concentration, while the Western and Eastern Basins had slightly higher values (Table 1). Notably, the lowest LM concentration in the Central Basin was identified at station M31, a site proximal to a cement factory and solid cargo handling ports. This reduced LM concentration is attributed to a dilution effect, specifically the concurrently recorded second-highest concentration of $CaCO_3$ at the same station. On the other hand, the highest LM value found at station M48, is characterized by a steep, sloping ground structure. This situation is assumed to be primarily driven by seafloor topography. Specifically, LM, which rapidly mobilizes from the upper slopes, accumulates much more than biogenic (organic, shell, frustules etc.) deposits in surface sediments found on steeply topographic gradients, particularly where deep currents lose velocity. A similar pattern, indicating the dominance of terrestrial material input influenced by slope, was also observed at stations M89 in the Central Basin and B01 and B10 in the Western Basin (Figure 1 and 3f).

The high abundance and dominance of LM throughout İzmit Bay confirms its role as the primary background matrix for İzmit Bay sediments. The significant negative correlation observed between the LM and the other measured components (i.e. BSi, TOM, TOC, and $CaCO_3$) is a direct consequence of the dilution effect (Table 2). Accordingly, the increase in the absolute concentrations of the biogenic and organic components causes a corresponding relative decrease in the background lithogenic fraction. The spatial trend of LM concentrations, which increase from east to west and from north to south, is consistent with the decreasing concentrations of fine-grained mud and biogenic/organic components across the study area. This inverse relationship further confirms the dominance of the dilution effect as the primary control on the observed sediment component distributions.

Conclusion

This study comprehensively examined the spatial distribution of major sediment components in the surface sediments of İzmit Bay, thereby attempting to understand the interaction between the bay's unique stratified water column, anthropogenic and industrial pollution, and continuously increasing nutrient loads. Our findings corroborate previous studies, confirming that the bay's surface sediments are strongly influenced by specific environmental factors; notably, the present results regarding chronic nutrient enrichment, eutrophication, mucilage occurrence, and localized pollution near discharge points align consistently with established regional patterns.

A particularly significant finding is the approximately 61% increase in average TOC levels in İzmit Bay since 1987, a substantial rise which underscores the persistent and escalating nature of organic enrichment within this semi-enclosed ecosystem, which is densely populated and heavily industrialized. Fundamentally, İzmit Bay serves as a major sink for both materials produced by the ecosystem's biological elements and pollutants of anthropogenic origin. To effectively mitigate the severe environmental degradation and establish preventative measures, we recommend sustaining the ongoing remediation projects on the removal of contaminated surface sediments accumulated within the Eastern Basin, which are confirmed to constitute a major pollutant reservoir. Furthermore, current WWTPs must be immediately upgraded with advanced technology to enhance the reduction of TN and TP discharge. Finally, long-term monitoring programs should be established to track the concentrations of BSi and TOC in the uppermost sediment layer as key indicators of eutrophication reversal, alongside continuous monitoring of primary production across the water column's different layers and the pollutant loads carried by streams flowing through the heavily industrialized zones.

Acknowledgments

This research was funded by the Turkish Scientific and Technological Research Council (Grant No: TÜBİTAK 107Y261) and the Kocaeli University Scientific Research Projects Unit (Grant No: KOU-BAPB 2008/017). The authors wish to thank the Gölcük Commandership of the Turkish Naval Forces, the Environment Protection and Control Department of Kocaeli Metropolitan Municipality, and İzmit Harbor authorities.

Competing interest: No potential conflict of interest declared by the authors.
Ethics committee approval: There is no necessity for ethical approval for this research
Author contributions: H.A.E. Designing, managing and writing the study; S.A. Analytical processes, preparation of maps and graphics; A.K. Analytical processes; M.Ç. Collection of samples

İzmit Körfezi'nde biyojenik ve litojenik sediment bileşenlerinin mekansal dağılımı: tabakalı bir kıyı ekosisteminde ötrofikasyon dinamiklerinin ve antropojenik kirlilik kaynaklarının değerlendirilmesi

Öz

Bu çalışmada, İzmit Körfezi (Marmara Denizi) yüzey sedimentlerindeki biyojenik silika (BSi), kalsiyum karbonat ($CaCO_3$), toplam organik madde (TOM), toplam organik karbon (TOK), litojenik madde (LM), kalsiyum (Ca) ve fosfor (P) derişimlerinin mekansal dağılımı ve aralarındaki ilişkiler incelenmiştir. Çalışmada, bu bileşenlerin ötrofikasyon ve

kirlilik süreçlerinin takibinde kullanılabilirliği de değerlendirilmiştir. Körfez genelindeki 56 istasyondan toplanan yüzey sedimentleri, klasik kimyasal ve yakma yöntemleri kullanılarak analiz edilmiş, Ca ve P derişimleri ICP-MS ile belirlenmiş ve dağılımları Kriging enterpolasyonu kullanılarak haritalandırılmıştır. Sonuçlar, İzmit Körfezi'nin karmaşık hidrodinamiğini ve ağır antropojenik baskılar nedeniyle sediment bileşenlerinin belirgin bölgesel farklılık gösterdiğini ortaya koymuştur. Diyatom aktivitesinin bir göstergesi olan BSi, en yüksek ortalama değerini (12,5%) sığ Doğu Havzası'nda almıştır. Yüksek BSi ve TOK-TOM derişimleri daha çok atıksu arıtma tesisi deşarj noktalarına yakın bölgelerde ölçülmüştür. Bu durum, besin yükünün (özellikle TN ve TP'nin) aşırı birincil üretimi ve sedimentte organik madde birikimini tetiklediğini göstermekte ve ciddi bir ötrofikasyon sorununa işaret etmektedir. Buna karşın, $CaCO_3$ derişimleri Merkez Basen'in kuzey kıyısında en yüksek değerini (16,0%) almıştır. Bu durum büyük ölçüde çimento üretimi ve bölgesel dolomit yataklarından kaynaklanan endüstriyel girdiyle ilişkilidir. Yüksek TOK ve TOM seviyelerinin, özellikle Merkez Basen'in derin, hipoksik/anoksik bölgelerinde bulunması, körfeze hem otokton (fitoplankton kaynaklı) hem de allokton (kara kökenli/endüstriyel) organik madde girişini göstermektedir. LM ile diğer biyojenik bileşenler arasındaki anlamlı negatif korelasyonlar, akarsu kaynaklı çamur girdisinin biyojenik bileşenler üzerinde seyreltme etkisini ortaya koymaktadır. Yüzey sedimenti TOK seviyelerinin 1987'den bu yana %61 oranında artışı ise İzmit Körfezi ekosistemindeki bozulmanın sürekli olarak tırmandığını göstermesi bakımından dikkate değerdir. Sonuç olarak, İzmit Körfezi yüzey sedimentlerindeki yüksek BSi, TOM, TOK ve P değerleri besin girdisinin tetiklediği ciddi ötrofikasyon sorunlarına, yüksek $CaCO_3$ ise esas olarak endüstriyel deşarjlara işaret etmektedir. Veriler, gelecekteki ötrofikasyon, aşırı alg çoğalmaları, deniz salyası oluşumu, oksijenin azalması/tükenmesi gibi sorunları önlemek için İzmit Körfezi'ne deşarj edilen besin tuzlarını azaltacak uygulamaların gerçekleştirilmesinin hayati önem taşıdığını göstermektedir.

Anahtar kelimeler: İzmit Körfezi (Marmara Denizi), biyojenik silika, toplam organik karbon, sediment biyojeokimyası, ötrofikasyon, kirlilik

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