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Original article

The impact of the marine sewage outfalls on the sediment quality: The Black Sea and the Marmara case

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ABSTRACT

Marine sewage outfalls are the cheapest method of disposal for municipalities with restricted funds, despite their negative effects on marine ecosystems. This study was conducted on the marine sewage outfalls of the Turkish cities Rize (Black Sea) and Yalova (Sea of Marmara). Heavy metals, polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), and organochlorine pesticides (OCPs) were investigated in the sediments for determine pollution degree. Two of Yalova stations were classified as having high contamination levels (1034.436 and 1476.483 ng/g, respectively) and all the other stations suffered moderate pollution in terms of $\sum_{16}$PAHs. $\sum$DTTs in sediments above probable effect levels (PELs), were observed both stations Yalova and Rize. The highest metal concentrations in the sediments from the eight stations ranged from 4.97 to 29.65 mg/kg for Ni; 7.57–44.14 mg/kg for Cr; 9.84–42.76 mg/kg for Cu; and 48.08–103.77 mg/kg for Zn. In sum, examination of pollutant sources provides clear evidence of an anthropogenic effect on the discharge environments.

1. Introduction

Discharging wastewaters via marine sewage outfalls is an efficient way for coastal settlements to dispose of their wastewater, however a huge amount of toxicants are transported to marine ecosystem via such outfalls. Marine sewage outfalls are the cheapest method of disposal for municipalities with restricted funds, despite their negative effects on marine ecosystems. Turkey has a large coastline (7144 km long) with a total of 28 cities and 221 municipalities in the coastal area. More than 53% of the country's population lives in these cities and more than 20% of the country's population lives in the coastal region. The Black Sea constitutes 18.77% of this coastline and the Sea of Marmara accounts for 13.56% (TUIK, 2019a). In this context according to the Municipal Wastewater Statistics for 2018, 1,949,475,000 m^3 of wastewater, which constitutes 40.7% of total wastewater, is treated with a pollutant removal level of 96.6%, and discharged to the marine environment via outfalls (TUIK, 2018a). Since most of the sewage discharged at marine outfalls have been processed using only physical methods, a serious amount of pollutants discharged into the marine environment, although the pollutants seem to be treated effectively.

Pollutants that constitute the subject of this study are heavy metals, polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), and organochlorine pesticides (OCPs). Heavy metals are pollutants, regardless of their source, and above certain limits they have a toxic effect on marine organisms. PAHs, which are trace organic pollutants, are hydrocarbon molecules containing two or more fused benzene rings. PAHs generally originate from fossil fuels and their combustion and spread over a wide environment through the atmosphere; 230,000 tons of PAHs are released into the marine environment around the world each year (Chongrong et al. 2019). PCBs and OCPs are synthetic organic compounds. PCBs were once widely used as dielectric fluids for capacitors and transformers (Schulz et al. 1989). OCPs are compounds with low production costs that are highly effective against pests (Jones and de Voogt, 1999); the most widely known OCPs are DDT, dieldrin, heptachlor, and chlordane. Also the pollutants mentioned above, which are mostly of anthropogenic origin, can accumulate in the tissues of fishes and crustaceans and via the

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tissues of marine organisms pass through the food chain and risk the health of human consumers.

The Black Sea and the Sea of Marmara, where the study was conducted, are very important fishing areas. According to TUIK (2018b) the majority of the Turkish fisheries marine capture fish is provided from the Black Sea (54.94%) and the Sea of Marmara (22.38%), as well as other marine species (87.63%) provided from the both seas. The Black Sea and the Sea of Marmara combined provide 80.51% of the Turkish marine fisheries production. The Sea of Marmara is a reproduction or nursery area for commercial fish species (Keskin and Kaygusuz 2010). In addition to Yalova (Sea of Marmara) and Rize (Black Sea) were selected as the sampling areas with other common and different aspects. Although the population of the city center is similar in both cities, Yalova more densely than Rize approximately 3.6 times in terms of the population density per square kilometer (TUIK, 2019a). While agricultural activities are carried out in both cities, the arable agricultural lands of the city of Rize are 3.5 times larger than the surface area of the city of Yalova (TUIK, 2019b). Unlike Rize, there are many industrial facilities around Yalova that discharge their waste into the sea.

In this paper the effects of heavy metals, PAHs, PCBs, and OCPs on sediments at marine sewage outfalls and surrounding areas were examined to provide a basis for environmental monitoring and pollution control. The general objectives of this study were: to assess the level of contamination on-site and to infer the sources of the pollutants.

2. Materials and methods

The study was conducted on the marine sewage outfalls of the Turkish cities Rize (Black Sea) and Yalova (Sea of Marmara). Sampling took place at a total of eight sediment stations, four of which (S1, S3, S5, S7) were discharge points and four of which (S2, S4, S6, S8) were on the shore approximately 50 m from the discharge points. Of the discharge points, one was from Rize city center (S1) and one from the Pazar district of Rize (S3) and two were from Yalova city center (S5, S7). The Yalova (S7) station's pipeline was broken in the 1999 Gölcük Earthquake and sewage discharge has been carried out intermittently at a depth of about 2.2 m at a distance of approximately 150 m from the coast for 18 years. The common feature of the stations is that all the sewer lines began to discharge at about the same time. Nevertheless, population density, industrial and agricultural activities, and treatment plant characteristics were taken into consideration while determining where the stations were sited. While physical treatment is available at Rize (S1 and S2) and Pazar (S3 and S4) stations, advanced biological treatment (BNR – Biological Nutrient Removal) is used at Yalova stations (S5, S6, S7, and S8). Sediment sampling was carried out in 2018 summer and each station was sampled a total of four times (Figs. 1 and 2) using a scuba diver survey, a total of 24 dives were performed, which lasted 36 h. Details of the stations are given in Table 1.

All sediment samples were preserved at −18 °C until analyzed (Csuros and Csuros 2002). Sediments were analyzed for total organic carbon (TOC), metal concentrations, PAHs, PCBs and OCPs. The sediment samples were dried for overnight at 45 °C and sieved manually with a set of sieves and classified as sand (0.063–2 mm) or Silt&Clay (<0.063 mm) based on their grain size (Folk 1974) before being subject to the acid digestion method (HNO_3 + H_2O_2) following Gedik et al. (2018), modified from United States Environmental Protection Agency - US EPA (1996), for heavy metal analysis. Metal concentrations (Cd, Pb, Ni, Fe, Zn, Cu, Al, Cr, Co, and Mn) were analyzed using an Inductively Coupled Plasma Optical Emission Spectrometer (ICP–OES). All metal concentration data were given as mg/kg dry weight (dw). TOC was determined by the solid sample combustion method using a solid sample combustion unit (SSM-5000A, Shimadzu) and laboratory TOC analyzer (TOC-L, Shimadzu). Oxidation-reduction potential and sediment pH (1:5 sediment:water) were measured according to Jackson (1958). Quality assurance and control was ensured by blank runs and triplicate analysis of each sample. The sediment samples were freeze-dried for 48 h before other analyses were performed and PAHs (ISO 11338–2, EPA Method 3540C), PCBs (ISO 10382), and OCPs (EPA 3535A, EPA 8270D) were analyzed using a Gas Chromatography - Tandem Mass Spectrometer (GC–MS-MS) after soxhlet extraction and cleanup at TUBITAK MAM (Gebze, Kocaeli, Turkey; Accreditation Certificate Number TS EN ISO/IEC 17025.) The limit of detection (LOD) = 0.05 μg/kg for (GC–MS-MS) analyses.

2.1. Statistical analysis

Statistical analysis of the data set was performed using IBM SPSS Statistics Software package (NY: IBM Corp., USA) and by JMP® Statistical Software package Version 14 (SAS Institute Inc., Cary, USA). The Mann-Whitney *U* test was performed to compare discharge points and nearby areas. ANOVA (one-way analysis of variance) followed by the Tukey Test was used to compare sampling stations and the significance level was set at $p < 0.05$.

3. Results and discussion

3.1. TOC, pH, ORP and sediment particle size fraction

Sediment TOC concentrations ranged from 1.43% to 2.66% and pH values ranged from 7.13 to 7.75; the lowest pH value was at station S5 and the highest TOC value occurred at station S6 (Table 2.) Organic matter content and pH values were similar for all stations. ORP values were positive for all stations, showing the effect of oxidation. The lowest ORP values were recorded at S1 and S2 stations and this may be explained by this treatment plant's use of physical methods instead of biological nutrient removal (BNR). The ratio of Sand/Silt&Clay values were higher at stations S5 and S6 and, according to Morillo et al. (2004), metals adhere to small particles in the sediment.

3.2. Metal concentrations

Metal concentrations (Cd, Pb, Ni, Fe, Zn, Cu, Al, Cr, Co, and Mn) were analyzed using an inductively coupled plasma optical emission spectrometer (ICP–OES). The elements Cd and Fe were not considered further in this study because Cd concentration was below the detection limit (detection limit = 0.05 mg kg^{-1}) and Fe concentrations were at the expected high values for all stations. The highest metal concentrations in the sediments from the eight stations ranged from 4.97 to 29.65 mg/kg for Ni; 7.57–44.14 mg/kg for Cr; 9.84–42.76 mg/kg for Cu; and 48.08–103.77 mg/kg for Zn (Fig. 3). Station S4 recorded the highest total metal concentration with a very high level of Manganese (Mn) compounds and the lowest level was found at S7. The values found in this study are lower than those reported for these regions in the literature. Pekey et al. (2004) reported Ni, Cr, Cu, and Zn concentrations, respectively, in the range of 38.4–70 mg/kg, 76.1–116 mg/kg, 60–139 mg/kg, and 510–1100 mg/kg in his study inside Izmit Bay, not far from the study area (S5, S6, S7, and S8). According to Topcuoğlu et al. (2002), metal concentrations ranged from 18.5 to 37 mg/kg for Ni, 21 to 38 mg/kg for Cr, 69.9 to 95 mg/kg for Cu, and 82.9 to 267 mg/kg for Zn in the Eastern Black Sea, while Ergül at al. (2002) reported Ni, Cr, Cu, and Zn concentrations, respectively, of between 23 and 26 mg/kg, 70 and 74 mg/kg, 52 and 56 mg/kg, and 169 and 182 mg/kg, in Yomra Bay.

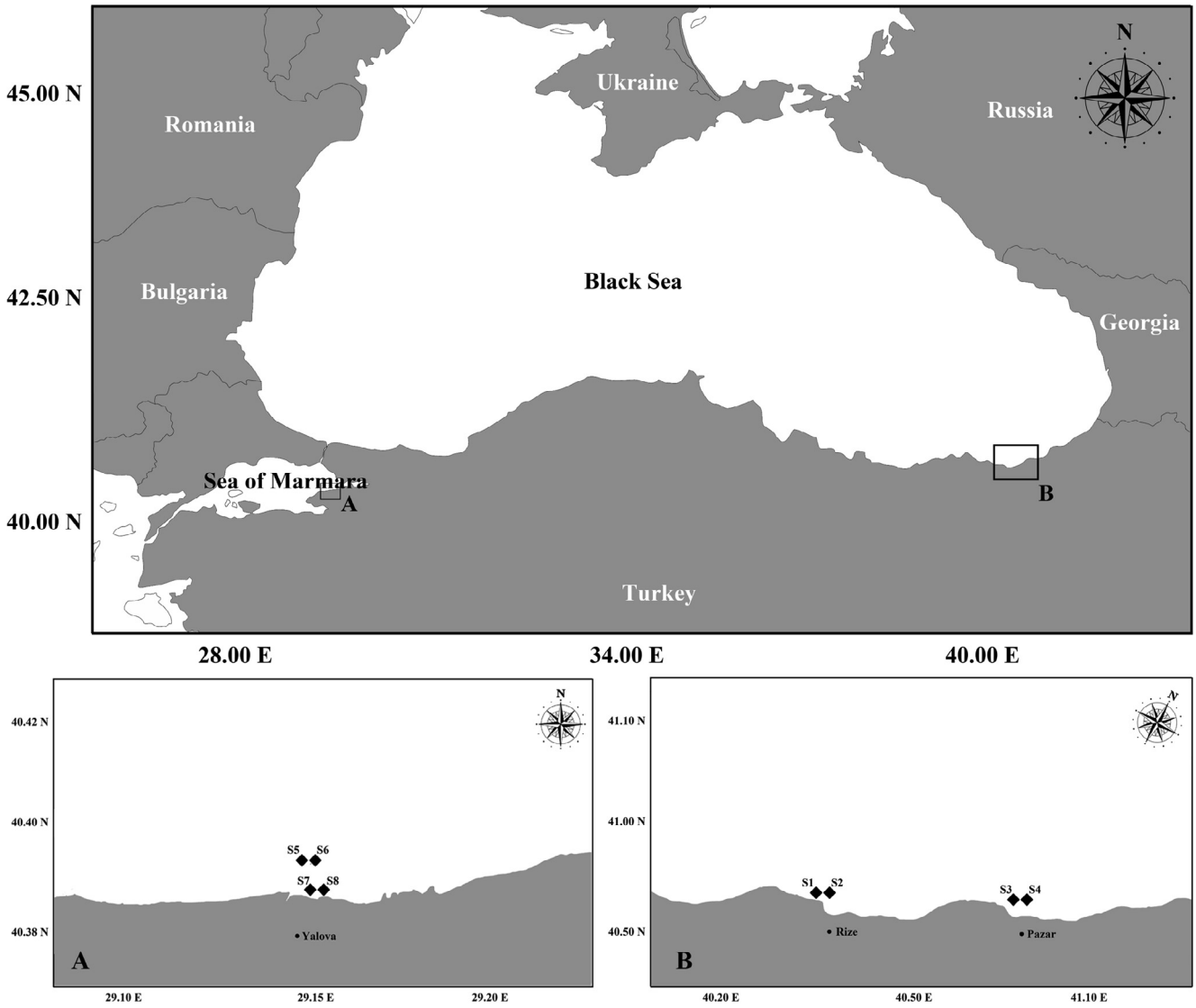

Fig. 1. Location of sediment sampling stations: S1, S3, S5, S7 are discharge points and S2, S4, S6, S8 are on the shore, about 50 m distant.

We compared the metal concentrations data obtained with US EPA Sediment Quality Guidelines (SQGs) (Table 3), which divided sediments into three classes: 1) non-polluted, 2) moderately polluted, and 3) heavily polluted (Perin et al., 1997; Pekey et al., 2004; Gedik and Boran, 2013).

The anthropogenic effects on the marine ecosystem are demonstrated by the outfall discharges. In their study Baltas et al. (2017) reported values of Cu, Zn, and Pb for three stations (one of them from the inner harbor) at Rize of 286.75 ± 5.64, 350.53 ± 7.47, and 37.00 ± 1.50 (mg kg^{-1}), respectively, and suggested that the Cu concentration could be caused by the transportation of copper from the ports of Hopa, Rize, and Surmene. These results are higher than our values and this may be due to the difference between sampling depths or the difference between sampling points in the two studies. In addition, Cu, Zn, and Pb are probably associated with discharge of sewage, industrial resources, motor vehicle emissions, automobile batteries, and gasoline additives (Tang et al. 2008; Huang et al., 1994; Yilmaz et al., 2018). While there are no large industrial facilities near Rize, it is known that there is intensive cultivation and production of tea in the region near S1, S2, S3 and S4 stations and, although it is prohibited, fertilizers may be used by farmers. According to Bat et al. (2009) the source of most of the pollutants in the Black Sea are shipping activities and untreated domestic, industrial, and agricultural wastes entering via rivers or directly discharged. This is also known to be the case for the Sea of Marmara. Therefore, it is not enough to comment on pollution at the outfalls and surrounding area by only considering heavy metal levels in the sediments, where they are potent indicators. To make predictions about heavy metal pollution, it is necessary to know their status both before and after measurement, so researchers have used many methods to evaluate contamination levels, using such metrics as enrichment factors, geoaccumulation indexes, contamination factors and contamination degrees.

3.3. Enrichment factor (EF) assessment

Calculation of the enrichment factor (EF) is the preferred approach for understanding anthropogenic effects on sediment quality (Alkan et al. 2015) because it distinguishes anthropogenic sources of heavy metal pollution from naturally occurring sources (Ozkan 2012). The EF is calculated as follows

$$Ef = \frac{\{(\frac{Metal}{Aluminium})Samples\}}{\{(\frac{Metal}{Aluminium})Background\}}$$

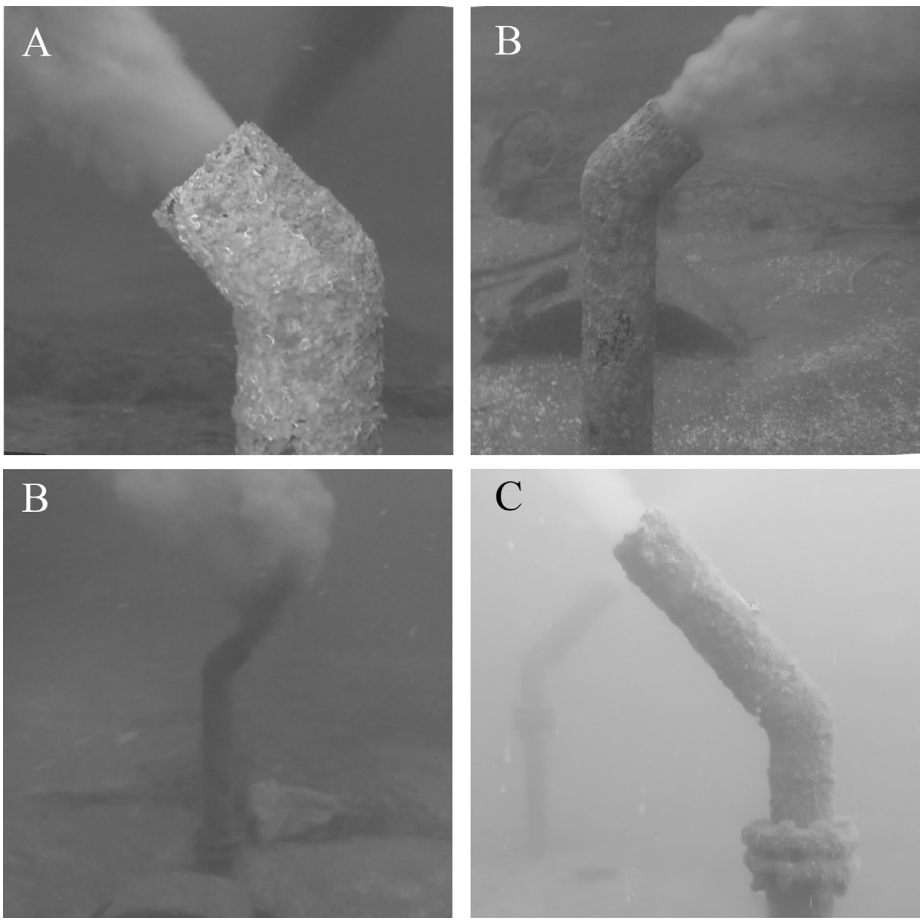

Fig. 2. Detail of outfalls at discharge points. A: Yalova (S5),B: Rize (S1), and C: Pazar (S3).

Table 1
Details of sampling stations.

ID	Stations	Location	Sediment Properties	Depth	Discharging From
S1	Rize Outfall	41° 02′ 47,80″ N 40° 29′ 59,00″ E	Coarse Sand	34 m	2017
S2	Shore of Rize Outfall	41° 02′ 47.56″ N 40° 30′ 01.11″ E	Coarse Sand	35 m	–
S3	Rize Pazar Outfall	41° 11′ 38.58″ N 40° 55′ 21.54″ E	Medium Sand	22 m	2016
S4	Shore of Rize Pazar Outfall	41° 11′ 38.54″N 40° 55′ 23.66″E	Medium Sand	22 m	–
S5	Yalova Outfall	40° 39′ 55.83″N 29° 14′ 52.81″ E	Fine	40 m	2017
S6	Shore of Yalova Outfall	40° 39′ 55.88″N 29° 14′ 54.95E	Fine	40 m	–
S7	Yalova Old Outfall	40° 39′ 34.26″N 29° 15′ 00.76″E	Coarse Sand	2 m	1999*
S8	Shore of Yalova Old Outfall	40° 39′ 34.22″N 29° 15′02.92″E	Coarse Sand	3 m	–

* This pipeline was broken in the 1999 Gölcük Earthquake.

Table 2
General properties of sediment samples.

Stations	S1	S2	S3	S4	S5	S6	S7	S8
TOC[a] (%)	1.59	1.58	2.06	1.98	2.41	2.66	1.68	1.43
pH	7.40	7.75	7.45	7.36	7.13	7.17	7.50	7.53
ORP[b]	162.4	168.5	207.3	183.3	191.0	196.3	192.4	193.6
Sand (%)	96.92	97.65	59.51	52.42	20.56	25.25	93.55	91.85
Silt&Clay (%)	3.08	2.35	40.49	47.58	79.44	74.75	6.45	8.15

[a] Total Organic Carbon – Dry weight.
[b] Oxidation–Reduction Potential (mV).

where $\{(\frac{Metal}{Aluminium})Samples\}$ is the ratio of the relevant metal concentration in the samples to the aluminum concentration and $\{(\frac{Metal}{Aluminium})Background\}$ is the ratio of the relevant metal concentration to aluminum concentration background values. In this study the background metal concentration values were obtained from Turekian and Wedepohl (1961) and the EFs calculated using the obtained data are given in Table 4.

EF values indicate levels where EF < 2 equates to low enrichment, 2 < EF < 5 is moderate enrichment, 5 < EF < 20 is significant enrichment, 20 < EF < 40 is very high enrichment, and EF > 40 is

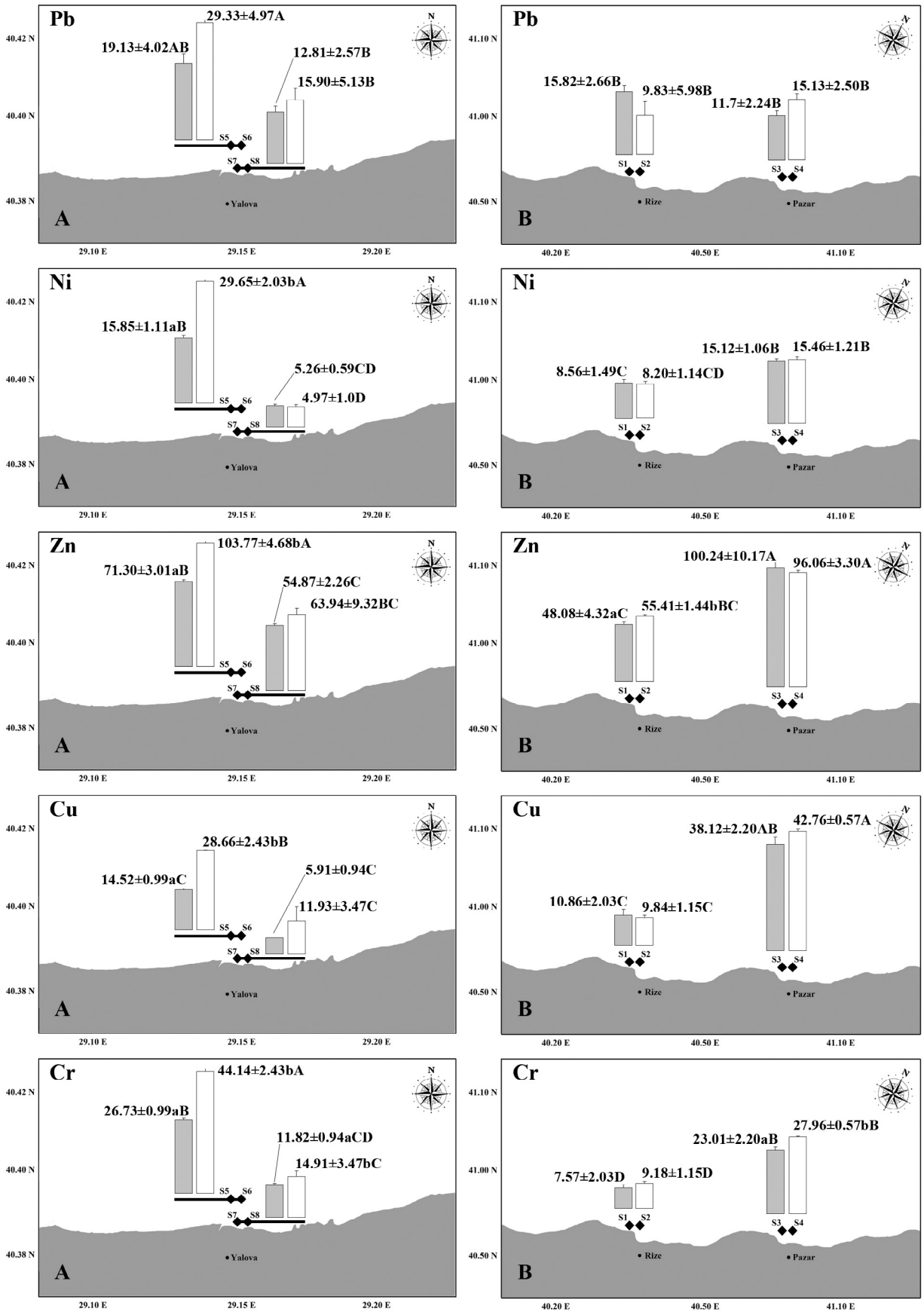

Fig. 3. Distribution of metal concentrations in the sampling areas. The results are given as mean ± standard deviation (mg kg^{-1}). Lower case letters (a, b) indicate significant differences ($p < 0.05$) among individual discharge points and nearby shorelines. Upper case letters (A, B, C, D) indicate significant differences ($p < 0.05$) among sampling stations.

Table 3
Metal Concentrations and Comparison with Sediment Quality Guidelines (SQGs) (mg kg^{-1}).

Stations	S1	S2	S3	S4	S5	S6	S7	S8	US EPA SQGs		
									Non.	Mod.	Heavy
Pb	15.82 ± 2.66B	9.83 ± 5.98B	11.7 ± 2.24B	15.13 ± 2.50B	19.13 ± 4.02AB	29.33 ± 4.97A	12.81 ± 2.57B	15.90 ± 5.13B	<40	40–60	>60
Ni	8.56 ± 1.49C	8.20 ± 1.14CD	15.12 ± 1.06B	15.46 ± 1.21B	15.85 ± 1.11aB	29.65 ± 2.03bA	5.26 ± 0.59CD	4.97 ± 1.0D	<20	20–50	>50
Zn	48.08 ± 4.32aC	55.41 ± 1.44bBC	100.24 ± 10.17A	96.06 ± 3.30A	71.30 ± 3.01aB	103.77 ± 4.68bA	54.87 ± 2.26C	63.94 ± 9.32BC	<90	90–200	>200
Cu	10.86 ± 2.03C	9.84 ± 1.15C	38.12 ± 2.20AB	42.76 ± 0.57A	14.52 ± 0.99aC	28.66 ± 2.43bB	5.91 ± 0.94C	11.93 ± 3.47C	<25	25–50	>50
Cr	7.57 ± 2.03D	9.18 ± 1.15D	23.01 ± 2.20aB	27.96 ± 0.57bB	26.73 ± 0.99aB	44.14 ± 2.43bA	11.82 ± 0.94aCD	14.91 ± 3.47bC	<25	25–75	>75
Co	10.87 ± 0.96CD	12.13 ± 1.15BC	21.36 ± 1.96A	19.74 ± 0.10A	10.23 ± 0.52aCD	14.82 ± 0.06bB	8.21 ± 0.56D	8.95 ± 1.0D	–	–	–
Mn	250.58 ± 40.23aD	449.88 ± 58.35bC	723.25 ± 138.99aB	1058.19 ± 29.09bA	148.87 ± 5.01aD	274.73 ± 14.29bD	141.25 ± 5.38D	156.75 ± 31.52D	<300	300–500	>500
Al*	2.14 ± 0.23	2.35 ± 0.25	4.82 ± 0.50	4.98 ± 0.14	1.96 ± 0.07	3.56 ± 0.16	0.90 ± 0.03	0.79 ± 0.05			

The results are given as mean ± standard deviation. Values in the same row followed by different lower case letters (a, b) show significant differences ($p < 0.05$) among individual discharge points and nearby shorelines. Values in the same row followed by different upper case letters (A, B, C, D) show significant differences ($p < 0.05$) among sampling stations. Al values given above for Enrichment Factor calculations.

extremely high enrichment (Alkan et al. 2015; Cukrov et al. 2011; Feng et al. 2011; Lianfeng et al. 2010). All elements demonstrated low levels of enrichment at S1(except for Pb and Co) and S3 while Co, Mn, and Cu were moderately enriched for stations S1, S2, S5, S7, S8, S4, and S8. Pb were moderately enriched at stations S1, S5 and S6 and Zn were moderately enriched at stations S5 and S6 but Pb and Zn were significantly enriched at S7 and S8 (Table 4). According to Tang et al. 2008, Cu, Pb, and Zn are probably associated with sewage discharge and the enrichment values found for these elements at stations S7, S8 would seem to agree with this hypothesis. Alkan et al. (2015) indicated that EF values above 1.5 suggest both natural and anthropogenic processes were impacting the sediment; this study shows that anthropogenic effects were present, in addition to natural processes, for at least one element at all stations.

3.4. Geoaccumulation index (I_{geo}) assessment

The geoaccumulation index (I_{geo}), as proposed by Müller (1979), is used to estimate the degree of metal concentration enrichment of the sediment, and is calculated as follows:

$$\boldsymbol{Igeo} = Log_2\left[\frac{Cn}{1.5Bn}\right]$$

where *Cn* is the concentration of the relevant element, *Bn* is the geochemical background value of the relevant element and 1.5 is a coefficient factor that compensates for variation. The geoaccumulation index was categorized into seven classes, according to Müller (1979) (Table 5).

When the obtained data were compared to the geoaccumulation index all stations qualified as Class 0 ($I_{geo} \leq 0$; uncontaminated), although elements such as Pb and Zn were at the threshold level for Class 1 (I_{geo} = 0–1; uncontaminated to moderately contaminated), especially at S6. These results reflects accumulation for elements Pb and Zn originating from sewage discharge.

3.5. Assessment using contamination factor (Cf) and contamination degree (Cd)

The contamination factor (Cf) is the ratio of the concentration of an element in the samples to background values for the element, using either mean shale values (Turekian and Wedepohl 1961) or mean crustal abundance (Taylor 1972). The degree of contamination (Cd) is the sum of the Cfs for all the sediment's heavy metals (Aksu et al. 1998). Cf is calculated as:

$$\boldsymbol{Cf} = \frac{\{(E.Consentration)Samples\}}{\{(E.Consentration)Background\}}$$

and Cd is calculated as:

$$\boldsymbol{Cd} = \sum_i^n \boldsymbol{Cf}$$

According to Ozkan (2012), Cd < 8 denotes a low degree of contamination, $8 \leq$ Cd < 24 indicates a moderate degree of contamination, $24 \leq$ Cd < 48 represents a considerable degree of contamination, and Cd > 48 denotes a very high degree of contamination. All the stations in the study demonstrated a low degree of contamination (Table 6).

According to Hakanson's (1980) approach, all the samples examined as described in Ozseker et al. 2016, in terms of both 'grade of ecological risk of single metal' and 'grade of potential ecological risk of environment' presented a 'low risk' for all the sampling stations.

Table 4
Enrichment factor calculations for determine contamination limits.

	Cu	Pb	Zn	Mn	Ni	Co	Cr
S1	0.90	2.96	1.89	1.10	0.47	2.14	0.31
S2	0.75	1.68	1.99	1.80	0.41	2.18	0.35
S3	1.41	0.93	1.75	1.41	0.37	1.87	0.42
S4	1.53	1.22	1.62	2.00	0.37	1.67	0.50
S5	1.32	3.90	3.06	0.71	0.95	2.20	1.21
S6	1.43	3.29	2.45	0.73	0.98	1.75	1.10
S7	1.16	5.66	5.11	1.47	0.68	3.82	1.16
S8	2.69	8.08	6.84	1.87	0.74	4.78	1.68

Table 5
Geoaccumulation Index Classes for determine contamination limits.

Class	Range	Soil or Sediment Quality
0	Igeo $\leq$ 0;	uncontaminated
1	Igeo = 0–1	uncontaminated to moderately contaminated
2	Igeo = 1–2	moderately contaminated
3	Igeo = 2–3	moderately to strongly contaminated
4	Igeo = 3–4	strongly contaminated
5	Igeo = 4–5	strongly to extremely contaminated
6	Igeo > 5	extremely contaminated

3.6. Polycyclic aromatic hydrocarbons (PAHs)

The 16 most common PAHs were used to determine PAH pollution at and around the discharge points. We compared values according to both the Canadian Sediment Quality Guidelines for the Protection of Aquatic Life (ISQGs and PELs) (CCME, 1999) and Threshold Effect Sediment Quality (TEL, PEL), and to median effect sediment quality (ERL, ERM) guideline values for organics (Long et al. 1995; MacDonald et al. 2000; Burton 2002) (Table 7).

There are two types of PAH sources in marine ecosystem: pyrolytic and petrogenic. While PAHs of pyrolytic origin are caused by incomplete combustion of organic matter, the source of petrogenic PAHs is mostly anthropogenic pollutants such as oil leaks and domestic waste. The origin of PAHs may be determined by various molecular indexes: a phenanthrene/anthracene ratio < 10 indicates pyrolytic origin and phenanthrene/anthracene > 10 indicates petrogenic sources. Moreover, fluoranthene/pyrene ratios greater than one are classically related to pyrolytic origins, namely coal combustion (Budzinski et al. 1997). Analysis of the sewage outfalls indicated a petrogenic PAH origin, for all stations (values from over 10 to 38), except for S6 and S7, according to the phenanthrene/anthracene ratio and for all stations (value under 1) except for S2 and S6, according to the fluoranthene/pyrene ratio.

When the important PAH congeners are evaluated individually, naphthalene values are above the interim sediment quality guidelines values (ISQGs) for all stations and for station S5 it is above effects range low (ERL). The reason for this is probably that naphthalene is used in a wide variety of industrial fields, as well as the intensive use of sink cleaners in homes. Phenanthrene and pyrene values are above threshold effect level (TEL) at S6. Pyrene is a low molecular weight PAH and is produced from a wide range of combustion conditions, but especially from vehicle traffic. Benz(a)anthracene values are above ISQGs at S6. Benzo(a)pyrene values are above the TEL at S5 and S6 and Benzo(b)fluoranthene values are above the TEL at S5, S6, and S7. PAH mixtures such as benzo(a)pyrene, benz(a)anthracene, benzo(b)fluoranthene, and dibenz(a,h)anthracene have all been reported to be carcinogenic (ATSDR, 1995).

Baumard et al. (1998) categorized PAH pollution in sediments into four classes: low (0–100 ng/g); moderate (100–1000 ng/g); high (1000–5000 ng/g); and very high (>5000). Stations S5 and S6 were classified as having high contamination levels (1034.436 and 1476.483 ng/g, respectively) and all the other stations suffered moderate pollution. When we examine each data element separately on a station basis, it can be seen that stations S5 and S6 are under intense pressure in terms of PAH contamination, due to factors such as excessive industrialization, population growth, and its location at the entrance of Izmit Bay. The many shipyards and industrial facilities in the area surrounding Izmit Bay can be considered the main causes of pollution in the region. Karakoc et al. (2002) reported $\sum_{16}$PAH in the range of 30.0–1670.0 mg/g dry weight in sediments from İzmit BAY in the Sea of Marmara and Readman et al. (2002) reported $\sum_{17}$PAH 10–550 ng/g dry weight from Black Sea coast sediments.

3.7. Organochlorine pesticides (OCPs) and polychlorinated biphenyls (PCBs)

In this study OCPs, such as p,p'-DDD, p,p'-DDE, p,p'-DDT, and HCHs (important commercial alpha, beta, delta, and gamma 'Lindane' isomers), were detected. However, heptachlor, aldrin, and endrin were not detected at any stations and dieldrin was only detected at one station (S1) at a level of 0.055 ng/g, therefore these OCP compounds are not discussed in this study. Polychlorinated Biphenyl (PCB) congeners PCB 101/118/138/153/180/28/31/52 were detected in the range 0.05–2.238 ng/g.

We compared values both according to Canadian Sediment Quality Guidelines for the Protection of Aquatic Life (ISQGs and PELs) (CCME 1999–2001) and Threshold Effect Sediment Quality (TEL, PEL) and Median effect sediment quality (ERL, ERM) guideline values for organics (Long et al. 1995; MacDonald et al. 2000).

Table 6
Contamination Factor and Contamination Degree for all samples.

Stations	Cu	Pb	Zn	Ni	Fe	Mn	Co	Cr	Cont degr.
S1	0.24	0.79	0.51	0.13	0.51	0.29	0.57	0.08	**3.12**
S2	0.22	0.49	0.58	0.12	0.58	0.53	0.64	0.10	**3.27**
S3	0.85	0.56	1.06	0.22	1.09	0.85	1,12	0.26	**6.00**
S4	0.95	0.76	1.01	0.23	1.11	1.24	1.04	0.31	**6.65**
S5	0.32	0.96	0.75	0.23	0.40	0.18	0.54	0.30	**3.68**
S6	0.64	1.47	1.09	0.44	0.70	0.32	0.78	0.49	**5.93**
S7	0.13	0.64	0.58	0.08	0.27	0.17	0.43	0.13	**2.43**
S8	0.27	0.79	0.67	0.07	0.28	0.18	0.47	0.17	**2.91**

Table 7
Measured PAHs levels and Comparison of Sediment Quality Guidelines (SQGs) (ng g^{-1}).

	Stations													
	S1	**S2**	**S3**	**S4**	**S5**	**S6**	**S7**	**S8**	**ISQGs**	**PELs**	**TEL**	**PEL**	**ERL**	**ERM**
Acenaphthene	0.2	0.192	1.083	0.196	1.177	4.066	0.497	0.314	6.71	88.9	10	90	20	500
Acenaphtylene	0.617	0.601	1.982	0.714	1.46	3.004	3.103	1.322	5.87	128	10	130	40	640
Anthracene	1.334	2.029	5.66	1.453	7.024	15.079	9.285	2.579	46.9	245	50	240	90	1100
Benz(a)anthracene	2.461	2.632	27.987	5.805	65.814	97.865	36.219	13.169	74.8	693	70	690	260	1600
Benzo(a)pyrene	4.002	3.697	25.243	8.153	103.932	170.679	49.735	25.382	88.8	763	90	760	430	1600
Benzo(b)fluoranthene	13.818	10.329	55.218	21.747	156.743	294.616	72.51	38.306	–	–	70	710	320	1880
Benzo(g,h,i)perylene	3.7	2.527	11.621	5.046	36.797	68.036	17.465	9.179	–	–	–	–	–	–
Benzo(k)fluoranthene	1.168	0.836	5.465	1.992	20.284	36.078	8.313	4.724	–	–	60	610	280	1620
Chyrsene	4.864	4.904	32.883	8.063	65.76	96.192	38.439	13.541	108	846	110	850	380	2800
Dibenz (a,h)anthracene	0.767	0.467	2.343	0.926	9.076	20.954	4.799	2.882	6.22	135	–	–	–	–
Fluoranthene	21.923	21.435	81.834	22.599	123.733	182.865	101.469	31.136	113	1494	110	1490	600	5100
Fluorene	2.756	2.456	5.544	2.479	6.486	8.197	5.812	2.999	21.2	144	20	140	20	540
Indeno(1,2,3-c,d)pyrene	5.251	3.49	14.925	6.963	52.998	94.773	22.746	13.12	–	–	–	–	–	–
Naphtalene	92.401	75.9	131.732	67.677	179.521	113.623	128.08	98.654	34.6	391	30	390	160	2100
Phenanthrene	51.631	52.241	61.138	27.383	74.231	90.798	73.383	51.502	86.7	544	90	540	240	1500
Pyrene	25.304	21.377	84.63	23.367	129.4	179.658	109.653	35.394	–	–	150	1400	660	2600

ISQGs, Interim sediment quality guidelines; **PELs**, probable effect levels; Canadian Sediment Quality Guidelines for the Protection of Aquatic Life (CCME, 1999) **TEL**, threshold effect level; **PEL**, probable effects level; Threshold Effect Sediment Quality Guideline values for organics **ERL**, effects range low; **ERM**, effect range median; Median Effect Sediment Quality Guideline values for organics. (Long et al. 1995; MacDonald et al. 2000).

Table 8
Measured OCPs and ∑PCB and Comparison of Sediment Quality Guidelines (SQGs) (ng g^{-1}).

Stations	**S1**	**S2**	**S3**	**S4**	**S5**	**S6**	**S7**	**S8**	**ISQGs**	**PELs**	**TEL**	**PEL**	**ERL**	**ERM**
DDD p,p	–	0.339	0.201	–	0.815	3.073	–	0.847	1.22	7.81	3.54	8.51	2	20
DDE p,p	0.405	0.232	0.306	0.172	1.673	1.891	0.621	0.469	2.07	3.74	1.42	6.8	2	15
DDT p,p	4.859	1.693	1.645	1.154	0.368	5.861	1.02	6.313	1.19	4.77	–	–	1	7
α-HCH alpha	18.75	4.47	0.646	0.786	0.983	2.737	0.941	3.406	–	–	–	–	–	–
ß-HCH beta	1.326	0.818	0.533	0.322	0.467	0.921	0.381	0.827	–	–	–	–	–	–
δ-HCH delta	2.579	1.911	0.328	0.307	0.413	0.964	0.328	1.070	–	–	–	–	–	–
ɣ - HCH 'Lindane'	4.358	1.848	0.224	0.247	0.341	1.215	0.284	1.272	0.32	0.99	0.09	1.38	–	–
$\sum_7$PCBs	0.665	0.798	0.833	0.890	1.305	2.4838	0.911	5.194	–	–	34	277	50	400

ISQGs, Interim sediment quality guidelines; **PELs**, probable effect levels; Canadian Sediment Quality Guidelines for the Protection of Aquatic Life (CCME 1999–2001) **TEL**, threshold effect level; **PEL**, probable effects level; Threshold Effect Sediment Quality Guideline values for organics. **ERL**, effects range low; **ERM**, effect range median; Median Effect Sediment Quality Guideline values for organics. (Long et al. 1995; MacDonald et al. 2000). **$\sum_7$PCBs** = 101 + 118 + 138 + 153 + 180 + 28/31 + 52 (PCB congeners).

The distribution of DDTs, HCHs, and ∑PCBs are shown in Table 8. High concentrations of DDTs, above probable effect levels (PELs), were observed at S8, S6, and S1, while the other stations exceeded effects range low and ISQG levels (ERL & ISQGs), except for S5. High concentrations of ɣ-HCH 'Lindane' were observed at stations S1, S2, S6, and S8, all above PELs.

This study was compared with studies carried out in the same seas on a dry weight basis and the results are as follows. Fillmann et al. (2002) reported ∑PCBs of 0.4–44 μg/kg, 0.3–4.7 μg/kg, 5.7–6.8 μg/kg, ∑DDTs of 0.2–7.2 μg/kg, 3.3–12 μg/kg, 35–65 μg/kg, and ∑HCHs of 0.08–1.1 μg/kg, 0.3–0.8 μg/kg, and 1.3–2.3 μg/kg, respectively, from the Bosporus (Turkey) and the Black Sea at Sochi (Russia) and Odessa (Ukraine). Burns and Villeneuve (1987) reported ∑PCBs of 0.8 μg/kg, ∑DDTs of 0.047 μg/kg, and ∑HCHs of 0.012 μg/kg for Mediterranean. Finally, Bakan and Ariman (2004) reported that ∑DDTs were 18–55 μg/kg and ∑HCHs were 5–16 μg/kg (wet wt. basis) on the Black Sea coast of Samsun, Turkey. ∑HCHs results were found higher than in the results of Fillmann et al. (2002) and Bakan and Ariman (2004) especially S1. Additionally, ∑DDTs results obtained in the present study were found to be in parallel with the results Fillmann et al. (2002), but lower than Bakan and Ariman (2004). This is a major pollution indicator and means that Turkey has not been able to eliminate the DDTs which have been banned since the 1980 s. However, the ∑PCB values of the sampling stations are below data reported in the literature given above or guide values and do not constitute a toxicological threat.

In the view of these outputs, it is known that both seas constituting the research area are vulnerable and prone to pollution. The dataset in this manuscript is significant due to the fact that the pollution status at the outfall area should continuously be surveyed.

4. Conclusions

This research represents a comprehensive study in the field of marine sewage outfall discharges, conducted by researchers performing diving surveys at outfalls and their surroundings. In the light of the results of this study, the following conclusions can be drawn. The marine sewage outfall discharges described in the study are still new discharges and their long-term effects should be investigated. Examination of pollutant sources provides clear evidence of an anthropogenic effect on the discharge environments. Although Yalova Station (S5 and S6) has an advanced biological treatment plant (BNR), Yalova discharges and the industrial activities in the region make significant contributions to pollution in this context. Moreover, taking into account the amount of OCPs found, the Rize station (S1) is affected by the thoughtless use of pesticides and fertilizers in intensive agricultural activities.

This study should be used as a baseline reference for further monitoring studies to be carried out at marine sewage outfalls.

The effect of increasing the depth of discharges and extending their distance from the shoreline could be evaluated to protect the coastal ecosystem. Considering that the discharge into marine environment starts from homes, it is very important to raise the awareness of people about pollutants and their effects and to encourage recycling and zero waste strategies.

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Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

References

Aksu, A.E., Yaşar, D., Uslu, O., 1998. Assessment of marine pollution in Izmir Bay: Heavy metal and organic compound concentrations in surficial sediments. Transl. J. Eng. Environ. Sci. 22, 387–415.

Alkan, N., Alkan, A., Akbaş, U., Fisher, A., 2015. Metal Pollution Assessment in Sediments of the Southeastern Black Sea Coast of Turkey. Soil Sediment Contamin.: Int. J. 24 (3), 290–305. https://doi.org/10.1080/15320383.2015.950723.

ATSDR, Agency for Toxic Substances and Disease Registry (ATSDR). (1995). Toxicological profile for polycyclic aromatic hydrocarbons (PAHs). Atlanta (GA): Department of Health and Human Services, Public Health Service, USA.

Bakan, G., Ariman, S., 2004. Persistent organochlorine residues in sediments along the coast of mid-Black Sea region of Turkey ISSN 0025-326X Mar. Pollut. Bull. 48 (11–12), 1031–1039. https://doi.org/10.1016/j.marpolbul.2003.12.005.

Baltas, H., Sirin, M., Dalgic, G., Bayrak, E.Y., Akdeniz, A., 2017. Assessment of metal concentrations (Cu, Zn, and Pb) in seawater, sediment and biota samples in the coastal area of Eastern Black Sea, Turkey. Mar Pollut Bull. 122 (1–2), 475–482. https://doi.org/10.1016/j.marpolbul.2017.06.059.

Bat, L., Gökkurt, O., Sezgin, M., Üstün, F., Sahin, F., 2009. Evaluation of the Black Sea Land Based Sources of Pollution the Coastal Region of Turkey. Open Mar. Biol. J. 3, 112–124. https://doi.org/10.2174/1874450800903010112. Electronic publication date 31/12/2009.

Baumard, P., Budzinski, H., Garrigues, P., 1998. Polycyclic aromatic hydrocarbons in sediments and mussels of the western Mediterranean sea. Environ. Toxicol. Chem. 17, 765–776. https://doi.org/10.1002/etc.5620170501.

Budzinski, H., Bellocq, J., Pierard, C., Garrigues, P., 1997. Evaluation of sediment contamination by polycyclic aromatic hydrocarbons in the Gironde estuary. Mar. Chem. 58, 85–97.

Burns, K.A., Villeneuve, J.P., 1987. Chlorinated hydrocarbons in the open Mediterranean ecosystem and implications for mass balance calculations. Mar. Chem. 20 (337), 359.

Burton Jr., G., 2002. Sediment quality criteria in use around the world. Limnology 3, 65–76. https://doi.org/10.1007/s102010200008.

Canadian Council of Ministers of the Environment (CCME). 1999. Canadian sediment quality guidelines for the protection of aquatic life: Summary tables. In: Canadian environmental quality guidelines. 1999. Canadian Council of Ministers of the Environment, Winnipeg.

Canadian Council of Ministers of the Environment. 2001. Canadian sediment quality guidelines for the protection of aquatic life: Polychlorinated biphenyls (PCBs). Updated. In: Canadian environmental quality guidelines, 1999, Canadian Council of Ministers of the Environment, Winnipeg.

Chongrong, Z., Baoqing, L., Huikai, W., et al., 2019. Distribution and sources of polycyclic aromatic hydrocarbons (PAHs) in Meizhou Bay sewage outfall and the surrounding ocean area. Meteorol. Environ. Res.; Cranston 10, 3, (Jun 2019), 77–80,83. http://doi.org/10.19547/j.issn2152-3940.2019.03.015.

Csuros, M., Csuros, C., 2002. Environmental sampling and analysis for metals. Lewis, Boca Raton.

Cukrov, N., Franciskovic-Bilinski, S., Hlaca, B., Barisic, D., 2011. A recent history of metal accumulation in the sediments of Rijeka harbor, Adriatic Sea. Croatia. Mar Pollut Bull. 62 (1), 154–167.

Feng, H., Jiang, H., Gao, W., Weinstein, M.P., Zhang, Q., Zhang, W., Yuet, L., 2011. Metal contamination in sediments of the western Bohai Bay and adjacent estuaries. China. J Environ Manage. 92, 1185–1197.

Fillmann, G., Readman, J.W., Tolosa, I., Bartocci, J., Villeneuve, J.P., Cattini, C., Mee, L. D., 2002. Persistent organochlorine residues insediments from Black Sea. Mar. Pollut. Bull. 44, 122–133.

Folk, R.L., 1974. Petrology of Sedimentary Rocks. Hemphill's, Austin, TX, USA, p. 182.

Gedik, K., Boran, M., 2013. Assessment of metal accumulation and ecological risk around Rize Harbor, Turkey (southeast black sea) affected by copper ore loading operations by using different sediment indexes. Bull Environ. Contam. Toxicol. 90, 2, 176–181. http://doi.org/10.1007/s00128-012-0894-2.

Gedik, K., Terzi, E., Yesilcicek, T., 2018. Biomonitoring of metal(oid)s in mining-affected Borcka Dam Lake coupled with public health outcomes. Hum. Ecolog. Risk Assess.: Int. J. 24 (8), 2247–2264. https://doi.org/10.1080/10807039.2018.1443390.

Hakanson, L., 1980. Ecological risk index for aquatic pollution control, a sedimetological approach. Water Res. 14, 975–1001. https://doi.org/10.1016/0043-1354(80)90143-8.

Huang, X.D., Olmez, I., Aras, N.K., Gordon, G.E., 1994. Emissions of traceelements from motor-vehicles: potential marker elements and source composition profile. Atmos. Environ. 28, 1385–1391.

Jackson, M., 1958. Soil Chemical Analysis. Prentice-Hall Inc, New Jersey, USA, p. 498.

Jones, K.C., de Voogt, P., 1999. Persistent Organic Pollutants (POPs): State of the Science. Environ. Pollut. 100, 209–221. https://doi.org/10.1016/S0269-7491(99)00098-6.

Karakoc, F.T., Tolun, L., Henkelmann, B., Klimm,C., Okay, O., Schramm, K.W., 2002. Polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs) distributions in the Bay of Marmara sea: İzmit Bay, Environ. Pollut., 119, 3, 383–397, ISSN 0269-7491, https://doi.org/10.1016/S0269-7491(01)00341-4.

Keskin, C., Kaygusuz, O., 2010. Length-weight relationships of fishes in shallow waters of Erdek Bay (Sea of Marmara, Turkey). European Journal of Biology. Cilt 69, Sayı 2, Sayfalar 87–94.

Lianfeng, W., Jiefang, D., Qiao, Y., Xinyi, L., 2010. Geoaccumulation index and enrichment factor to assess heavy metal contamination in estuarine intertidal sediments and their adjacent arable soils in Dalian, Northeastern China. 2010 4th International Conference on Bioinformatics and Biomedical Engineering (iCBBE), 18–20 June 2010, Chengdu, China.

Long, E.R., Macdonald, D.D., Smith, S.L., Calder, F.D., 1995. Incidence of adverse biological effects within ranges of chemical concentrations in marine and estuarine sediments. Environ. Manage. 19, 81–97.

MacDonald, D., Ingersoll, C., Berger, T., 2000. Development and Evaluation of Consensus-Based Sediment Quality Guidelines for Freshwater Ecosystems. Arch. Environ. Contam. Toxicol. 39, 20–31. https://doi.org/10.1007/s002440010075.

Morillo, J., Usero, J., Gracia, I., 2004. Heavy metal distribution in marine sediments from the southwest coast of Spain. Chemosphere 55, 431–442. https://doi.org/10.1016/j.chemosphere.2003.10.047.

Müller, G., 1979. Schwer metalle in den sedimentn des Rhiens-Verenderrungen seit. Umsechan 79, 778–783.

Ozkan, E.Y., 2012. A New Assessment of Heavy Metal Contaminations in an Eutrophicated Bay (Inner Izmir Bay, Turkey). Turkish J. Fisheries Aquatic Sci. 12, 135–147. https://doi.org/10.4194/1303-2712-v12_1_16.

Ozseker, K., Seyhan, K., Eruz, C., 2016. Ecological risk assessment and spatial distribution of heavy metals in sediment and pore water around Trabzon harbour, Turkey. Fresenius Environ. Bull., 25

Pekey, H., Karakaş, D., Ayberk, S., Tolun, L., Bakoğlu, M., 2004. Ecological risk assessment using trace elements from surface sediments of İzmit Bay (Northeastern Marmara Sea) Turkey, Mar. Pollut. Bull., 48, 9–10, 946–953, https://doi.org/10.1016/j.marpolbul.2003.11.023.

Perin, G., Bonardi, M., Fabris, R., et al., 1997. Heavy metal pollution in central Venice Lagoon bottom sediments: Evaluation of the metal bioavailability by geochemical speciation procedure. Environ. Tech. 18, 593–604. https://doi.org/10.1080/09593331808616577.

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

Schulz, D.E., Petrick, G., Duinker, J.C., 1989. Complete characterisation of polychlorinated biphenyl congeners in commercial Aroclor and Clophen mixtures by multidimensional gas chromatography–electron capture detection. Environ. Sci. Technol. 23, 852–859.

Tang, C.W.Y., Ip, C.C.M., Zhang, G., Shin, P.K.S., Qian, P.Y., Li, X.D., 2008. The spatial and temporal distribution of heavy metals in sediments of Victoria Harbour, Hong Kong. Mar. Pollut. Bull. 57, 816–825.

Taylor, S.R., 1972. Abundance of chemical elements in the continental crust: A new table. Geochim. Cosmochim. Acta 28, 1273–1286. https://doi.org/10.1016/0016-7037(64)90129-2.

TUIK (Turkish Statistical Institute). 2018a. Municipal Wastewater Statistics. Amount of wastewater discharged from municipal sewerage by receiving bodies. TURKEY.

TUIK (Turkish Statistical Institute). 2018b. Turkey Fisheries Statistics. TURKEY.

TUIK (Turkish Statistical Institute). 2019a. Population Statistics. Population of provinces by years. TURKEY.

TUIK (Turkish Statistical Institute). 2019b. Agricultural land statistics. TURKEY.

Turekian, K.K., Wedepohl, D.H., 1961. Distribution of the elements in some major units of the earth's crust. Bull. Geolog. Soc. Am. 72, 175–192. https://doi.org/10.1130/0016-7606(1961)72[175:DOTEIS]2.0.CO;2.

US EPA (US Environmental Protection Agency). 1996. Acid digestion of sediments, sludges, and soils. EPA Method 3050B. Washington, DC, USA.

Yilmaz, A., Yanar, A., Alkan, E., 2018. Review of Heavy Metal Accumulation in Aquatic Environment of Northern East Mediterrenean Sea Part II: Some Non-Essential Metals. Pollution 4 (1), 143–181. https://doi.org/10.22059/poll.2017.236121.287.