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Original Research

Assessment of Arsenic and Heavy Metal Pollution in Surface Sediments of the Ergene River, Turkey

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Abstract

20 surface sediments recovered from the Ergene River have been analyzed in order to assess the extent of anthropogenic inputs into the river. The results of enrichment factor (EF), contamination factor (CF), and pollution load index (PLI) reveal that the sediments of the Ergene River were not polluted with Cu, Fe, Mn, and Ni, but were moderately polluted with As, Cr, Pb, V, and Zn. The highest CF and PLI of As, Cr, and V were observed near the industrial district of Çorlu. These CF and PLI values indicated anthropogenic influence caused by the input of untreated industrial wastewater and domestic sewage.

Keywords: sediment pollution, enrichment factor, heavy metals, Ergene River, Maritza River

Introduction

The Ergene River was used as drinking water for animals and agricultural irrigation 30 years ago. However, the rapid development of Edirne, Kırklareli and Tekirdağ cities in the past few decades has resulted in growing pressure on the local environment. On the other hand, the high industrial activities have basically concentrated in the upper part of the river basin especially in the last decade. The Ergene River, a major source of water, carries a pollution load from industrial plants, unnatural fertilizers used in agriculture, and urban wastewaters originating in the basin to the Maritza River [1-3]. Throughout the hydrological cycle, far less than 1% of pollutants remain dissolved in water, whereas over 99% are stored in sediments, which are the major sinks and carriers for contaminants in aquatic environments [4]. The River Ergene is the main tributary of the Maritza, joining the Maritza just before its confluence with the Aegean Sea and during transport to the sea suspended sediment with heavy metals, which have a high affinity for fine-grained particles, may settle and be deposited in the bottom of the Ergene sediments under favorable hydraulic conditions. The enrichment of heavy metal in the sediments can result from both anthropogenic activities and natural processions. Weathering of soils and rocks in drainage basins are the primary sources for the lithogenic contribution of heavy metals into the aquatic system [5-7]. The main anthropogenic sources of heavy metals pollution are mining and smelting operations, urban and industrial waste water, combustion of fossil fuels, processing and manufacturing industries, and waste disposal, including dumping, fertilizer, and pesticides in agricultural fields [8, 9]

According to the Ministry of the Environment and Forestry of Turkey (MEFT) approximately 2,037 industrial plants in the region are concentrated in Çorlu, Çerkezköy, Muratlı, and Lüleburgaz districts in the Ergene drainage area. As a consequence of the rapid industrialization, urbanization, and agricultural activities, environmental problems may have occurred in this basin. However, possible negative effects of these problems on Ergene sediment quality have not yet been comprehended. Several studies have recently been conducted in the Ergene, focusing mainly on

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water quality [1, 3, 10-12] and its impact on agricultural produce [13, 14]. There is almost no information available about metal contamination in the sediments of the Ergene and its tributaries. The aims of this study are to:

1) Determine the distribution of heavy metals in freshly deposited sediments of the Ergene and its tributaries
2) Assess the degree of heavy metal pollution by using enrichment factor, contamination factor, and pollution load index
3) Identify the bioavailability and ecological risk of these metals.

Study Area Description

The Ergene River is one of the last tributaries of the Maritza River. This river is 285 km long in the Thrace drainage basin, covering an area of 11,325 km^2 in north-western Turkey [1, 12]. The most important tributaries of the Ergene River are Çorlu, Paşaköy, Sulucak, Lüleburgaz, Teke, Ova, Sinanlı, Hayrabolu, and Basamaklar streams. The Ergene River originates in the Istranca Mountains of north-western Turkey, runs through the Thrace Basin, and receives pollution load from agriculture plus domestic and various industrial wastewaters (mainly tannery, textile, metal, automotive, electrical appliance, beverage, chemical, plastic, paper, wood, and food factories). While the Ergene is used for drinking water at its source, its water quality deteriorates and the water even loses its irrigation quality after passing through the polluted urban sites. The high industrial activities are basically concentrated in the upper part of the river basin in Çorlu, Çerkezköy, Muratlı, and Lüleburgaz districts. The 1.03 million population (based on the 2012 census) and 2,037 industrial plants located in the basin are considered major sources of pollution for the Ergene [15].

The climate of the Ergene basin is under the influence of Mediterranean, the Black Sea, and the Continent: the local topography and the distance from the seas are, however, a source of climatic diversity. The main climate types prevailing in the Thrace basin are hot and dry in summer, cold and rainy in winter and spring. The annual mean rainfall varied between 530 mm and 726 mm, with the lowest and the highest average temperature of 3.5ºC and 23.5ºC, respectively [15, 16]. Maximum flows occur from November through December, whereas minimum flows occur from July through September. The annual mean flow and precipitation of the Ergene are 28 m^3/sn and 665 mm, respectively [12].

The geology of the region is composed of various magmatic (tuff and andesite), metamorphic (gneiss, marble and

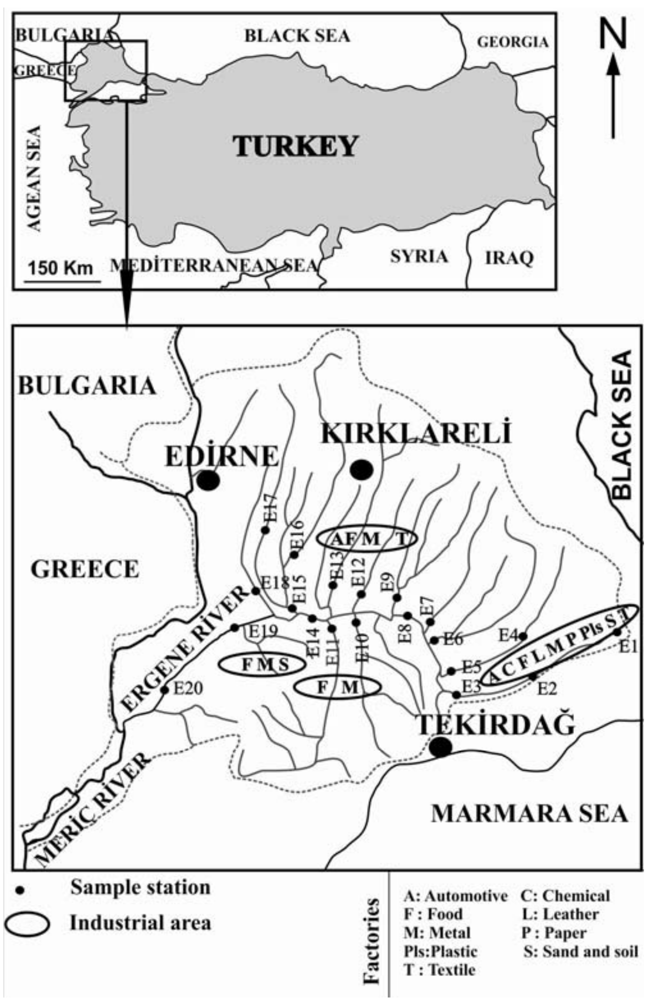

Fig. 1. Study area, industrial plants, and sample locations of the Ergene River.

mica schist), and sedimentary rocks (alluvium, gravelstone, sandstone, claystone, and shale). A part of the richest mineral belt of the continent consisting of Cu and Mo ore, coal, dolomite, marble, clay, and quartz sand deposits fall within the basin.

Materials and Methods

Sediment Sampling

20 freshly deposited bottom sediment samples were collected from the Ergene River and its tributaries with an ekman grab sampler during a 9-day period from 21-29 November 2012 (Fig. 1). The sampling locations were selected on the main river as well as its tributaries so that the sources of polluting metals in the drainage area could be delineated. Coordinates of the sampling points were recorded using GPS. The freshly deposited sediment samples were taken from the upper 1 cm of the surface sediment and placed in polyethylene bags. The samples were put in cooling boxes at 4ºC during transportation to the laboratory and stored in a deep freeze before the drying and grinding. The bulk sediment samples were divided into three sub-samples for the determinations of total organic carbon, grain size and heavy metals analysis.

Total Organic Carbon Analysis

Total organic carbon was determined using Walkley-Black method [17]. The analysis is based on the exothermic heating and oxidation of organic matter with potassium dichromate and concentrated sulfuric acid, followed by back-titration with ferrous ammonium sulfate using phenylamine as an indicator.

Grain Size Analysis

Gravel and sand were determined in a representative portion of each sample using sieving techniques. 0.5% of sodium hexametaphosphate was added to the samples, aiming to make the sediments disperse completely. The fine fraction (silt and clay) of river sediments was determined in Micromeritics Sedigraph 5100, after the removal of sand (>63 lm) by wet sieving.

Heavy Metals Analysis

Approximately 0.2 g was analyzed for Al, As, Cr, Cu, Fe, Mn, Ni, Pb, V, and Zn with inductively coupled plasma-mass spectrometer (ICP-MS) after total digestion. Sample solutions were analyzed for metals of interest using Agilent 7500 ICP-MS (Tokyo, Japan) at the Department of Geological Engineering laboratory of Mersin University, Turkey. The accuracy of analytical procedures for total metal determinations was checked using the reference material NIST SRM 2710 (Montana soil). Replicate analysis of NIST SRM 2710 showed good accuracy, with recovery rates for metals between 93% and 103% (Table 1).

Table 1. Accuracy of ICP-MS analyses used in this study as determined by analysis of NIST SRM 2710 (Montana soil) reference material.

Element	NİST certified value ($mg \cdot kg^{-1}$)	Measured value (This study, $mg \cdot kg^{-1}$)	Recovery %
Al	64,400±8,000	67,000	103
As	626±38	666	100
Cr	39*	38	97
Cu	2950±130	3,082	100
Fe	33,800±1,000	34,400	101
Ni	14.3±1	13.6	96
Pb	5,532±80	5,421	99
V	76.6±2.3	80.3	102
Zn	6,952±91	6,358	93

*noncertified values

Result and Discussion

General Characteristic of Ergene River Sediments

Grain size composition and total organic carbon (TOC) contents were determined in order to get general characteristics of freshly deposited sediment samples in the Ergene River and its tributaries. It is well established that grain size and TOC contents are significant factors influencing the distribution of trace metals [18, 19]. For these reasons, grain size, TOC, and statistical parameters such as minimum, maximum, mean, and median values were determined and shown in Table 2.

The content of the four fractions varies significantly in the region. The average grain size of sediments in the river was 6.24 Φ, corresponding to silt. The relative percentage of grain size in the sediments of this river were within the ranges (30.4-74.9%) for clay, (9.8-37.9%) for silt, (0.7-57.6%) for sand, and (0-4.2%) for gravel. This result indicated that the studied sediments were predominantly composed of clay with an average of 55.75%, followed by silt (average 24.24%) and sand (average 18.65%). The least important constituent was gravel (average 1.36%). A microscopic examination of gravel and sand fractions from the Ergene River indicated the presence of calcite, muscovite, amphibole, plagioclase quartz, and rock fragments. On the basis of grain size analysis, it was easy to conclude that the Ergene River sediments were richest in clay. This fact was expected since the Ergene River flows through the Thrace Basin, which is rich in clay [20].

Total organic carbon (TOC) contents of the sediment samples in the study area ranged from 1 to 6.8%, averaging 4.4%. The highest values (> 5 dry wt. %) were found in stations E1, E2, E3, E7, E8, E13, E14, and E17, where abundant plants leaves and wood fragments were present.

Table 2. Statistical summary of grain size and organic matter values in the Ergene River sediments.

Sample	Gravel %	Sand %	Silt %	Clay %	TOC %
E1	1.94	32.90	14.20	50.95	5.35
E2	0.66	10.91	37.92	50.51	6.68
E3	0.82	3.65	26.86	68.67	6.80
E4	0.01	51.17	13.47	35.35	0.96
E5	0.07	33.61	19.25	47.07	2.83
E6	0.55	27.35	20.77	51.34	3.54
E7	2.17	57.65	9.81	30.38	5.78
E8	2.69	6.19	19.77	71.35	6.58
E9	0.55	18.64	31.36	49.46	3.28
E10	0.91	5.52	21.90	71.68	2.51
E11	2.64	16.58	19.15	61.63	4.23
E12	0.68	35.35	24.12	39.85	3.80
E13	3.44	32.71	23.11	40.74	5.81
E14	4.19	8.22	32.32	55.27	6.58
E15	0.78	2.03	36.64	60.55	3.46
E16	0.22	23.83	35.24	40.71	1.80
E17	0.23	1.34	23.53	74.91	5.40
E18	4.19	0.72	20.35	74.74	4.27
E19	0.09	3.60	27.27	69.05	4.22
E20	0.31	0.98	27.83	70.87	4.80
Minimum	0.01	0.72	9.81	30.38	0.96
Maximum	4.19	57.65	37.92	74.91	6.80
Mean	1.36	18.65	24.24	55.75	4.43
Median	0.73	13.75	23.32	53.31	4.25

Metal Concentrations in Ergene River Bed Sediments

Concentration values and basic statistics of the measured heavy metals with shale average [21] are shown in Table 3. The total concentrations (mg·kg^{-1}) varied from 40,610 to 91,340 (average 72,848±11,730) for Al, 11 to 52 (average 25±10) for As, 95 to 304 (average 160±49) for Cr, 23 to 203 (average 65±46) for Cu, 13,950 to 39,560 (average 26,935±7,373) for Fe, 133 to 865 (average 356±167) for Mn, 19 to 155 (average 64±35) for Ni, 77 to 145 (average 99±15) for Pb, 258 to 966 (average 486±177) for V, and 74 to 385 (average 177±101) for Zn. A comparison of metal concentrations in the sediment with the average shale is generally taken as a quick and practical method of metals enrichment [7]. This comparison revealed that most of the samples from the Ergene River were polluted with As, Cr, Pb, V, and Zn. On the contrary, the samples studied had Al, Cu (except stations E2, E3, E6, E8, and E14), Fe, Mn, and Ni values similar to those for average shale, which indicated that there were no major sources of pollution for these elements in the Ergene River. The station near the industrial plants (E2) in the Çorlu Stream had the highest values of As (52 mg/kg), Cr (304 mg/kg), and V (966 mg/kg). This area is affected by the wastewater and water-runoff from local industrial and agriculture activities. This is also supported by the local occurrence of the highest and second highest Corg values (> 6.80 and 6.68%) at stations E2 and E3 in the Çorlu Stream. The main anthropogenic sources of Arsenic, Cr, and V for the study area can be listed as follows: arsenic is used in pigments, pesticides, and herbicides, and in alloys with lead and copper; chromium is used for Cr alloys, oxidizing agents, Cr-plating, corrosion inhibitors, ceramics, glass, and pigment manufacturing in the textile industries, and leather tanning companies (which are mostly concentrated in the study area). The most common use of vanadium is in alloys for making rust-resistant steel used in manufacturing tools, engines, and gears. These elements point to the trace elements from iron and steel industries in the area, which use coal with a high content of As and V as fuel [23, 24].

The variation in the Pb values measured in the study area showed that the Ergene River is potentially Pb-enriched (Table 3). Domestic and industrial effluents and atmospheric deposition may be the major anthropogenic sources of the observed high level of Pb. This element is used in industry in plumbing (pipes), solder, gasoline (significantly curtailed), drying agent for oils, glass, plumber's cement, covering of steel to prevent rust, batteries, as a pigment in paint (significantly curtailed), hair dye, and as a pigment in plastics caulking and cable sheathing, which are mostly concentrated in the study area[15].

A relatively high Zn concentration was observed at sites E2 (334 mg·kg^{-1}), E8 (385 mg·kg^{-1}), E14 (350 mg·kg^{-1}), and E20 (374 mg·kg^{-1}). This distribution might be related to nearby industrial and residential activities. Anthropogenic sources of Zn are significant, arising mainly from industrial activities such as mining, coal, and waste combustion and steel processing. A major use of Zn is as an anti-corrosion coating. It is also used as a constituent of brass, as a white pigment in paint and rubber products, and in the manufacture of dry batteries. Such activities are mostly concentrated in the Thrace Basin [15]. A large amount of urban sewage and industrial wastewater is discharged into the river, which might explain the high level of Zn accumulation in sediments.

As, Cr, Cu, Pb, and Zn values obtained from the current study also were compared with those from other rivers around the world and within Turkey itself (Table 4). The levels of As in the river sediments of the study area were found to be more polluted than the Tigris. The average concentrations of Cr in the Ergene river sediments were higher than those of other rivers such as the Po, the Danube, the Achankovil the Odiel and the Tigris rivers, and significantly lower than the Nilüfer River. By comparison, our mean values for Cu and Zn were lower than or comparable to

Table 3. Select element concentrations and basic statistical parameters in the sediment samples of the Ergene River and its comparison with shale average [21], effect range low (ERL), and effect range medium (ERM) values [22].

Sample	Al	As	Cr	Cu	Fe	Mn	Ni	Pb	V	Zn
	mg·kg^{-1}									
E1	76760	37	221	33	22900	224	34	99	716	93
E2	81710	52	304	98	35470	458	60	106	966	334
E3	77280	32	190	103	32640	235	77	96	637	192
E4	63090	14	122	26	17730	318	35	94	346	74
E5	71290	36	218	48	25290	430	65	124	705	119
E6	59260	31	168	203	21070	432	54	91	539	139
E7	40610	27	174	38	14350	133	51	77	425	94
E8	72390	20	149	138	29570	234	85	101	390	385
E9	66120	23	142	33	22090	211	59	85	380	106
E10	83370	13	98	48	39560	519	155	80	306	162
E11	71170	25	162	40	31390	469	124	88	440	109
E12	65690	17	115	54	22570	246	65	110	318	189
E13	60880	13	101	23	13950	188	19	91	271	126
E14	70920	11	95	121	28720	341	87	99	258	350
E15	79610	31	171	63	32950	332	108	97	551	170
E16	74130	30	169	23	25090	431	23	96	563	84
E17	91340	30	163	51	34260	207	44	103	559	192
E18	89580	28	157	43	35780	865	68	103	545	127
E19	77410	22	164	37	21230	359	27	98	450	128
E20	84340	16	120	75	32080	492	48	145	361	374
Minimum	40610	11	95	23	13950	133	19	77	258	74
Maximum	91340	52	304	203	39560	865	155	145	966	385
Mean	72848	25	160	65	26935	356	64	99	486	177
Median	73260	26	163	48	27005	337	60	98	445	134
Shale [21]	80000	6.6	100	57	47000	850	95	20	130	80
ERL [22]		8.2	81	34	-	-	20.9	46.7	-	150
PEL [39]		17	90	197	-	-	36	91.3	-	315
ERM [22]		70	370	270	-	-	51.6	218	-	410

Table 4. Mean values of heavy metals and As concentration in different rivers of the world (mg·kg^{-1}).

	As	Cr	Cu	Pb	Zn	Reference
Ergene River, Turkey	25	160	65	99	177	Present study
Nilüfer River, Turkey	-	462	113	33	1117	[6]
Tigris River, Turkey	6	136	1258	380	510	[25]
Po River, Italy	-	-	77	53	303	[19]
Danube River, Serbia		54	78	68	343	[26]
Achankovil River, India	-	-	224	72	415	[27]
Odiel River, Spain	-	80	1282	649	954	[28]

those of other studies indicated in Table 4. The mean level of Pb of the study area was found to be more polluted than those of the Nilüfer, the Po, the Danube and the Achankovil rivers, whereas Pb contents of the Ergene sediment were lower than those of the Tigris and Odiel rivers (Table 4). The above comparisons suggest that river sediments in the Ergene show significant As, Cr, and Pb pollution.

Environmental Quality Assessment of Recently Deposited Sediments from the Ergene River

Anthropogenic Arsenic and Heavy Metal Accumulation in Sediments

The enrichment factor (EF) is used to assess heavy metal contamination in the sediments of the Ergene River. EF is a common method for estimating the anthropogenic impact on sediments by calculating differentiates between the metals originating from human activities and those from natural provenance. Heavy metal concentrations are generally normalized by conservative elements, such as Al, Fe, Li, and Sc [6, 29-31]. In this study, we selected Al as a conservative tracer. This element is a major constituent of clay minerals and has been used successfully by several researchers [6, 8, 32]. The EF is calculated by the following equation:

$$EF = \frac{(Mx/Alx)_{Sample}}{(Mx/Alx)_{Shale}}$$

...where (*Mx/Alx*)*Sample* and (*Mx/Alx*)*Shale* are the concentration ratios of metals to Al in the investigated samples and in the background or reference materials. There were no data about background values for the investigated Ergene sediments and soil of close areas. Thus, we adopted the geochemical average shale values for EF calculation. Shale values are 80,000 mg·kg^{-1} for Al, 6.6 mg·kg^{-1} for As, 100 mg·kg^{-1} for Cr, 57 mg·kg^{-1} for Cu, 47,000 mg·kg^{-1} for Fe, 850 mg·kg^{-1} for Mn, 95 mg·kg^{-1} for Ni, 20 mg·kg^{-1} for Pb, 130 mg·kg^{-1} for V, and 80 mg·kg^{-1} for Zn [21]. EF values were interpreted as the levels of metal pollution categorized by Sutherland [9]; EF≤2 suggests deficiency of minimal enrichment, EF: 2-5 moderate enrichment, EF: 5-20 significant enrichment, EF: 20-40 very high enrichment, and EF>40: extremely high enrichment. Enrichment factor values were calculated to determine if the levels of metals in the sediments of the Ergene River were of anthropogenic origin. EF value of < 2 indicates that heavy metal is entirely provided from crustal contribution in sediment, while values greater than 2 are considered to indicate an important proportion of non-crustal materials delivered from either natural processes and/or anthropogenic influences [9]. EF of arsenic and heavy metals with statistical parameters in the studied sediments are shown in Table 5. The result indicated that the mean EF values of Cu, Fe, Mn, and Ni were lower than 2, showing a minimal anthropogenic impact on the heavy metals concentration level in the Ergene river sediments. For this reason, it could be deduced that Cu, Fe, Mn, and Ni contamination in the studied river might entirely come from crustal material according to the scale suggested by Sutherland [9]. Contamination from these four heavy metals should therefore not pose a current major concern. On the other hand, as shown in Table 5, the enrichment factors of As (except E10), Pb, and V are greater than 2 in all stations, and of Zn in most of the stations and Cr for six samples, indicating a moderate to significant contamination of the area by those metals (Table 5). The mean EF values of the metals and arsenic exhibited the following sequence: Pb (5.5) > As (4.3) > V (4.2) > Zn (2.4) > Cr (1.8) > Cu (1.3) > Ni (0.8) > Fe (0.6) > Mn (0.5). Pb had the highest EF values among the 10 metals studied. The EF values for Pb were greater than three (e.g., 3.9-7.6) which indicates a high degree of Pb contamination. As had the second highest EF values (e.g., 1.8-8) among the metals studied. The high mean EF values (EF>2) indicate that the source of accumulation of As, Pb, V, and Zn originated mainly from anthropogenic contributions.

Assessment of Arsenic and Heavy Metal Using Contamination Factor (CF)

CF is a useful indicator reflecting the status and the degree of environmental contamination [33] and has been widely used by many researchers to evaluate anthropogenic influences of heavy metals in sediments [33-35]. The contamination degree of heavy metals in the Ergene River sediments was also assessed on the basis of the contamination factor, which was calculated as the ratio between the sediment metal content at a given station and average shale values of the metal [21]. The contamination factor is measured by the following equation [36].

$$CF = \frac{Metal\ concentration\ in\ sediment}{World\ shale\ average\ for\ the\ metal}$$

Statistical parameters for contamination factor of the surficial river-bed sediments along the Ergene River are presented in Table 6. As shown in Table 6, sediments in the Ergene River showed a wide range of metal enrichment. CF values were interpreted as suggested by Hakanson [36], where: CF < 1 indicates low contamination; 1 < CF < 3 is moderate contamination; 3 < CF < 6 is considerable contamination; and CF > 6 is very high contamination. In general, the mean values showed considerable contamination for As, Pb, and V, moderate contamination for Cr, Cu, and Zn, and no enrichment for Al, Fe, Mn, and Ni according to Hakanson's CF classification [36]. The highest and second highest CF of As (7.8 and 5.6), Cr (3.0 and 2.2), and V (7.4 and 5.5) were found in the sediments collected from stations E1 and E2 in the Çorlu Stream, which collects huge amounts of textile and leather industries, and also wastewaters originating from various other industries and municipalities [1, 15]. Therefore, this river highlights the major contribution of the anthropogenic origin of those elements. On the basis of the mean values of CF, the degree of heavy metal and arsenic contamination in the surface sediments of the Ergene yielded the following sequence: Pb (5) > As (3.8)

Table 5. Select element enrichment factors (EF) and basic statistical parameters in the sediments of the Ergene River.

Sample	Enrichment factor								
	As	Cr	Cu	Fe	Mn	Ni	Pb	V	Zn
E1	5.8	2.3	0.6	0.5	0.3	0.4	5.1	5.7	1.2
E2	7.7	3.0	1.7	0.7	0.5	0.6	5.2	7.3	4.1
E3	5.0	2.0	1.9	0.7	0.3	0.8	5.0	5.1	2.5
E4	2.6	1.6	0.6	0.5	0.5	0.5	5.9	3.4	1.2
E5	6.1	2.4	1.0	0.6	0.6	0.8	7.0	6.1	1.7
E6	6.4	2.3	4.8	0.6	0.7	0.8	6.2	5.6	2.4
E7	8.0	3.4	1.3	0.6	0.3	1.1	7.6	6.4	2.3
E8	3.4	1.7	2.7	0.7	0.3	1.0	5.6	3.3	5.3
E9	4.1	1.7	0.7	0.6	0.3	0.8	5.1	3.5	1.6
E10	1.8	0.9	0.8	0.8	0.6	1.6	3.9	2.3	1.9
E11	4.2	1.8	0.8	0.8	0.6	1.5	4.9	3.8	1.5
E12	3.1	1.4	1.1	0.6	0.4	0.8	6.7	3.0	2.9
E13	2.6	1.3	0.5	0.4	0.3	0.3	6.0	2.7	2.1
E14	2.1	1.1	2.4	0.7	0.5	1.0	5.6	2.2	4.9
E15	4.7	1.7	1.1	0.7	0.4	1.1	4.9	4.3	2.1
E16	5.0	1.8	0.4	0.6	0.5	0.3	5.2	4.7	1.1
E17	3.9	1.4	0.8	0.6	0.2	0.4	4.5	3.8	2.1
E18	3.7	1.4	0.7	0.7	0.9	0.6	4.6	3.7	1.4
E19	3.4	1.7	0.7	0.5	0.4	0.3	5.0	3.6	1.7
E20	2.3	1.1	1.2	0.6	0.5	0.5	6.9	2.6	4.4
Minimum	1.8	0.9	0.4	0.4	0.2	0.3	3.9	2.2	1.1
Maximum	8.0	3.4	4.8	0.8	0.9	1.6	7.6	7.3	5.3
Mean	4.3	1.8	1.3	0.6	0.5	0.8	5.5	4.2	2.4
Median	4.0	1.7	0.9	0.6	0.5	0.8	5.2	3.8	2.1

> V (3.7) > Zn (2.2) > Cr (1.6) > Cu (1.1) > Al (0.9) > Ni (0.7) > Fe (0.6) > Mn (0.4). The results were consistent with enrichment factor values.

Assessment of Sediment Contamination by Calculating the Pollution Load Index (PLI)

To evaluate sediment environmental quality, an integrated pollution load index (PLI) of 10 elements was calculated according to Tomlinson et al. [37]. The PLI has been determined as the nth root of the product of the n CF:

$$PLI = (CF_1 \times CF_2 \times CF_3 \times CF_4 \times \ldots\ldots \times CF_n)^{1/n}$$

...where *CF* is the contamination factor and n is the number of heavy metals considered. The PLI gives an evaluation of general toxicity status for a sample and also it is a result of the contribution of 10 elements. The calculated PLI values and statistical parameters of the freshly deposited sediments from the Ergene are shown in Table 6. The PLI value in the studied samples varied from 0.81 to 2.11 with an average of 1.38. PLI values were interpreted as suggested by Tomlinson et al. [37], where A PLI value greater than 1 indicates that the site is polluted, whereas a PLI less or equal to 1 indicates no pollution. Present sediments were moderately polluted, since PLI of most samples was higher than one (Table 6). According to the mean PLI value; the Ergene River sediments were moderately polluted. The highest PLI value in the studied samples was observed at E2 in Çorlu Stream with a value of 2.11, indicating that the sediment of E2 was highly polluted (2 < PLI ≤ 3), while most of other sites where PLI was between 1 and 2 must be classified as moderately polluted (Table 6). The PLI were found to be low (PLI<1) in three stations, indicating that the sediments of E4, E7, and E13 weren't affected by pollution. An overall higher PLI value (PLI>1.5) can be ascribed to the influence of external discrete sources like sewage, industrial, and agricultural runoff.

Toxicity Assessment-Based ERL (Effect Range Low), PEL (Probable effects level), and ERM (Effect Range Medium)

Because of the lack of Turkish regulations, we compared metal concentrations in our sediment samples to various marine-sediment-quality guidelines [38]. It is important to determine whether the concentrations of arsenic and heavy metals found in the sediments pose a threat to aquatic life. In this study, arsenic and heavy metal concentrations in the assessed sediment samples were compared with sediment quality guidelines (SQGs) such as ERL, PEL, and ERM values [22, 38]. Chemical concentrations corresponding to the 10^{th} and 50^{th} percentiles of adverse biological effects are called ERL and ERM, respectively. The ERL represent chemical concentrations below which adverse biological effects were rarely observed, while the ERM represent concentrations above which effects were more frequently observed. The ERL, PEL, and ERM values for As, Cr, Cu, Pb, Ni, and Zn as reported by Long et al. [22] and MacDonald et al. [39] are presented in Table 3.

Sediment concentration results showed that 60% of Ni values in the Ergene sediments exceeded its ERM value of NOAA. Some of the sediment sample metals concentrations were between ERL and ERM values for As (100%), Cr (100%), Cu (75%), Ni (35%), Pb (100%), and Zn (45%). We concluded that Ni can cause extreme or midrange to extreme effects. Concentrations of Cr, As, and Pb are near PEL, while Cu and Zn have concentrations around ERL. These metals could more likely be toxic to benthic fauna and produce adverse effects on the entire ecosystem.

Conclusion

The Ergene River sediment is subjected to varying degrees of pollution caused by the input of numerous untreated or partially treated wastewaters from industrial,

Table 6. Select element contamination factors (CF), pollution load index (PLI), and basic statistical parameters for sediments of all sites studied in the Ergene River.

Sample	Contamination Factor										PLI
	Al	As	Cr	Cu	Fe	Mn	Ni	Pb	V	Zn	
E1	1.0	5.6	2.2	0.6	0.5	0.3	0.4	4.9	5.5	1.2	1.26
E2	1.0	7.8	3.0	1.7	0.8	0.5	0.6	5.3	7.4	4.2	2.11
E3	1.0	4.8	1.9	1.8	0.7	0.3	0.8	4.8	4.9	2.4	1.64
E4	0.8	2.1	1.2	0.4	0.4	0.4	0.4	4.7	2.7	0.9	0.94
E5	0.9	5.5	2.2	0.9	0.5	0.5	0.7	6.2	5.4	1.5	1.56
E6	0.7	4.7	1.7	3.6	0.4	0.5	0.6	4.6	4.1	1.7	1.57
E7	0.5	4.1	1.7	0.7	0.3	0.2	0.5	3.9	3.3	1.2	0.99
E8	0.9	3.1	1.5	2.4	0.6	0.3	0.9	5.0	3.0	4.8	1.60
E9	0.8	3.4	1.4	0.6	0.5	0.2	0.6	4.2	2.9	1.3	1.11
E10	1.0	1.9	1.0	0.8	0.8	0.6	1.6	4.0	2.4	2.0	1.39
E11	0.9	3.7	1.6	0.7	0.7	0.6	1.3	4.4	3.4	1.4	1.43
E12	0.8	2.5	1.1	0.9	0.5	0.3	0.7	5.5	2.4	2.4	1.21
E13	0.8	1.9	1.0	0.4	0.3	0.2	0.2	4.5	2.1	1.6	0.81
E14	0.9	1.7	1.0	2.1	0.6	0.4	0.9	4.9	2.0	4.4	1.41
E15	1.0	4.7	1.7	1.1	0.7	0.4	1.1	4.9	4.2	2.1	1.61
E16	0.9	4.6	1.7	0.4	0.5	0.5	0.2	4.8	4.3	1.0	1.15
E17	1.1	4.5	1.6	0.9	0.7	0.2	0.5	5.2	4.3	2.4	1.42
E18	1.1	4.2	1.6	0.8	0.8	1.0	0.7	5.2	4.2	1.6	1.59
E19	1.0	3.3	1.6	0.6	0.5	0.4	0.3	4.9	3.5	1.6	1.17
E20	1.1	2.4	1.2	1.3	0.7	0.6	0.5	7.2	2.8	4.7	1.54
Minimum	0.50	1.7	1.0	0.4	0.3	0.2	0.2	3.9	2.0	0.9	0.81
Maximum	1.10	7.8	3.0	3.6	0.8	1.0	1.6	7.2	7.4	4.8	2.11
Mean	0.91	3.8	1.6	1.1	0.6	0.4	0.7	5.0	3.7	2.2	1.38
Median	0.90	3.9	1.6	0.9	0.6	0.4	0.6	4.9	3.5	1.7	1.42

domestic, and agricultural activities. The impact of anthropogenic heavy metal and arsenic pollution in the Ergene sediments was evaluated using enrichment factor (EF), contamination factor (CF), pollution load index (PLI), and ecological risk. The largest pollution values were found in the upper part of the Ergene River with a decrease toward the Maritza River. The mean CF and EF values of heavy metal and arsenic decreased in the order of Pb > As > V > Zn > Cr > Cu > Al > Ni > Fe > Mn in river sediments. The results of EF and CF revealed that sediments of the Ergene River were highly enriched in As, Pb, V, and Zn compared to their shale levels, whereas Al, Fe, Mn, and Ni were generally within the natural levels. The highest CF and PLI of As, Cr, and V values were observed near the industrial district of Çorlu (sampling site E2). These CF and PLI values indicated anthropogenic influence caused by the input of untreated industrial wastewater and domestic sewage (station E2). The sediment's heavy metal (Cr, Cu, Ni, Pb, and Zn) and arsenic content was evaluated in relation to SQGs to assess their pollution level and toxicological significance. The results indicated that Ni (60% of the samples) appeared to be the pollutant with the greatest potential to cause adverse effects on biota, while As, Cr, Cu (75%), Pb, and Zn (45%) may adversely affect some benthic species occasionally, as suggested by the sediment quality guidelines.

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