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Original Research

Evaluation of Contamination by Selected Elements in a Turkish Port

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Abstract

Enrichment factor and geoaccumulation index analyses revealed significant anthropogenic pollution by Al, As, Cu, La, Mo, Pb, Se, and Zn in the surface sediments of cores from Ambarlı Port Area, whereas Ba, Fe, Ni, Sr in all sediments could be considered to be derived from pollution-free sources. Pb^{210} dating shows deposition in the upper 2 cm between 1979 and 2009, indicating anthropogenic contamination of Al, As, Cu, La, Mo, Pb, Se, and Zn in sediments. As, Cr, Cu, Pb, and Zn in the upper parts may occasionally have reached toxic biological levels. The toxicity order for benthic organisms was Ni>Cr>As>Zn>Cu>Pb.

Keywords: metals, sediment contamination, Ambarlı Port, Marmara Sea

Introduction

When metals are released into marine environment, they soon are transferred to and eventually settle in the sediment phase by adsorption on the surface of suspended particulate matter [1]. Their occurrence in water and sediment thence indicates the presence of natural or anthropogenic sources. Over the past century, anthropogenic metals have been discharged into marine environment due to rapid industrialization [2, 3]. Discharge of urban and industrial wastewater, mining and smelting operations, combustion of fossil fuels, processing and manufacturing industries, and waste disposal (including dumping, shipping, and boating activities), etc., are primary anthropogenic sources of pollution [4, 5].

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One of the most useful approaches to establishing the effects of anthropogenic and natural processes on the depositional environment is the analysis of marine sediments. The determination of total sediment concentrations of metals has been used extensively for purposes of pollution monitoring [3, 6-8]. Furthermore, the vertical concentration profile of metals in sediment cores can be used to reveal the degree of metal pollution history in recent decades [9, 10]. Since 1960, the Ambarlı Port area has faced environmental pollution due to ever increasing urban and industrial development. Possible major sources of pollution in the port area include port activities, thermal power plant emissions, fuel oil tanker terminal waste, and domestic wastewater of Avcılar and Küçükçekmece provinces, which was directly discharged without any treatment into the Marmara Sea before 2004. Although several surface sediment contamination studies have been conducted recently in the Marmara, these studies focus mainly on metals [3, 7, 8] and organic pollution [11] in other areas. There is almost no information available for metal contamination in Ambarlı Port Area core sediments.

The aim of this study is to contribute to a better understanding of the pollution history of the Ambarlı Port Area in the Marmara Sea and to assess sediment quality and ecotoxicological risk using different sediment quality guidelines (SQGs), geoaccumulation index (I_{geo}), and enrichments factors (EF). Compatibility with sediment quality guidelines aids in protecting the aquatic biota from the deleterious effects associated with sediment-bound contaminants, to rank and/or prioritize contaminated areas or chemicals of concern for further investigation, and to evaluate the spatial patterns of sediment contamination and direct monitoring programs [12]. On the other hand, EF [13, 14] and I_{geo} [15] values of marine sediments help to identify anthropogenic influences and the levels of environmental contamination with respect to reference values, respectively.

Site Description

Ambarlı Port is 34 km away from the city center of İstanbul and located on the north shore of the Sea of Marmara (Fig. 1). It is a so-called the "port-terminal" complex, consisting of seven separate shipping terminals; each owned by different entrepreneurs and served since 1989. A consortium-type management was formed to organize and manage the infra-structure of the complex. Each terminal, however, is independent from others. Several are engaged in container the business, whereas the remaining ones are in bulk, ro/ro, and general cargo. Ambarlı Port, since the first day of operation, has served traffic-wise not only the Istanbul metropolitan area but also Thrace and the Black Sea countries. The Port complex handled 2,686,000 TEU containers, 2,763,000 metric tons of general cargo, 259,000 liquid ton cargo, and 223,000 numbers of conveyances in 2011. The study area is potentially affected by any possible shipping casualty to occur within the Sea of Marmara. One of the most serious shipping casualties, which gave rise to heavy oil pollution, occurred by way of a collision. Almost 96,000 tons crude oil from the Romanian tanker Independenta spilled over the Sea of Marmara in 1979; this accident affected the whole area – the study area inclusive.

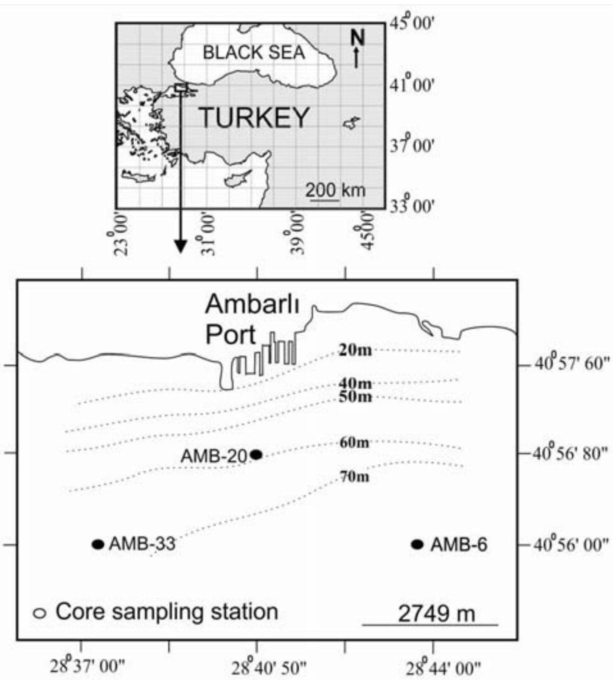

Fig. 1. Map of the area studied, showing the location of the sampling points and bathymetric contour.

Material and Methods

Three sediment cores from the seabed of the Ambarlı Port area were collected using a stainless gravity corer sampler on board the R. V. Arar of Istanbul University, Institute of Marine Sciences and Management, during a cruise held in May 2009 at the following locations (latitude and longitude, respectively): AMB-6 (40º56'00"N, 28º43'35"E), AMB-20 (40º56'80"N, 28º40'50"E), and AMB-33 (40º56'00"N, 28º37'60"E). The sample locations were determined to represent the recent impacts of Ambarlı Port activities, such as berthing spaces for vessels, waiting for a berth at the anchorage on sediment quality. A gravity core sampler was driven into the sediment by gravity, and the sediment core was retained in a PVC tube. The diameter of the PVC coring tube was 70 mm, and up to 118 cm sediment profiles were obtained. The sediment penetration depth ranged from 72 to 118 cm and never exceeded the length of the sampling tube (3.5 m). Cores AMB-6, AMB-20, and AMB-33 were recovered at a water depth of 78, 61, and 64 m, respectively. The locations of cores are shown in Fig. 1. The cores were split into two halves in laboratory and lithologically described. Half of each core was used beforehand for core scanner analysis and then the upper 5 cm of the cores were subsampled at 5 mm intervals. They were dried in an oven at 35ºC for 48 h, then ground lightly in an agate mortar for homogenization; then digested for inductively-coupled plasma mass spectrometric (ICP-MS) measurements.

X-ray fluorescence (XRF) data used in this study were produced by the ITRAX XRF core scanner from İstanbul Technical University Laboratory. All the core sections were measured with ITRAX Core Scanner with an optical image resolution of 0.1 mm·pixel^{-1}, using 30 kV X-ray voltage, and an X-ray current of 50 mA with a step size of 0.5 mm, counting for 10 seconds at each step with the select elements of Al, As, Ba, Cr, Cu, Fe, La, Mo, Ni, Pb, Se, Sr, V, and Zn. Resulting data were given on the basis of element peak areas as count per second (cps). Element concentrations are not directly available from the XRF measurements and the processing software, but the obtained values can be used as estimates of relative concentrations or in a semi-quantitative manner. These values were used for EF and I_{geo} calculations.

The upper 5 cm of each core were subsampled at 5-mm resolution and Al, As, Ba, Cr, Cu, Fe, La, Mo, Ni, Pb, Se,

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
Fe	33,800±1,000	34,400	101
As	626±38	666	100
Ba	707±51	769	101
Cr	39*	38	97
Cu	2,950±130	3,082	100
La	34*	33	97
Mo	19*	20	105
Ni	14.3±1	13,6	96
Pb	5,532±80	5,421	99
Se	nr	91	-
Sr	330	342	104
V	76.6±2,3	80,3	102
Zn	6,952±91	6,358	93

*noncertified values. nr – no range reported by the laboratory

Sr, V, and Zn concentrations were determined by inductively coupled plasma-mass spectrometry (ICP-MS) after total digestion. ICP-MS analyses were performed in the Department of Geological Engineering Laboratory of Mersin University, Turkey. Concentrations of 14 elements (Al, As, Ba, Cr, Cu, Fe, La, Mo, Ni, Pb, Se, Sr, V, and Zn) in the extract solutions were determined in triplicate by Agilent 7500ce ICP-MS (Tokyo, Japan) equipped with a reaction cell in the form of octopole reaction system (ORS). The accuracy of the select elements analyses was checked by analyzing the reference material NIST SRM 2710 (Montana soil). The difference between the measured and reference concentrations were generally between 0 and 7% (Table 1).

In the present study, enrichment factor (EF) and geoaccumulation index (I_{geo}) were used to assess the level of contamination and the possible anthropogenic impact in sediments of the Ambarlı Port area. The EF method normalizes the measured metal content with respect to a sample reference metal sample such as Al or Fe [2, 16-18]. For this study we chose Fe as the normalizing element, because the natural concentrations of Fe in the core sediments were more uniform than of Al. EF is expressed by the following equation:

$$EF = (M/Fe)_{sample}/(M/Fe)_{background}$$

...where $(M/Fe)_{sample}$ is the metal/Fe ratio in the sample of interest and $(M/Fe)_{background}$ is the natural background value of the metal/Fe ratio. For EF calculations, average values of each element unaffected from pollution below 30 cm core depth are used as the background values. EF values were interpreted as the levels of metal pollution categorized by Sutherland [19]: EF≤2 suggesting 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.

Like the metal enrichment factor, I_{geo} can be used as a reference to estimate the extent of metal pollution [8, 18, 20]. To evaluate the intensity of historical metal pollution in the Ambarlı Port area sediments, the I_{geo} introduced by Müller [15] was calculated as follows:

$$I_{geo} = \log_2[Cn/(1.5*Bn)]$$

...where Cn is the measured concentration of the examined metal (n) in the sediment and Bn is the geochemical background concentration of the metal (n); the background matrix correlation factor of 1.5 is due to lithogenic effects. The background values of the metals in the Ambarlı Port area also were adopted for I_{geo} calculations as in EF calculations. Müller [15] defined seven classes of the I_{geo} ranging from Class 0 (I_{geo}<0, unpolluted) to Class 6 (I_{geo}>5, extremely polluted), the latter reflecting at least 100-fold enrichment factor above background values.

Results and Discussion

Three core samples collected within the Ambarlı Port area were scanned with an XRF core scanner to determine the historical profile of select elements, also aiming to reveal the starting point of recent anthropogenic pollution. XRF counts of the select elements in the core sediments have shown the following variations: 4,000-44,500 cps for Al, 0-17 cps for As, 8-305 cps for Ba, 9-902 cps for Cr, 6-1,423 cps for Cu, 4,300-55,600 cps for Fe, 0-109 for La, 0-16 cps for Mo, 35-480 cps for Ni, 15-266 cps for Pb, 0-4 for Se, 0-110 cps for Sr, 13-206 cps for V, and 21-1,398 cps for Zn. All these results indicate that the upper parts of the cores up to 5 cm from the surface were enriched with the elements in question. For this reason, all the selected elements in the specified layer of the cores were measured by ICP-MS to determine their concentrations. The levels of Al, As, Ba, Cr, Cu, Fe, La, Mo, Ni, Pb, Se, Sr, V, and Zn in cores as a function of depth are shown in Table 2. AMB-6, AMB-20, and AMB-33 core sediments collected from the Ambarlı Port area would naturally be expected to be affected by the port activities in the region, leaving some geochemical signatures. It can be seen from Table 2 that the metal levels appear to be uniformly distributed with depth, except for the first uppermost 2 cm of all the cores; i.e. AMB-6 for Al, As, Ba, Cr, Cu, La, Mo, Ni, Pb, Se, V, and Zn; AMB-20 for Al, As, Cu, La, Mo and Se; and AMB-33 for As, Cu, Mo, and Zn. The current findings are also supported by the EF and I_{geo} data. In the present study, enrichment factor is used to assess the level of contamination and possible anthropogenic impact in core sediment samples. The mean EF values of Al, As, Ba, Cr, Cu, Fe, La, Mo, Ni,

Table 2. Concentrations of select elements (mg·kg^{-1}) in three core sediments from the Ambarlı Port area, compared with ERL and ERM values.

cm	Al	Fe	As	Ba	Cr	Cu	La	Mo	Ni	Pb	Se	Sr	V	Zn
Core AMB-6														
0-0.5	55,170	31,270	48	358	339	140	82	1.47	59	62	6.02	281	171	315
0.5-1	54,690	32,010	44	350	270	85	60	0.85	59	49	4.40	277	148	287
1-1.5	55,810	32,110	38	354	240	25	29	0.17	60	44	1.16	279	121	201
1.5-2	56,850	32,290	22	357	169	24	29	0.17	64	39	2.04	276	105	144
2-2.5	54,310	30,670	35	347	226	22	29	0.19	59	39	0.40	269	116	172
2.5-3	55,830	32,370	24	358	171	22	30	0.25	63	38	1.84	280	103	160
3-3.5	56,430	32,120	21	357	156	20	30	0.04	61	33	1.44	278	100	151
3.5-4	56,540	32,880	21	366	157	21	31	0.06	63	33	2.23	282	100	146
4-4.5	57,850	33,150	19	364	146	21	31	0.32	65	32	1.33	281	102	133
4.5-5	55,370	32,130	20	369	152	21	30	0.11	64	33	1.80	286	99	130
Core AMB-20														
0-0.5	52,770	31,540	53	1356	310	210	72	2.00	70	57	4.90	277	177	329
0.5-1	51,470	26,140	40	859	238	123	50	1.85	66	40	2.94	287	140	244
1-1.5	48,460	25,880	21	711	148	21	29	1.47	69	34	0.74	239	113	106
1.5-2	52,940	30,370	25	570	178	23	30	1.38	79	32	0.52	203	109	102
2-2.5	50,150	28,800	23	461	162	21	27	0.46	70	31	0.47	230	118	105
2.5-3	52,150	26,830	27	468	188	18	28	0.33	69	26	0.39	213	105	101
3-3.5	53,860	27,600	27	540	195	20	31	0.35	85	35	0.81	224	103	95
3.5-4	51,280	24,520	24	590	171	17	30	0.54	61	37	1.47	255	113	94
4-4.5	52,940	26,860	27	532	194	19	30	0.45	69	29	1.33	250	105	94
4.5-5	50,510	25,180	24	527	166	18	29	0.37	63	28	1.23	253	111	86
Core AMB-33														
0-0.5	52,990	29,250	44	468	305	220	68	1.10	67	96	4.09	397	160	346
0.5-1	51,920	28,940	37	447	244	125	44	0.85	63	48	2.6	418	121	230
1-1.5	54,550	30,140	25	508	197	25	30	0.47	66	45	1.3	375	104	117
1.5-2	54,320	30,320	24	434	194	24	35	0.45	65	58	1.9	373	102	130
2-2.5	53,310	29,800	24	425	189	22	31	0.38	64	42	2	366	100	111
2.5-3	52,990	29,510	27	434	179	21	30	0.30	62	40	1.92	370	118	109
3-3.5	55,770	31,200	23	419	189	21	34	0.39	67	48	2.12	375	103	106
3.5-4	50,690	27,770	18	399	148	18	33	0.17	58	40	2.13	342	105	95
4-4.5	52,710	29,220	20	414	161	19	30	0.39	62	39	1.83	376	113	105
4.5-5	54,390	30,500	22	414	177	19	30	0.25	67	38	1.81	348	115	100
ERL[a]	-	-	8.2	-	81	34	-	-	20.9	47	-	-	-	150
ERM[a]	-	-	70	-	370	270	-	-	51.6	218	-	-	-	410

ERL – Effect range low; ERM – Effect range medium; concentrations are in mg·kg^{-1}; [a] – [28].

Table 3. Metal concentrations in sediments from different coastal environments in the world.

	References	Al	As	Cu	Cr	Mo	Pb	Zn
		(%)	(mg·kg^{-1})					
This study		4.8-5.8	18-53	17-280	146-339	0.04-2	26-96	86-346
Marmara Sea	[3]	2.4-8.8	nr	7-80	31-654	nr	11-68	38-162
Keratsini Harbor	[4]	nr	0-1813	195-518	264-860	nr	521-1,263	409-6,725
Saros Gulf	[6]	nr	nr	6-44	nr	nr	2-80	23-154
İzmit Bay	[7]	nr	20-27	60-139	58-116	2.9-9.9	24-178	500-1,190
İstanbul Strait	[8]	1.3-7.2	4.8-18	7.6-180	18-222	nr	4.5-461	16-859
Nemrut Bay	[16]	nr	14-20	9.6-44	36-99	nr	22-89	75-271
Rijeka Harbor	[21]	nr	9.5-38	31-429	43-119	nr	24-637	70-1,260
Gemlik Gulf	[24]	3.6-8	9-32	7-88	40-205	0.2-64	18-66	40-352
Daya Bay	[25]	nr	7.7-31	4.9-24	22-48	nr	22-111	57-120
Venice Lagoon	[26]	nr	5-132	nr	nr	nr	21-929	101-8,295
Naples Harbor	[27]	nr	1-1121	12-5743	7-1,798	nr	19-3,083	17-7234

nr – not reported

Pb, Se, V, and Zn are lower than 2. According to the five-category system proposed by Sutherland [19], the mean calculated EFs suggest deficiency to low enrichment (EF < 2) in the core sediments below 2 cm sea floor. On the other hand, the results show that some metals are moderately(2<EF<5) or significantly enriched (5<EF<20) in the surface sediment layer between 0 and 2 cm below sea floor (bsf) in cores AMB-6 (Al, As, Ba, Cr, Cu, La, Mo, Ni, Pb, Se, V, and Zn), AMB-20 (Al, As, Cu, La, Mo, Se and Zn), and AMB-33 (As, Cu, Mo, and Zn). Moreover, very high enrichment of Cu (EF=30) contamination is found at 0-1 cm bsf in core AMB-33 (Fig. 2). On the basis of the mean

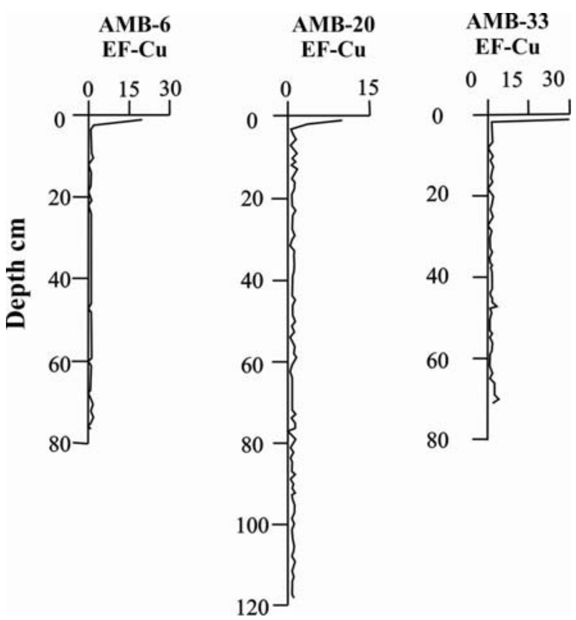

Fig. 2. Enrichment factor (EF) for Cu in the three sediment cores of Ambarlı Port area.

values of EFs in all the cores, sediments are enriched for metals in the following order: Cu > As > Al > Zn > Mo > Se > Cr > Pb > V > Ni > La > Ba > Sr. Like the metal enrichment factor, the geo-accumulation index can be used as a reference to estimate the extent of pollution [8, 18, 21]. The I_{geo} results reveal that sediments of the Ambarlı Port area remain unpolluted as all of the I_{geo} values are less than zero for Fe, Ba, Ni, and Sr, whereas some intervals of the core sediments were characterized as unpolluted to moderately or moderately polluted ($0 \leq I_{geo} \leq 2$) for Al, As, Cu, La, Mo, Se, and Zn from surface up to 2 cm bsf of the cores. In addition to these findings, the sediments have been moderately to strongly polluted ($2 \leq I_{geo} \leq 3$) by Cu in AMB-6, strongly polluted ($3 \leq I_{geo} \leq 4$) by Zn in AMB-33, and strongly to extremely polluted ($4 \leq I_{geo} \leq 5$) by Cu in AMB-33 cores at 0-1 cm intervals (Fig. 3). The data indicate that metal (Al, As, Cu, La, Mo, Se, and Zn) contamination began from 2 cm bsf, corresponding to ca. 1979, based on the average linear sedimentation rate (0.5 mm/a) in core AMB-6 [22]. Since that date, the pollution intensities of Al, As, Cu, La, Mo, Se, and Zn have increased in the Ambarlı Port area. The results of EF and I_{geo} reveal that sediments of the Ambarlı Port area are highly enriched in metals compared to their shale levels. The highest EF and I_{geo} of selected elements are observed in the upper part of the cores. A possible source of enrichment should be the anthropogenic influence caused by the input of untreated domestic wastewater until 2004, and port activities since 1979.

In general, EF values below 2 cm of the cores ranging from 0.5 to ~2 can be considered to be similar to that of the deeper or deficiency to minimal enrichment as implied by Sutherland's EF classification [19]. Our findings imply that the core sediments below 2 cm were unaffected by any human influence, and port activities and were derived pre-

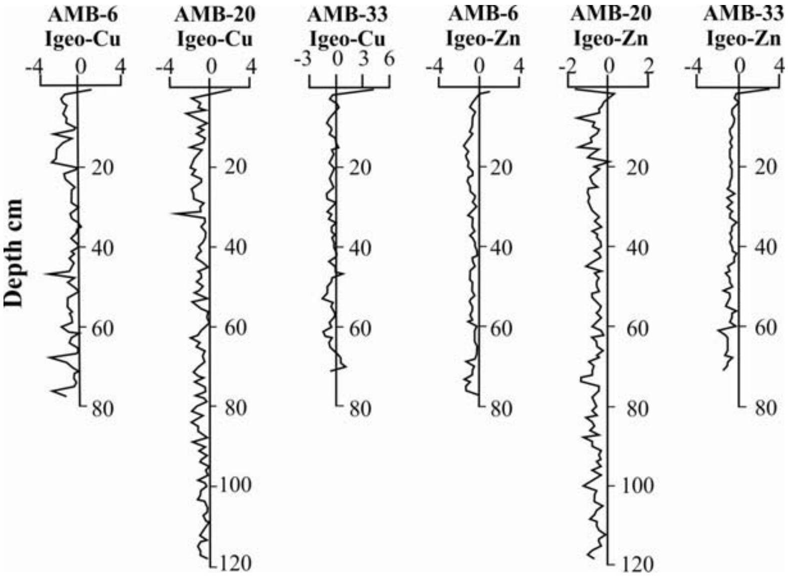

Fig. 3. Distribution of geoaccumulation index (I_{geo}) for Cu and Zn in cores AMB-6, AMB-20, and AMB-33.

dominantly from natural lithological sources. In contrast, the enrichment factors of select elements above 2 cm of the cores were found to be evidently higher than 2, indicating that anthropogenic contamination may be a major concern for these elements in the Ambarlı Port area sediments; ICP-MS analyses revealed that average concentrations for certain elements between the surface and following 5 cm are Al 5.4%, As 28 $mg\cdot kg^{-1}$, Ba 485 $mg\cdot kg^{-1}$, Cr 199 $mg\cdot kg^{-1}$, Cu 50 $mg\cdot kg^{-1}$, Fe 3%, La 37 $mg\cdot kg^{-1}$, Mo 0.59 $mg\cdot kg^{-1}$, Ni 65 $mg\cdot kg^{-1}$, Pb 41 $mg\cdot kg^{-1}$, Se 2 v, Sr 299 $mg\cdot kg^{-1}$, V 116 $mg\cdot kg^{-1}$, and Zn 155 $mg\cdot kg^{-1}$. The average concentrations of As, Cr, Pb, Se, and Zn in the 5 cm of cores are higher than the shale average of these elements [23]. On the other hand, the mean values of Ba, Cu, La, and V are lower, whereas the maximum values of Ba, Cu, La, and V in the upper layers of the sediment cores are higher than the shale average [23]. All these findings indicate that the study area has been contaminated in recent decades.

A comparison of Al, As, Cr, Cu, Mo, Pb, and Zn concentrations in the 5 cm section of the core sediments with the results from other regions of Turkey and large industrialized/urban ports and estuaries in the world are shown in Table 3. The concentrations of As, Cr, and Cu in the Ambarlı Port area were higher than those recorded for sediments in different marine parts of Turkey and other countries such as Gemlik Gulf [24], İstanbul Strait [8], Nemrut Bay [16], Daya Bay [25], and Venice Lagoon [26], but were lower than those of Naples Harbor [27] and Keratsini Harbor [4]. Our values for Al and Mo were lower than or comparable to those of other studies indicated in Table 3. The levels of Pb and Zn of the study area are found to be more polluted than those of Saros Gulf [6], the northern shelf of the Marmara Sea [3], and Nemrut Bay [16], whereas Pb and Zn contents of the core sediment are lower than those of İzmit Bay [7], İstanbul Strait [8], Venice Lagoon [26], Naples Harbor [27], Rijeka Harbor [21], and Keratsini [4]. These results stress that As, Cr, and Cu contaminations in the uppermost part of the Ambarlı Port cores exceed those observed in other neighboring marine environments. According to Pb-210, dating results of the sediment core [22], the average sedimentation rate was 0.5 mm/a, whereupon the depth of 0-2 cm of cores was deposited during the period from 1979 to 2009. This implied that anthropogenic contamination of Al, Cu, La, Mo, Pb, Se, and Zn in sediments should be no earlier than 1979, as Ambarlı Port has been in service since 1989. Therefore, the uppermost 1.14 cm portion of the core sediment reflected the effects of Ambarlı Port activities corresponding to the accumulation periods from 1989 to 2009.

To estimate the possible environmental consequences of metals analyzed, our ICP-MS results also were compared to sediment quality guidelines (SQGs), such as effect-range low (ERL) and effect-range median (ERM), as proposed by Long et al. [28]. Considering the results, the metal concentrations of Cu, Pb, and Zn (for AMB-20 and AMB-33) below 1 cm of the cores were below ERL, which represents a minimal-effects range intended to estimate conditions where biological effects are rarely observed, whereas some of the sediment samples were between ERL and ERM values for As (100%), Cr (100%), Cu (20%), Pb (17%), and Zn (33%), which represent a range within which biological effects occur occasionally (Table 2). Nickel in AMB-6, AMB-20, and AMB-33 cores sediments exceeded the ERM level (Table 2), potentiating adverse effects on the organisms.

Conclusion

The recent impacts of Ambarlı Port activities on sediment quality were studied by way of geochemical analysis and evaluated accordingly through EF and I_{geo} values reached through three cores collected from the area. Depicted and analyzed data showed that the area has been polluted by Al, As, Cu, La, Mo, Pb, Se, and Zn since 1979. The ongoing pollution also has been indicated by the I_{geo} and EF values. Seemingly, port activities have played a significant role on the continuing pollution since 1989. The concentration values of As, Cu, Cr, Pb, and Zn were found to lie between ERL and ERM values, hence acting as rarely toxic on the benthic organisms. All Ni values, in contrast, exceeded the ERM values, thus making Ni the most toxic element. Consequently, based on possible toxic effects on the benthic organisms, the toxicity order was Ni>Cr>As>Zn>Cu>Pb. Overall, the current study reveals that consumption of mussels and similar benthic organisms may create health problems for those who live in the region.

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References

1. FÖRSTNER U., WITTMANN G.T.W. Metal pollution in the aquatic environment. Heidelberg: Springer. **1979**.
2. SARI E. Source and distribution of heavy metals in river sediments from the southern drainage basin of the sea of Marmara, Turkey. Fresen. Environ. Bull. **7**, (12a), 2007, **2008**.
3. ALGAN O., BALKIS N., ÇAĞATAY M.N., SARI E. The sources of metal contents in the shelf sediments from the Marmara Sea, Turkey. Environ. Geol. **46**, 932, **2004**
4. GALANOPOULOU S., VGENOPOULOS A., CONISPOLIATIS N. Anthropogenic Heavy Metal Pollution in the Surficial Sediments of the Keratsini Harbor, Saronikos Gulf, Greece. Water Air Soil Poll. **202**, 121, **2009**.
5. ZOURARAH B., MAANAN M., ROBIN M., CARRUESCO C. Sedimentary records of anthropogenic contribution to heavy metal content in Oum Er Bia estuary (Morocco). Environ. Chem. Lett. **7**, 67, **2009**.
6. SARI E., ÇAĞATAY M.N. Distributions of heavy metals in the surface sediments of the Gulf of Saros, NE Aegean Sea. Environ. Int. **26**, 169, **2001**.
7. PEKEY H. Heavy metal pollution assessment in sediments of the Izmit Bay, Turkey. Environ. Monit. Assess. **123**, 219, **2006**.
8. OKAY O.S., PEKEY H., MORKOC E., BASAK S., BAYKAL B. Metals in the surface sediments of Istanbul Strait (Turkey). J. Environ. Sci. Heal A. **43**, 1725, **2008**.
9. HARIKUMAR P.S., NASIR U.P. Ecotoxicological impact assessment of heavy metals in core sediments of a tropical estuary. Ecotox. Environ. Safe. **73**, 1742, **2010**.
10. YUAN G.L., LIU C., CHEN L., YANG Z.F. Inputting history of heavy metals into the inland lake recorded in sediment profiles: Poyang Lake in China. J. Hazard. Mater. **185**, 336, **2011**.
11. TAŞ S., YILMAZ N., OKUS E. Phytoplankton as an Indicator of Improving Water Quality in the Golden Horn Estuary. Estuar. Coast. **32**, 1205, **2009**.
12. FARKAS A., ERRATİCO C., VİGANO L. Assessment of the environmental significance of heavy metal pollution in surficial sediments of the River Po. Chemosphere **68**, 761, **2007**.
13. TUREKIAN K. K., WEDEPOHL K. H. Distribution of the elements in some major units of the earth's crust. Geol. Soc. Amer. Bull. **72**, 175, **1961**.
14. CLEMENS R., DE CARIAT P. Intrinsic Flaws of Element Enrichment Factors (EFs) in Environmental Geochemistry. Environ. Sci. Technol. **34**, 5084, **2000**.
15. MÜLLER G. Schwermetalle in den sediment des Rheins, Veranderungem Seit 1971. Umschau **79**, 778, **1979**.
16. ESEN E., KUCUKSEZGIN F., ULUTURHAN E. Assessment of trace metal pollution in surface sediments of Nemrut Bay, Aegean Sea Environ. Monit. Assess. **160**, 257, **2010**.
17. FERNANDES L., NAYAK G.N., ILANGOVAN D., BOROLE D.V. Accumulation of sediment, organic matter and trace metals with space and time, in a creek along Mumbai coast, India. Estuar Coast Shelf S. **91**, 388, **2011**.
18. FENG H., JIANG H., GAO W., WEINSTEIN M.P., ZHANG Q., ZHANG W., YU L., YUAN D., TAO J. Metal contamination in sediments of the western Bohai Bay and adjacent estuaries, China. J. Environ. Manage. **92**, 1185, **2011**.
19. SUTHERLAND R.A. Bed sediment-associated trace metals in an urban stream, Oahu, Hawaii. Environ. Geol. **39**, 611, **2000**.
20. ZHANG L., YE X., FENG H., JING Y., OUYANG T., YU X., LIANG R., GAO C., CHEN W. Heavy metal contamination in western Xiamen Bay sediments and its vicinity, China. Mar. Pollut. Bull. **54**, 974, **2007**.
21. CUKROV N., FRANCISKOVIC-BILINSKI S., HLACA B., BARISIC D. A recent history of metal accumulation in the sediments of Rijeka harbor, Adriatic Sea, Croatia. Mar. Pollut. Bull. **62**, 154, **2011**.
22. SARI E., ÜNLÜ S., BALCI N.C., KOLDEMIR B. Investigation of present pollution in Ambarli Harbour sediment. Final project (ÇAYDAG/108Y260) report which, supported by Turkish scientific and technical research council. İstanbul, Istanbul University Marine Science and Management. **2011** [In Turkish].
23. KRAUSKOPF K.B. Introduction to geochemistry. 2nd ed. Republic of Singapore: Keong Printing Co. Pte. Ltd. **1985**.
24. ÇAĞATAY N., SANCAR Ü., ÇAKIR Z., ERYILMAZ F.Y., ERYILMAZ M., SARI E., AKÇER S., BILTEKIN D. Sediment geochemistry atlas of the Sea of Marmara. Final project (YDABCAG/103Y053) report which, supported by Turkish scientific and technical research council. İstanbul. pp. 85, **2006** [In Turkish].
25. DU J.Z., MU H.D., SONG H.Q., YAN S.P., GU Y.J., ZHANG J. 100 years of sediment history of heavy metals in daya bay, china. Water Air and Soil Poll. **190**, 343, **2008**.
26. BELLUCCI L.G., FRIGNANI M., PAOLUCCI D., RAVANELLI M. Distribution of heavy metals in sediments of the Venice Lagoon: the role of the industrial area. Sci Total Environ. **295**, 35, **2002**.
27. SPROVIERI M., FEO M.L., PREVEDELLO L., MANTA D.S., SAMMARTINO S., TAMBURRINO S., MARSELLA E. Heavy metals, polycyclic aromatic hydrocarbons and polychlorinated biphenyls in surface sediments of the Naples harbour (southern Italy). Chemosphere **67**, 998, **2007**.
28. LONG E.R., MACDONALD D.D., SMITH S.L., CALDER F.D. Incidence of Adverse Biological Effects Within Ranges of Chemical Concentrations in Marine and Estuarine Sediments. Environ. Manage. **19**, 81, **1995**.